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THE PRODUCTION OF PYROLYTIC OIL FROM SCRAP TIRE TUBES

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Abstract

Scrap tires represent major environmental problem, they are usually dumped in landfill sites, or burned in cement kilns. However, because of the elevated emissions of polyaromatic hydrocarbons (PAH) and of heavy metals (e.g. zinc) expensive gas cleaning systems have to be installed in order to perform this process in an environmentally responsible fashion.

Pyrolysis may be an environmentally friendly process to transform used tires into useful products. Pyrolysis means heating solid waste in the absence of oxygen yields oil, gases and carbonaceous char. This process transforms used tires into gas, pyrolytic oil and carbon black. Researchers have shown that the conversion of used tires into oil is a feasible process. The derived oils may be used directly as fuel.

Dealing with scrape tire is too hard, so it replaced by scrap tire tube which easier to treat. The main purpose of the present work was to prepare pyrolytic oil from waste tire tubes. A bench-scale batch system to experiment and develop pyrolysis of used tires tubes. Yields are oil, carbon black, and gas. The maximum recovery of pyrolytic oil was performed at 415°C. The specific gravity of oil was 0.95. It was rich in benzol and other petrochemical components.

Keywords: Pyrolysis, Pyrolytic oil, scrap tire, tire tube, thermal conversion

Introduction

Power generation from residual biomass and MSWs can follow different conversion routes, known as waste to energy processes. These processes include thermochemical (combustion, gasification and pyrolysis) and biochemical (fermentation and bio-digestion) pathways which lead to liquid, solid and gas fractions with high added value in a wide range of applications. Nevertheless, the liquid fraction is particularly more interesting as an energy source because has higher energy density (in volume basis), as compared with gases and solids. Similarly, it can be easily storable, transportable and hence, distributable. In this sense, among all the conversion processes, several authors have highlighted that

Aylon *et al*. (2010), Murillo *et al*. (2006), and Williams *et al*. (2013). Pyrolysis is much attractive due mainly to its less environmental impact and the possibility to recover liquid and solid compounds with wide potential in the energy and material sectors]. Therefore, it is considered that the energy contained in any feedstock is recovered in a cleaner way in contrast to other processes such as combustion and gasification. In pyrolysis, lower amounts of nitrogen oxides (NOx) and sulfur oxides (SO_2) are produced due to the inert atmosphere and the lower operating temperatures. Even so, despite these advantages, the selection of any transformation pathway must be based on a detailed understanding of the feedstock physical-chemical properties and the goal fractions to be achieved (liquid, solid or gas).

Scrap tires are highly flammable, resistant to decay and provide an ideal breeding ground for mosquitoes, rodents, fires and deadly diseases. It is very difficult to recycle profitably. Current Tire Recycling Options, repurposing, stacking abandoned tires into highway safety barricades, shredding them into granulates for rubber flooring, roofing or playground surfacing. The disposal of scrap automotive tires is an increasing environmental and economic problem. Traditionally the route to dispose has been via landfill sites or open dumping, but pyrolysis of tires is currently receiving renewed attention. The derived oils may be used directly as fuels, or added to petroleum refinery feedstocks, or as a source of refined chemicals; gases derived from the pyrolysis of tires are of high calorific value and sufficient to provide the energy requirements for the pyrolysis process plant; and the char may lso be useful as a solid fuel, as substitute carbon black or activated carbon. Williams *et al*. (2010)

Pyrolysis of waste tire, using heat in the absence of oxygen yields steel, oil, gases and carbonaceous char, which is a form of carbon. Tire material has high volatile and fixed carbon contents with heating values greater than that of coal and biomass. These properties make it an ideal raw material for thermochemical processes. Pyrolysis can be an alternative for waste tire management. After tire pyrolysis, three phases are obtained: gas, liquid, and solid. While solid and liquid products are recovered, stored, and possibly commercialized, the gas fraction can be used in situ, contributing to design a cost-effective and thermally integrated process. Aylo'n *et al*. (2008) Different experimental systems have been used to perform waste tire pyrolysis. The use of a thermo balance has been reported in order to obtain kinetic information, fluidized bed reactors, batch reactors, and many configurations based on fixed bed reactors have also been reported. However, there are few works regarding waste tire processing in continuous reactors. Asmin Shah *et al*. (2006) Ether used a moving bed reactor with a batch feeding system. In addition, the aim of the process was to perform total tire combustion in a supplementary reactor where the gas and solid fractions were burnt together. Aylo'n *et al*. (2008) have developed a reactor for polymer degradation, but it can be operated only up to 100kg/h. The vacuum pyrolysis of used tires enables the recovery of useful products, such as pyrolytic oil and pyrolytic carbon black (CBp). The light part of the pyrolytic oil contains dl-limonene which has a high price on the market. The naphtha fraction (initial boiling point (IBP) < 160ºC) can be used as a high octane number component for gasoline. The middle distillate (IBP 204oC) demonstrated mechanical and lubricating properties similar to those of the commercial aromatic oil. The heavy oil was tested as a feedstock for The production of needle coke. The surface chemistry of the recovered CBp has been compared with that of commercial carbon black through ESCA analysis. It was found that the surface morphology of CBp produced by vacuum pyrolysis, as opposed to atmospheric pyrolysis, resembles that of commercial carbon black. The CBp contains a higher concentration of inorganic compounds (especially ZnO and S) than commercial carbon black.

