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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<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, 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 posttreatment.

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.

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#### 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).

\* Corresponding author. *E-mail address:* besmakhiari@yahoo.com (B. Khiari). 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.



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<sub>2</sub>/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<sub>2</sub>O<sub>3</sub> 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 (Rofigul 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<sub>2</sub>O<sub>3</sub>), calcium carbonate (CaCO<sub>3</sub>) 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

Table	1
C1	

Characterization of used tyres.





Fig. 1. Experimental set-up.

flow rates and especially suitable for handling solids of different sizes and types (in this case supports and catalysts, too) without segregation problems.

The pyrolysis experiments were carried out in a batch reactor under atmospheric pressure. Fixed amounts of waste tyre and supported catalyst (catalyst/OS) were loaded in a reactor in two levels which were placed at the mid height of the reactor, the distance separating the two levels being 5 cm.

Heating was controlled via an external electrical heater (2) and temperature inside the reactor was monitored using three thermocouples  $(T_1, T_2, T_3)$ 

The acquisition device (3) registered the values of temperatures evolution inside the reactor  $(T_1, T_2, T_3)$  and the reference temperature  $(T_R)$ , allowed the control of thermal profile all along the process.

A water cooling condenser (6) was connected to the reactor to condense the pyrolysis vapors. The liquid was collected in a glass vessel (7) immersed in an ice bucket (8) whereas gases went to the gas-chromatograph with thermal conductivity detector (GC/TCD) for analysis (9).

The yields of pyrolysis liquid and solid were determined for each experiment by weighing their amount and the gas was calculated by difference. The experimental assembly is outlined in a previous paper using one stage process (Kordoghli et al., 2017).

In this section, different catalysts supported on oyster shells (OS) are studied on two levels to better understand their effects on the thermal decomposition of tyres, appreciating the influence of direct and indirect contact between raw materials and the catalytic bed.

Attention was focused on the characteristics of the produced gas in order to test the supported catalyst and its good position. For this, applied heating rate varied from 1 to 5 °C/min to identify any changes in term of releasing vapors and gas composition (during sampling).

The main gas species produced during the pyrolysis process were  $H_2$ ,  $CH_4$ , CO and light hydrocarbons ( $C_2H_4$ ,  $C_3H_6$  and  $C_4H_{10}$ ).

# 3. Results and discussions

# 3.1. Influence of supported catalyst on the pyrolysis by-product yields

It was noticed that MgO and Al<sub>2</sub>O<sub>3</sub> have almost a similar influence in the conversion rate and the percentage of gas produced. CaCO<sub>3</sub> induced the higher percentage of gas but its conversion rate was not satisfactory.

MgO/OS with two catalytic beds provided a good compromise between the largest conversion rate and a high yield of gas (Fig.2)

# 3.2. Influence of supported catalysts on the energetic characteristics of obtained products

Analyses of the three byproducts were performed in order to evaluate their energetic potential. With regard to the solid residue, elemental analyses (C, H, O, N, S), calorific value and ash yield analysis were performed. The chemical composition of the gas and its calorific value at different thermal ranges were determined, too. As for the liquid phase, there has been interest only on its calorific value.

# 3.2.1. Analysis of liquid and solid by-products

The results on solid characterization are presented in Table 2, while in Fig. 3 the values of HHV of solids and liquids are seen.

It can be concluded that by adding MgO/OS and  $Al_2O_3/OS$  in two stages, the pyrolysis reactions were more effective than those induced by CaCO<sub>3</sub>/OS and ZSM-5/OS and this, in terms of percentage of hydrogen remaining in the solid residue, conversion rate and temperature of the first appearance of the liquid.



Fig. 2. The yields of by-products obtained in simple non-catalytic pyrolysis and two-level catalyzed pyrolysis.

The presence of supported catalysts in two stages reduced the sulfur content and the carbon content of the carbonaceous residues.

