Effect of heating power on the scrap tires pyrolysis derived oil

Radwan Alkhatib [a,b], Khaled Loubar [a,*], Sary Awad [a], Eskandar Mounif [b], Mohand Tazerout [a]

[a] GEPEA, UMR 6144, Ecole des Mines de Nantes, La chantrerie, 4 rue Alfred Kastler B.P. 20722, 44307 Nantes Cedex 3, France
[b] Higher Institute for Applied Science and Technology, B.P. 31983, Damascus, Syria

ARTICLE INFO

ABSTRACT

Experimental investigation is carried out in order to study the effect of power input on the pyrolysis process of waste tires (WT). Three different power input levels i.e., 750 W, 1500 W and 3000 W have been used to heat the reactor to 500 °C. The part of energy that was effectively consumed for thermal cracking of rubber and in evaporating the volatile products was deduced by subtracting reactor heating energy (blank tests) from total power input. Changes in physico-chemical characteristics of products were noticed while changing power inputs, which can be the consequence of changes in energy distribution between heating and cracking processes. In addition to the liquid product yield, its tar content is considered to be one of the most important characteristics according to the European standard EN590. From one side, the yield of liquid product for both 1500 W and 3000 W is higher than 45% while it is around 40% for 750 W. On the other side, tar content in the liquid product is higher than 35% at 1500 W and 3000 W power inputs while it is around 11% at 750 W. When high power is introduced to the reactor, it promotes the cracking of CC and CH bonds leading to higher liquid yield and H_2 formation during the pyrolysis. Furthermore, it promotes dehydrogenation/cyclization/aromatization/reactions leading to tar and coke formation. Diels–Alders reaction mechanism explains as well the tar yield in the liquid product via dehydrogenation/aromatization/cyclization/reactions.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Each year 1.3–1.5 billion tires reach the end of their life cycle all over the world. For instance, the USA production accounts 500 million tires alone and European Union produces around 289 million tires/year [1,2]. Approximately 64% of these tires go to landfill or they are illegally dumped or stockpiled. Waste tires (WT) resist degradation due to the vulcanization process during its production. Thus, in landfills, tires do not degrade easily, but tend to float on the top over time, due to trapped gases, breaking landfill covers. Although initially, WT do not represent immediate danger, its inappropriate disposal or production in large quantities can seriously pollute the environment or cause problems when they are not properly treated. Both, environmental concerns and high oil prices have increased the interest in solid waste treatment in recent years. Specially, rubber is among the problematic waste materials on one hand and a valuable potential as recycled raw materials on the other hand.

Tires consist mainly of natural rubber (NR) 10–30%, styrene–butadiene rubber (SBR) 30–50%, butadiene rubber (BR) up to 30%, carbon black ≈30%, sulphur ≈1%, and small quantity of organic and inorganic additives; depending on the manufacturer [3–4]. This means that tires are composed mainly of long-chain hydrocarbons, and reprocessing tires to utilize these hydrocarbons could introduce an economical way to treat this form of waste.

Pyrolysis of WT is currently receiving high interest and seems to be more attractive as a method to treat the huge quantities of disposal WT. Pyrolysis is a favourable method because of the high conversion rate to oil that can be obtained, in addition to a high calorific value gas which may be used to fuel the process and a residual char which may also be useful either as a smokeless fuel, carbon black or activated charcoal [5]. The main advantage of pyrolysis is that it could deal with waste, which is otherwise difficult to be recycled.

Pyrolysis is, in general, an endothermic process that implies many reactions such as cracking, dehydrogenation, and cyclisation/aromatization which are affected by temperature. Therefore, temperature has a considerable effect on the products and conver-

sion rate and, for this reason, it is the governing factor/parameter. In addition, other parameters such as heating rate (HR), particle size, pyrolysis time and volatile residence time involved in the process also have remarkable effects [3]. For this reason, depending on the final objective of the pyrolysis, it is necessary to find the optimal conditions for the feedstock.

Many efforts have been paid over the last few decades to produce oil fuel from WT by pyrolysis. As the quality of produced oil depends on the above mentioned conditions, fuel characterization is a very important step on the waste-to-fuel chain.

Tar content represents one of the most important aspects that should be taken in account for the optimization of pyrolysis conditions. Tar is known as bitumen or asphalt which is a sticky, black and highly viscous liquid or semi-solid form of petroleum with boiling points range higher than 360 °C [6]. Its chemical structure shows that it is a complex of heavy polyaromatic hydrocarbons (PAHs), so any reaction of dehydrogenation/aromatization/cyclization will cause tar formation. Bibliographic survey [1–3,7–10] shows that all the conditions of pyrolysis contribute – at different scales – to the promotion of these reactions. However, temperature and HR stay the most influencing parameters. In other words, temperature and HR express the quantities of heat (energy) used during the pyrolysis process.