The composition of the inorganic part depends on the pyrolysis conditions. An acid-base demineralization treatment was shown to significantly reduce the ash concentration of the CBp, thereby improving its quality. The pyrolysis process feasibility looks promising.

Pyrolysis of rubber is an old concept. Rubber is treated at high temperatures in the absence of air to prevent oxidation. The long polymer chains of the rubber decompose at high temperatures to smaller hydrocarbon molecules. C. Roy *et al*. (1999)

When the pyrolysis is performed under vacuum, the spectrum and quality of products obtained is distinct from the other (usually atmospheric pressure) pyrolysis process. The advantage of a reduced pressure is that secondary decomposition reactions of the gaseous hydrocarbons are limited. Preliminary studies of the tire vacuum pyrolysis process were performed with a bench scale reactor and with cross-ply tires as feedstock.

Properties of Pyrolysis Products

Distillation of the pyrolytic oil yields approximately 20% light naphtha, 6.8% heavy naphtha, 30.7% middle distillate, and 42.5% bottom distillation residue. Benzene, toluene, xylene and other benzene-derivatives were identified in the naphtha fraction, as well as a valuable chemical, dl-limonene, which was found to be present with a concentration of 15% by weight.

The pyrolytic light naphtha has a relatively high concentration of sulfur, mercaptans and nitrogenous compounds due to the thermal decomposition of the additives originally present in the tires as vulcanization agents.

The relatively high levels of sulfur, nitrogenous, olefinic and diolefinic compounds in the pyrolytic light naphtha make it an unsuitable blend for gasoline.

Reforming processing is required to convert it to a high value gasoline component. Comparison of the pyrolytic naphtha and commercial petroleum naphtha indicates that the pyrolysis light naphtha is a more complex mixture than the petroleum naphtha.

Fossil fuel is basically composed of homologous series of compounds such as n-alkanes, iso-alkanes and anti-iso-alkanes. On the contrary, pyrolysis light naphtha is a heterogenous mixture of various compounds with higher isomerization which were produced during the tire thermal decomposition. Another potential application for the pyrolytic oil is the fabrication of coke. It was confirmed earlier that coal tar recovered by thermal decomposition of coal can easily be used in electrode coke manufacturing.

The composition and character of the pyrolytic oil are basic to the quality of the coke and hence its potential usage. Sulfur content and metallic constituents in the feedstock have an important effect on the quality of the coke. The metallic constituents in coke, in particular vanadium, are almost as important as sulfur in determining the coke quality. The presence of nitrogen in the coke is the result of the thermal decomposition of additives originally used in tires, such as organic accelerators, antidegradants and antiozonants, for example sulfenamide and nitrile compounds. The asphaltenes content of the oil is sufficiently high and the viscosity is suitable for the transportation of the oil.

The toluene insolubles content is too low to affect the quality of the coke. Pyrolytic oil has almost the same carbon content as the usual petroleum feedstock. However, high carbon content results in a higher yield and a better quality of coke [7].

Characteristics of feedstocks

The combined carbon and hydrogen content of tries exceeds 80 percent by weight (dry basis). These elements form the principal constituents of the solid, liquid and gaseous pyrolysis products. Waste tires are richer in these elements, and have a higher heat content then either waste plastics or municipal solid waste. At least one developer plans to blend shredded tires with an equal amount of waste oil (lubricating oil, transmission fluid, or automotive coolant) to improve economics and operations.

In addition to natural and synthetic rubber, tires are also contain a variety of other materials, including styrene-butadiene copolymers, butyl, EPOM, cis-o-poly-butadiene, aramid, steel, glass fibers, nylonrayon, polyester, antioxidants, antiozonants, vulcanization accelerators, extending oils, zinc oxide, tackifiers, stearic acid, sulfur, clay fillers, various pigments, and carbon black. Aa consequence of antimony, arsenic, barium, beryllium, boron compounds, cadmium, calcium and magnesium carbonates, cobalt, copper, lead , mercury, potassium, and sodium unavoidable.