It was noticed that the liquid produced during pyrolysis of used tyres in the presence of ZSM-5/OS is lighter than that obtained by adding CaCO<sub>3</sub>/OS, which confirms the difference obtained in calculating gross calorific value (the calorific value increases with the carbon chain).

Furthermore,  $Al_2O_3/OS$  gave a viscous liquid of darker color, while the MgO gave a less dense and clearer liquid than all other tests in two stages.

#### 3.2.2. Analysis of gaseous by-products

Being the main aim of this paper, the influence of used catalytic systems on gas quality and quantity, as well as the evolution of major species all along the process was monitored. The curves are presented in Figs. 4–12 showing the evolution of different identified species during the process.

Fig. 13 gives the calorific values of the gas produced by the twolevel pyrolysis.

It was found that the main components of the generated gases are hydrogen (H<sub>2</sub>) and methane (CH<sub>4</sub>), but important amounts of carbon monoxide (CO), ethane (C<sub>2</sub>H<sub>6</sub>), ethene (C<sub>2</sub>H<sub>4</sub>), propane (C<sub>3</sub>H<sub>8</sub>), propene (C<sub>3</sub>H<sub>6</sub>), and butane (C<sub>4</sub>H<sub>10</sub>) were also found in several thermal ranges. Hydrogen sulfide (H<sub>2</sub>S) was identified, too.

It was noticed that, contrary to what was observed with the tests in a single level of catalytic bed of oyster shells (Kordoghli et al.2016), the formation of the  $H_2$  in the presence of MgO is not more intensive. On the other hand, CaCO<sub>3</sub> catalyst becomes more effective in the generation of  $H_2$  and  $CH_4$ . The values obtained showed that the pyrolysis on 2 oysters' shells floors was favored by CaCO<sub>3</sub>.

Regarding the evolution of hydrocarbon, the gas produced from the pyrolysis with  $Al_2O_3/OS$  registered a considerable presence of  $C_2H_2 + C_2H_4$ ,  $C_3H_8$ ,  $C_3H_6$ , which significantly increased its calorific value compared to other catalysts and compared to tests with only one stage (Kordoghli et al., 2017).

The formation of  $C_4H_{10}$  was different following the type of catalyst and the range of decomposition: it was intense (between 20 and 28%) with MgO from 255 to 320 °C which increased its LHV; it remains constant (between 9 and 12%) up to 400 °C with the CaCO<sub>3</sub>, then it is no longer detected. Al<sub>2</sub>O<sub>3</sub> marked the longest interval of the formation of butane with a variable concentration following 3 phases, which was joined by an important LHV. Finally with the ZSM-5, the concentration of butane was constant between 295 and 385 °C, followed by a sudden decrease.

In the other hand, CO was intensively produced in the presence of  $CaCO_3$  starting from 355 °C, and with quantities exceeding those obtained with the non catalytic pyrolysis. It was concluded that this was the time of the beginning of the decomposition of the major components of tyres.

As far as  $H_2S$  is concerned, all catalysts are active in its capture or its transformation in the range of (335–400 °C). But beyond 415 °C, only CaCO<sub>3</sub> was able to capture  $H_2S$  and reduce its volume concentration in the pyrolysis gases compared to the conventional

I able 2		
Analysis	of solid	residue.

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Fig. 3. The High Heating Value (HHV) of solid and liquid by-products.

pyrolysis and to other tests with a single catalytic bed based on oyster shells.

To summarize, if we try to produce a gas rich in  $H_2$  with low percentages of  $H_2S$ , CaCO<sub>3</sub>/OS on two levels seems to be the most appropriate, although it has a relatively modest percentage of C<sub>3</sub>H6 and C<sub>3</sub>H<sub>8</sub>, and consequently a low calorific value. This deficiency is compensated by the percentage of butane up to 400 °C, since this molecule is found in a relatively high concentration (more than 10%).

