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Impact of different catalysis supported by oyster shells on the pyrolysis of tyre wastes in a single and a double fixed bed reactor

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ABSTRACT

The treatment and disposal of tyres from vehicles has long been of considerable environmental importance. Studies have been undertaken to reduce their environmental impact.

In this study, an alternative gas was produced from automobile tyre wastes by the means of a controlled pyrolysis. To do so, a novel catalytic system was designed with the aim of increasing the rate of conversion and improving the quality of the pyrolysis products. This work aimed also to reduce the severity of the overall reactions, by using powder catalysts (MgO, Al_2O_3, $CaCO_3$, and zeolite ZSM-5) uniformly distributed on two layers of oyster shells (OS) particles. The catalyst/tyres mass ratio was kept for all the tests at 1/30. The pyrolysis reactor was maintained at 500 °C and the influence of each catalyst and of the number of shell beds (0, 1 or 2), on the yield and composition of the derived products, was examined.

The gas yields could contribute by 1.2% of total consumption in Tunisia. Furthermore, some combinations could upgrade the derived gas and made it possible to use it as such or with the minimum of post-treatment.

It was found that, with the use of supported catalyst, the gas produced is 45% greater compared to classical thermal pyrolysis. The Heating value of the produced gas was also improved by the use of supported catalysts; it was found 16% greater with the use of Al_2O_3/OS compared to non-catalytic pyrolysis.

When compared to the gas obtained from only one catalytic supported bed, the sulfur content was reduced by 80% with the use of $CaCO_3$/OS on two catalytic beds.

1. Introduction

Scrap tyres are a growing environmental problem because they are not biodegradable and their components cannot readily be recovered. When the waste tyres are disposed of at dump sites, they can also cause serious human health, environmental and atmospheric problems (Sienkiewicz et al., 2017). Besides, in such places waste tyres keep destroying the ecology by bacteria growth, hosting insects as mosquitoes and pests through soil and groundwater (Poyraz et al., 2013). Moreover, it causes high fire risk and then, uncontrolled emissions (Abdulkadir and Recep, 2016).

Many scientific works, legal aspects and budget programs have been developed to deal with the increasing amounts of these materials (Daniel et al., 2013; Sienkiewicz et al., 2012).

In addition, energy recovery seems to have a high potential in processing and valorizing waste tyres (Aylon et al., 2010).

Therefore, researchers and senior scientist have been working on various utilization techniques, such as pyrolysis (Daniel et al., 2013; Fernández et al., 2012; Oyedun et al., 2012), co-pyrolysis (Acevedo and Barriocanal, 2014; Martínez et al., 2014; Onay and Koca, 2015), incineration/combustion (Tang et al., 2016) and gasification (Karatas et al. 2012). However, most of these methods have noticeable drawbacks and limitations (Abdulkadir and Recep, 2016). Pyrolysis is receiving renewed interest and attention to tackle the tyre waste disposal problem while allowing energy recovery.

In this process, the heat breaks down chemical bonds and decomposes the compound structure under non-oxygen atmosphere at high temperatures. Thereby, the high molecular weight polymers in tyre rubber are reduced to low ones in forms of gas, solid and liquid that can be used as chemical energy resources.

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The inorganic residues such as steel and carbon black still remain solid at the end of this process (Islam et al., 2013).

Several technologies have been studied for tyre pyrolysis, but those that have reached a larger scale development are units provided with fixed bed (Ucar et al.,2005), bubbling fluidized bed (Conesa et al., 1997; Kaminsky and Mennerich, 2001; Ono et al.,2001), circulating fluidized bed (Dai et al., 2001; William and Brindle, 2003), vacuum moving bed (Lopez et al., 2009; Roy et al., 1997; Roy et al., 1999; Zhang et al., 2008), and rotary kilns (Diez et al., 2005; Li et al. 2004).

All these reactors/configurations have advantages and disadvantages in terms of technical, economical and ecological parameters and are used for different energy applications (Martinez et al., 2013).

Further developments in the process of tyre waste recycling have included the use of catalysts. Thus, previous studies mainly correspond to the reforming of the stream product, obtained by thermal pyrolysis of tyres, carried out in fixed bed (Williams and Brindle, 2002a, 2002b; Shen et al., 2006; Shen et al., 2007a; Shen et al. 2007b) or in fluidized bed (Williams and Brindle, 2002a, 2002b), and they show a significant catalyst effect on product distribution and a dependence of results on catalyst properties. For example, Ni catalysts have been extensively used for biomass gasification tar conversion because of their high tar destruction activity, but other advantages are to be mentioned such as methane reforming and water gas shift activity, allowing adjustment of the H_2/CO ratio in the syngas (Michel et al., 2011).