Composition of Waste Tire

(a) Typical Composition of a Tire

Synthetic Rubber

Natural Rubber

Sulfur and sulfur compounds

Silica

Phenolic resin

Oil: aromatic, naphthenic, paraffinic

Fabric: Polyester, Nylon, Etc.

Petroleum waxes

Pigments: zinc oxide, titanium dioxide, etc.

Carbon black

Fatty acids

Inert materials

Steel Wire

(b) Typical Composition by Weight

This lists the major classes of materials used to manufacture tires by the percentage of the total weight of the finished tire that each material class represents.

Passenger Tire	
Natural rubber	14 %
Synthetic rubber	27%
Carbon black	28%
Steel	14 - 15%

Fabric, fillers, accelerators, antiozonants, etc.16 - 17%

Average weight: New 25 lbs, Scrap 22.5 lbs.

Truck Tire

Natural rubber	27 %
Synthetic rubber	14%
Carbon black	28%
Steel	14 - 15%

Fabric, fillers, accelerators, antiozonants, etc.16 - 17%

Average weight: New 120 lbs., Scrap 110 lbs.

Materials and Methods

Taking samples from tire is too difficult because cutting to small pieces need hard machine like (kossra) and then the fiber and steel must be extracted from it, instead of that, the sample was produced from a waste tire tube. For pyrolysis, representative sample of the whole tire tube cutting into 5-10 mm wide pieces were used. The pyrolysis experiments were carried out in Pyrex glass batch reactor under atmospheric pressure. A fixed amount of waste tire tube rubber was loaded in reactor and heated at 4000C, the temperature controlled at that value for 2hrs using controller J type. Heating was via an external electrical heater and temperature was monitored using thermocouple connected to the controller. Using nitrogen gas to carry gaseous products and passing through condenser cooled by chilled water. The condensable gas was trapped as liquid phase, where the liquid hydrocarbons were collected. Liquid and solid (carbon black) pyrolysis yield were determined for each experiment by weighing the amount of each obtained and calculating the corresponding percentage. Non condensable gases yield was determined by difference. Lab. Scale Experimental system is designed to make the process of pyrolysis, as in Figure (1).

Fig. 1: Lab Scale Pyrolysis Experimental System.

The system contains of:

1. Tube furnace, manufactured locally, 70 cm height, max. Operating temperature is 600^{o}C.
2. Pyrex Reactor, it consists of a glass column reactor length of 70 cm and the inner diameter of 3 cm thickness of 1.5 mm and contains within it the stainless steel carrier basket 50cm height 2.5 cm inner diameter the effective height available for reactant material is 50 cm.
3. Chiller,
4. Condenser,
5. Thermocouple,
6. Gas Washing Bottle,
7. Bio-oil Product container.

These apparatuses are shown in Figure (2).

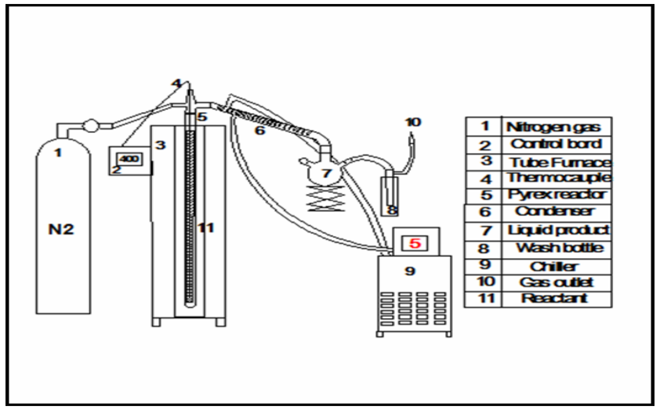

Fig. 2: Schematic diagram for Pyrolysis Experiment System.

The pyrolysis experiments must carried out in a Pyrex glass batch reactor under atmospheric pressure as shown in Fig. 2. A fixed amount of waste tires was loaded in a reactor and heated from room temperature to a final temperature at 400°C, 430°C, and 460°C for 2hrs.

The input material for experiments is shown in Figure 3 and the output solid material and liquid material are shown in Figures (4) and (5) respectively.

Fig 3: Input tire tube material.

Fig. 5: Output Liquid, Pyrolytic oil.

Results and Discussion

The bio-oils from our experiments are dark brown viscous liquid. Certain amount of shredded tire tube placed in stainless steel basket, which inserted in the core of pyrex reactor.