If we focused on a more advanced gas conversion, it is recommended to use  $Al_2O_3$  on two floors of OS, but with a post-treatment to reduce the percentage of  $H_2S$  formed.

# 3.2.3. Characteristics of catalytic bed at the end of the reaction

During two-level catalyzed pyrolysis of used tyres, no coke was deposed on the catalyst beds. However, various amount of lightbrown gel was found on the oyster shell particles, particularly in the second catalyzed bed. This gel corresponds to high molecular weight molecules that have failed to react with the catalyst. As the reactor temperature at the outlet level was lower than their evaporation temperature, these molecules cannot leave the reactor and they re-condense.

It was noted that by adding a second catalyst bed, a gel was deposited on the second bed (farthest from the raw material). The support and the catalyst of the second bed (where contact was direct with the raw material) were dry. The short residence time at the final temperature could cause the gel deposit.

# 3.3. Influence of the number of the catalyst/OS beds

According to the results mentioned in a previous paper (Kordoghli et al. 2016), the influence of the number of the catalytic bed (0, 1 or 2) on the process of pyrolysis in general and the production of gas in particular was studied.

Economically, the use of two catalytic beds may increase the cost of the installation, but on the other hand, the conversion will be improved, especially if the position of the second bed is changed

Processing conditions	Elemental and	Elemental analysis (wt.%)					
	С	Н	Ν	S	0		
Simple non-catalytic pyrolysis	87.35	1.05	0.24	2.70	0.42	8.24	
Pyrolysis catalyzed by CaCO <sub>3</sub> /OS	79.49	1.16	0.31	2.17	5.55	11.32	
Pyrolysis catalyzed by ZSM-5/OS	84.11	1.29	0.17	2.50	5.66	6.27	
Pyrolysis catalyzed by Al <sub>2</sub> O <sub>3</sub> /OS	87.04	1.14	0.27	2.59	0.8	8.16	
Pyrolysis catalyzed by MgO/OS	86.17	1.29	0.29	2.53	2.4	7.32	
5 5 5 6 1							



Fig. 4. The evolution of H<sub>2</sub> in the pyrolysis gas during the process.







Fig. 6. The evolution of  $C_2H_6$  in the pyrolysis gas during the process.

(avoiding the loss of heat load). Besides, the addition of the second bed can contribute to the increase of the amount of gas that can offset the cost increase of the plant. The goal is to appreciate the right position for the best conversion and the largest proportion of gas. Direct and indirect influences are discussed:



**Fig. 7.** The evolution of  $C_2H_4$  in the pyrolysis gas during the process.



Fig. 8. The evolution of  $C_3H_8$  in the pyrolysis gas during the process.



Fig. 9. The evolution of  $C_3H_6$  in the pyrolysis gas during the process.



Fig. 10. The evolution of  $C_4H_{10}$  in the pyrolysis gas during the process.







Fig. 12. The evolution of H<sub>2</sub>S in the pyrolysis gas during the process.

- direct effect : the contact of the pyrolysis vapors with the particles of solid support covered with catalyst should bring changes on yields of liquid and gaseous products, as well as the chemical composition of such products;
- indirect effect: the catalyst bed was an "obstacle" to the general dynamics of the process. The temperature at which the material starts to generate condensable and non-condensable components may provide more or less significant changes in the overall process

To begin the comparison, we present the temperature curves recorded in the reactor (Fig. 14) on the first and second level as well as on the level of tyres itself.

According to thermogravimetric study mentioned in a previous paper (Kordoghli et al., 2017), the endothermic time disappears in the presence of catalysts, confirming the good effect on the process (Fig. 14). However, the loss of the thermal load prevents us to achieve the catalytic pyrolysis of vapors (Fig. 15). Indeed, the temperature of the second catalyst bed is not favorable.



Fig. 13. The Low Heating Value (LHV) of gas produced by two levels of catalyst-supported pyrolysis.