Rodrigues et al. [11] found that 75 wt% of the pyrolytic oils had a boiling point below 370 °C, which is lower than the 95% set by EN590 for diesel oil. Chaala and Roy [12] found that heavy oil fraction with boiling point higher than 350 °C is 56 wt%. This is attributed to a stronger effect of thermal cracking on conversion products.

The objective of this work is to study the effect of the power inputs (expressed sometimes indirectly as HR) over different heating programs on the liquid product yield and its tar content. Two series of experiments have been realized for three different values of power inputs. In the first series, pyrolysis takes place without limiting the heating rate. The maximum temperature was set to 500 °C. In this case, the resistance is used at its maximum power. While in the second series, the time of heating between 250 °C and 500 °C is limited (250 min). In this case, the heating procedure is fluctuating up and down to control and equilibrate between the time and the temperature till arriving to 500 °C. The temperatures 250 °C and 500 °C have been chosen depending on the thermogravimetric analysis (TGA) results [13]. No inert gas current has been used during the pyrolysis, but the system was only purged for 30 min before the beginning of heating. Thus, volatiles leave reactor under the effects of thermal expansion and evaporation. Three power inputs values were investigated 750, 1500 and 3000 W.

2. Material and methods
2.1. Raw materials

Waste passenger car shredded tires have been brought from a WT Collection Company in France. Shreds dimensions ranged between $1 \times 1 \times 1 \, cm^3$ and $6 \times 5 \times 1 \, cm^3$.

2.2. Pyrolysis reactor

A 19 cm diameter and 24 cm height cylindrical, stainless steel, fixed-bed, external electrical wall heated batch reactor was used. Its total capacity of WT is ≈1500 g. The reactor was purged using a 100 ml/min nitrogen flow for 30 min before the beginning of each experiment to make sure that the system is filled with inert gas and no oxidation process will take place. This is verified by gas analysis at the end of purging. The produced volatiles are evaporated out of the reactor into a water-cooled (15 °C) condenser, where liquid fraction is condensed in the receiving flask. Samples of noncondensing gases are taken each 10–15 min to be analyzed by a micro GC instrument in order to identify the gas composition.

Two thermocouples are attached to the reactor, the first is located in the middle of the reactor (central point), while the second is located on the outlet of reactor before the condenser. The first thermocouple measures the temperature inside the reactor while the second one measures the temperature of produced vapour. The reactor is heated up to 500 °C, then the temperature is stabilized at 500 °C for 30 min (it is chosen depending on the results of TGA, gas analysis and temperature of outlet volatile).

The collected liquid in the receiving flask is filtered from carbon soot, solid particles and heavy gum compounds (<1%). Then the liquid is characterized (density, viscosity, flash point, Gross Calorific Values (GCV) and GC–MS).

2.3. Measuring equipments

Flash point was measured using NORMALAB NPM 440 instrument; it measures up to 350 °C. Viscosity was measured using AND vibro viscometer SV-10, with measuring range 0.3–10,000 mPa.s. GC–MS analyses were performed using a PerkinElmer gas chromatograph Clarus 680 connected to a mass spectrometer PerkinElmer Clarus 600S operating with electron ionisation at 70 eV. GC separation was conducted with a ALB^{TM}-5 ms Supleco capillary column (30 m × 0.25 mm × 0.25 μm film thickness) with the following thermal program: from 60 °C to 180 °C at 7 °C/min, held at 180 (1 min) then ramped to 250 °C at 5 °C/min and to 350 °C at 2 °C/min, held at 350 °C for 5 min. In addition, GCV has been obtained using Parr 6200 calorimeter; upper limit of detection 55 kJ/g. Gaseous products (H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, CO, CO_2, O_2 and N_2) were analyzed using a Micro-GC: Agilent technologies 3000A with a thermal conductivity detector.

2.4. Distillation system

Distillation system is composed of a 500 ml plated bottom flask, a plated heater with stirrer, a 60 cm condenser and two thermocouples for measuring the temperatures of both gas and liquid phases.

3. Results and discussion

3.1. First series: different power inputs and different residence times

The objective of this series is to investigate the effect of power input on the tar content. Heating up to 500 °C is carried out without limiting in heating rate or residence time. Behaviour of temperature and energy consumption within the pyrolysis process is shown in Figs. 1 and 2.

Table 1
Liquid products' characteristics with different power, series 1.

Experiment No.	Power input (W)	HR (°C/min)	Yield (wt%)	Density (kg/l)	Viscosity (mPas @ 40 °C)	GCV (MJ/kg)	Flash point (°C)
1	750	1.81	40.51	0.85	1.17	43.43	25
2	1500	7.14	53.49	0.91	3.3	43.47	nd[a]
3	3000	16.31	50.86	0.93	2.35	43.47	