In addition, the catalyst may be selected according to the following criteria (Michel et al., 2011):

1. Activity in the pyrolysis of heavy hydrocarbon and aromatic compounds.
2. Ability to provide a suitable gas ratio for special purpose
3. Resistance to deactivation due to coking, sintering and impurity fouling.
4. Stability and reusability.
5. Mechanical strength.
6. Cost and availability.

Researchers used various catalysts in tyres pyrolysis. Shen et al. (2007a), using a catalytic pyrolysis reactor, reached the result that zeolite USY catalyst and ZSM-5 catalyst reduced oil yield, maximizing at the same time the gas yield. Shah et al. (2009) studied catalytic pyrolysis of End of Life Tyres and concluded that the use of Al_2O_3 as a catalyst produced higher liquid yield and reduced gas yield. San Miguel et al., 2006) produced larger fraction of light hydrocarbons and with ash content on solid products to the levels of 3.7%.

In the other hand, NaOH can promote the rapid cracking of organic compounds scrap tyres rubber into small molecular compounds, even at low temperatures (Rofiqul Islam et al., 2010).

As well, Ni-Mg-Al catalyst was used by Williams et al. (2010), to increase the yield of gas product from 22% without catalyst into 43% with catalyst, and the H2 concentration, as well, in the gas by-product was changed from 26% into 67% in respect.

Sermin et al. (2012), pyrolysed individual scrap tyres (ST), oily sludge (OS), bilge water oil (BW) and a mix of (OS:BW:ST 1:1:2) in presence/absence of catalysts. The used catalyst were FCC (fluid catalytic cracking used in refinery, commercial catalyst) and RM (Red Mud, disposal catalyst) with ratio 1:5 (catalyst: feedstock) mass rate. The catalysts were laid between two layers of quartz wool in a stainless-steel net basket that was placed in the middle part of the reactor, being in contact with the gaseous products from primary degradation of materials. The result showed that the catalysts didn't have significant effects on the yields of both gas and liquid products for the pyrolysis of scrap tyres. But they had big effect on the composition of liquid.

In this work, the influence of different catalysts on upgrading the pyrolysis of waste tyres has been investigated. Special attention has been given to the gas fraction, highlighting its properties as alternative fuel. The main properties of the pyrolytic products are pointed out.

2. Experimental setup and procedure

2.1. Materials

The raw materials tested in this study are light automobile tyres. The pieces were not shredded and contained all reinforced materials (wires, fibers). The raw material is used directly in the reactor for economic reasons since the removal of the metal and textile is a process that consumes more time and a lot of energy. Thus, the metal separation process was performed at the end of pyrolysis tests, which required a simple grinding of the solid residue and a metal separation using a magnetic stirrer.

To achieve high production yields by implementing small amounts of catalysts, supported catalysts are employed. Often they are in the form of fine divided solid having a high specific surface. This specific surface area is dependent on the unique properties of size and/or internal porosity of supports used. In addition, the use of a support allows limitation of powder agglomeration, thereby providing more stability for catalysts.

Four catalysts were then used in this work: zeolite (ZSM-5), alumina (Al_2O_3), calcium carbonate ($CaCO_3$) and magnesium oxide (MgO). All catalysts were Sigma Aldrich analytically pure compounds, in powder form. To ensure the catalyst/tyres ratio of 1/30, for each test, two batch-catalytic systems have been prepared by mixing fixed amounts of oyster shells and catalyst powder. The choice of abandoned oyster shells is explained by the huge amounts of this household and industrial waste which can cause problems including noxious odor and illegal dumping into the sea. Efforts have been made to assess effective alternatives to use such wastes for energy or chemical recovery. Moreover, the project aims to manage the waste tyres by using other wastes (such as oyster shells or egg shells) to find environmentally safe and profitable uses which may contribute to the improvement of efficiency in economic and environmental terms of process.

2.2. Proximate and ultimate analyses of tyres

The used Scrap tyre pieces are very heterogeneous in size, shape and composition, depending on the tyre grade, age and manufacturer. They have been characterized and the results are presented in Table 1. The elemental analysis has been done on a C, H, N, S–O Analyzer (Flash EA 1112 Series), with detection limit of 0.05, while the higher heating value was determined with an isoperibolic calorimeter (6200 Parr Instruments). The thermochemical behavior of this tyre in presence and absence of catalysts has been studied in a previous paper using thermogravimetric analysis (Kordoghli et al., 2016). GC/TCD analysis of the pyrolytic gas produced from used tyres was performed at each 10 °C during the active decomposition range identified by TGA (255–500 °C). In order to ensure its repeatability, each test was repeated three times

2.3. Laboratory-scale installation

The experimental setup used in this paper is shown in Fig. 1.

The fixed bed reactor (1) with two-level catalytic beds (4, 5) has a simple design, yet being very versatile concerning gas and solid