Fig. 14. Temperature profiles in the reactor in non catalytic pyrolysis.



Fig. 15. Example of Temperature profiles in the reactor in catalytic pyrolysis with Al<sub>2</sub>O<sub>3</sub>/OS.

Compared to the pyrolysis with one bed of shells of oysters, the two beds configuration reduces  $H_2S$  up to 70% with CaCO<sub>3</sub>/OS (Fig. 16). This latter combination did also reduce the percentage of  $H_2S$  by about 40% in comparison with the non catalytic pyrolysis (Fig. 17).

In this work, it is found that by adding the catalyst bed on two levels, the gas quantity increased. But, a single bed of  $Al_2O_3$  gives better yields.

Finally, energy potentially recovered from gaseous by-product is analyzed. It is noticed that for  $Al_2O_3/OS$  on two levels, the LHV







Fig. 17. Comparison of H<sub>2</sub>S capture between non catalytic pyrolysis, two levels of CaCO<sub>3</sub>/OS and two levels of ZSM-5/OS.

of the gas may reach 36 MJ/N m<sup>3</sup>, while reminding that we have used only 1 g of catalyst for each catalytic bed.

# 4. Conclusions

This is an original work using for the first time powder catalysts (MgO, Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub> and zeolite ZSM-5) uniformly distributed on two layers of oyster shells (OS) particles within a fixed bed pyrolysis reactor, in order to obtain more gas and liquid and less black carbon. The catalyst/tyres mass ratio was kept for all tests at 1/30.

The influence of catalysts on gas fraction in terms of yield, composition, distribution, and heating value during the main thermal range of the decomposition process was investigated.

Depending on used catalyst, pyrolysis products yields ranged from 36 to 43 wt.% for char, from 24 to 34 wt.% for liquid, and from 22 to 30 wt.% for gas.

Compared to the non-catalytic pyrolysis, it was found that the liquid yield decreased in all cases. The gas yield grows in presence of CaCO<sub>3</sub>/OS ranging from 24.6 wt.% (simple pyrolysis) to 30.01 wt. %. On the other hand, ZSM-5/OS and CaCO<sub>3</sub>/OS did not bring significant changes in products yield, but there are considerable influences on the evolution of gas composition during the tyres decomposition.

It was also shown that CaCO<sub>3</sub> and ZSM-5 zeolite provide the highest concentrations of CH<sub>4</sub> and H<sub>2</sub>.

Besides, the zeolite spread on two layers of oyster shells, is the only catalyst system which generates more hydrogen than methane in the last part of the tyre pyrolysis (440–500 °C).

In the other hand, MgO/oyster provides a good compromise between the largest conversion rate and the highest gas yield.

Al<sub>2</sub>O<sub>3</sub>/oyster provides a good compromise between a high gas yield and a high calorific value.

It is concluded that the supported catalyst in two levels increases the percentage of hydrocarbons C<sub>2</sub> and C<sub>4</sub> in all cases.