Experiments were done to detect temperature effect on the production of Pyrolytic-oil from Scrap tire tube.

Five experiments were conducted at different temperatures, a 400, 415, 430. 445 and 460 °C for the reactor and the results are listed in Table (1). The calculated yield of products are listed in Table (2).

Table 1: Input and Outputs of Experiments

Experiment No.	Temp. of Reaction, (°C)	Mass of Input, (gm)	Mass of Output, solid (gm)	Mass of Output, Liquid (gm)	Loss of Mass, (gm)
1	460	60	26.6	12.87	20.53
2	445	60	27.3	13,05	19.65
3	430	60	29.54	14.41	16.04
4	415	60	31.15	12.55	16.3
5	400	60	33.25	11.82	14.93

Table 2: Calculated Yield of Products

Experiment No.	Temp. of Reaction, (°C)	Solid, Yield %	Liquid, Yield %	Gas, Yield %
1	460	44.3	21.4	34.2
2	445	45.9	21.7	32.7
3	430	49.2	24.0	26.7
4	415	51.9	20.9	27.1
5	400	55.42	19.7	24.8

Yield Percent of products shown in Figure (6)

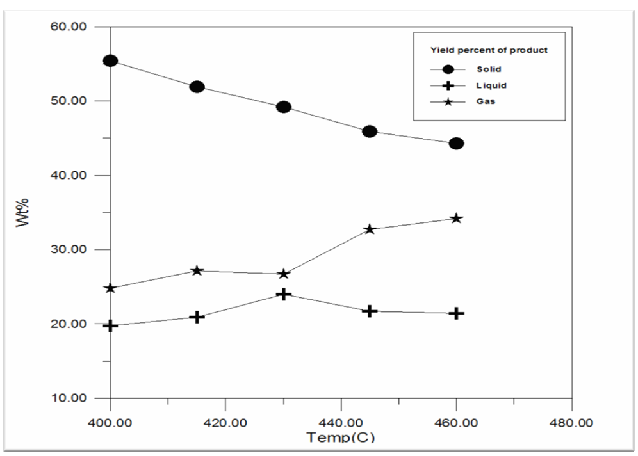

Fig 6: Yield Percent of Gas, Liquid and Solid products.

(A) Gas chromatography Mass spectrometry analysis of pyrolytic oil

The GC/MS analysis was carried out to characterize the component contained in pyrolytic oil. The characteristics mass spectrum 0f pyrolytic oil is shown in Figure (7) with retention time between 2.792 min to 30.672 min are listed in table (2). The compounds identified in the chromatogram detailed in table (3) with carbon number between C4 to C27

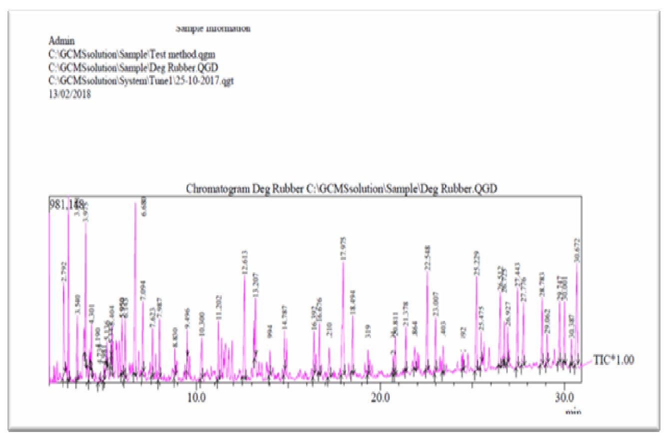

Fig. 7: GC/MS Mass Spectrum of Tire Tube Pyrolytic oil

Table (2) GC/ MS Analysis of Tire Tube Pyrolytic oil

Conclusion

Pyrolysis can convert scrap tire, usually considered as waste substance, into several kinds of pyrolytic products which are valuable such as – pyrolytic oil – Can used as fuel in electricity power generation plants, Boilers, Diesel Pumps, Furnace, etc. –Hydrocarbon Gas—Can used as source of heat for the pyrolysis plant itself – Carbon Black—Can used in Rubber Industry, Plastic, Paints, Inks, etc.

The Pyrolytic oil product can easily store and transferred to consuming sector. It can be upgraded and separated into different components such as naphtha, light and heavy oil and a distillation residue. All these outputs have a commercial value.

A proper choice of the pyrolysis will yield a pyrolytic carbon black which is close in properties to commercial rubber-grade carbon black. An additional potential market for carbon black is filler for road asphalt. The commercial value of the products can make the tire pyrolysis process both ecological friendly and economical attractive.

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