#### References

- Abdulkadir, A., Recep, Y., 2016. Rotary kiln and batch pyrolysis of waste tyre to produce gasoline and diesel like fuels. Energy Convers. Manage. 111, 261–270.
- Acevedo, B., Barriocanal, C., 2014. Fuel-oils from co-pyrolysis of scrap tyres with coal and a bituminous waste: influence of oven configuration. Fuel 125, 155-163.
- Aylon, E., Fernandez-Colino, A., Murillo, R., Navarro, M.V., Garcia, T., Mastral, A.M., 2010. Valorisation of waste tyre by pyrolysis in a moving bed reactor. Waste Manage. 30, 1220-1224.
- Conesa, I.A., Marcilla, A., Font, R., Caballero, I.A.I., 1997, Kinetic model for the continuous pyrolysis of two types of polyethylene in a fluidized bed reactor. J. Anal. Appl. Pyrol. 40-41, 419-431.
- Dai, X., Yin, X., Wu, C., Zhang, W., Chen, Y., 2001. Pyrolysis of waste tyres in a circulating fluidized-bed reactor. Energy 26 (4), 385-399.
- Diez, C., Sanchez, M.E., Haxaire, P., Martinez, O., Moran, A.I., 2005, Pyrolysis of tyres: a comparison of the results from a fixed-bed laboratory reactor and a pilot plant (rotatory reactor). J. Anal. Appl. Pyrol. 74 (1-2), 254-258.
- Daniel, J., Murillo, R., García, T., Veses, A., 2013. Demonstration of the waste tyre pyrolysis process on pilot scale in a continuous auger reactor. I. Hazard. Mater. 261 637-645
- Fernández, A.M., Barriocanal, C., Alvarez, R., 2012. Pyrolysis of a waste from the grinding of scrap tyres. J. Hazard. Mater. 203-204, 236-243.
- Islam, M.R., Islam, M.N., Mustafi, N.N., Rahim, M.A., Haniu, H., 2013, Thermal recycling of solid tyre wastes for alternative liquid fuel: the first commercial step in Bangladesh. Procedia Eng. 56, 573-582.
- Kaminsky, W., Mennerich, C.J., 2001. Pyrolysis of synthetic tyre rubber in a fluidised-bed reactor to yield 1,3-butadiene, styrene and carbon black. J. Anal. Appl. Pyrol. 58-59, 803-811.
- Karatas, H., Olgun, H., Akgun, F., 2012. Experimental results of gasification of waste tyre with air & steam and steam in a bubbling fluidized bed gasifier. Fuel Process Technol 102 166-174
- Kordoghli, S., Paraschiv, M., Tazerout, M., Khiari, B., Zagrouba, F., 2016. Novel catalytic systems for waste tyres pyrolysis: optimization of gas fraction. J. Energy Resour. Technol. 139 (3), 1-11. http://dx.doi.org/10.1115/1.4034979 (IERT-16-1090).
- Kordoghli, S., Paraschiv, M., Kuncser, R., Tazerout, M., Zagrouba, F., 2017. Catalysts influence on thermochemical decomposition of waste tyres. Environ. Progr. Sustain. Energy. http://dx.doi.org/10.1002/ep.12605.
- Li, S.Q., Yao, Q., Chi, Y., Yan, J.H., Cen, K.F., 2004. Pilot-scale pyrolysis of scrap tyres in a continuous rotary kiln reactor. Ind. Eng. Chem. Res. 43 (17), 5133-5145.
- Lopez, G., Aguado, R., Olazar, M., Arabiourrutia, M., Bilbao, J., 2009. Kinetics of scrap
- tyre pyrolysis under vacuum conditions. Waste Manage. 29 (10), 2649–2655. Martinez, D.M., Puy, N., Murillo, R., Garcia, T., Navarro, M.V., Mastral, A.M., 2013. Waste tyre pyrolysis - a review. Renew. Sustain. Energy Rev. 23, 179-213.
- Martínez, J.D., Veses, A., Mastral, A.M., Murillo, R., Navarro, M.V., Puy, N., Artigues, A., Bartrolí, J., García, T., 2014. Copyrolysis of biomass with waste tyres: upgrading of liquid bio-fuel. Fuel Process. Technol. 119, 263-271.
- Michel, R., Rapagnà, S., Marcello, M.D., Burg, P., Matt, M., Courson, C., Gruber, R., 2011. Catalytic steam gasification of miscanthus × giganteus in fluidised bed reactor on olivine based catalysts. Fuel Process. Technol. 192 (6), 1169-1177.

Onay, O., Koca, H., 2015. Determination of synergetic effect in co-pyrolysis of lignite and waste tyre. Fuel 150, 169-174.

- Ono, A., Kurita, M., Nagashima, T., Horio, M., 2001. Evaluation of waste pyrolysis characteristics in a pressurized fluidized bed reactor. Waste Manage. 21 (5), 451-456
- Oyedun, A., Lam, K., Fittkau, M., Hui, C., 2012. Optimisation of particle size in waste tyre pyrolysis. Fuel 95, 417-424
- Poyraz, S., Liu, Z., Liu, Y., Zhang, X., 2013. Devulcanization of scrap ground tyre rubber and successive carbon nanotube growth by microwave irradiation. Curr. Org. Chem. 17 (20), 2243-2248.
- Rofiqul Islam, M., Parveen, M., Haniu, H., Islam Sarker, M.R., 2010. Innovation in pyrolysis technology for management of scrap tyres: a solution of energy and environment. Int. J. Environ. Sci. Dev. 1 (1), 89-96.
- Roy, C., Chaala, A., Darmstadt, H.J., 1999. The vacuum pyrolysis of used tyres: enduses for oil and carbon black products. J. Anal. Appl. Pyrol. 51 (1-2), 201-221.
- Roy, C., Darmstadt, H., Bellanal, B., Amen-Chen, C., 1997. Characterization of naphtha and carbon black obtained by vacuum pyrolysis of polyisoprene rubber. Fuel Process. Technol. 50 (1), 87-103.
- San Miguel, G., Aguado, J., Serrano, D.P., Escola, J.M., 2006. Thermal and catalytic conversion of used tyre rubber and its polymeric constituents using Py-GC/MS. Appl. Catal. B: Environ. 64 (3-4), 209-219.
- Shah, J., Jan, M.R., Mabood, F., 2009. Recovery of value-added products from the catalytic pyrolysis of waste tyre. Energy Convers. Manage. 50 (4), 991-994.
- Sermin, Ö., Mihai, B., Cornelia, V., Jale, Y., 2012. Copyrolysis of scrap tyres with oily wastes. J. Anal. Appl. Pyrol. 94, 184-189.

Shen, B., Wu, C., Wang, R., Guo, B., Liang, C., 2006. Pyrolysis of scrap tyres with zeolite USY. J. Hazard. Mater. 137 (2), 1065–1073.

- Shen, B., Wu, C., Guo, B., Wang, R., Liang, C., 2007a. Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts. Appl. Catal. B: Environ. 73 (1–2), 150–157.
- Shen, B., Wu, C., Liang, C., Guo, B., Wang, R., 2007b. Pyrolysis of waste tyres: the influence of USY catalyst/tyre ratio on products. J. Anal. Appl. Pyrol. 78 (2), 243– 249.
- Sienkiewicz, M., Janik, H., Borzedowska-Labuda, K., Kucinska-Lipka, 2017. Environmentally friendly polymer-rubber composites obtained from waste tyres: a review. J. Clean Prod. 147, 560–571.
- Sienkiewicz, M., Kućinska-lipka, J., Janik, H., Balas, A., 2012. Progress in used tyres management in the European Union: a review. Waste Manage. 32 (10), 1742– 1751.
- Tang, Y., Ma, X., Zhang, C., Yu, Q., Fan, Y., 2016. Effects of sorbents on the heavy metals control during tyre rubber and polyethylene combustion in CO<sub>2</sub>/O<sub>2</sub> and N<sub>2</sub>/O<sub>2</sub> atmospheres. Fuel 165, 272–278.

- Ucar, S., Karagoz, S., Ozkan, A.R., Yanik, J., 2005. Evaluation of two different scrap tyres as hydrocarbon source by pyrolysis. Fuel 84 (14-15), 1884–1892.
- William, P.T., Brindle, A.J., 2003. Fluidised bed pyrolysis and catalytic pyrolysis of scrap tyre. Environ. Technol. 24 (7), 921–929.
- Williams, P.T., Brindle, A.J., 2002a. Catalytic pyrolysis of tyres: influence of catalyst temperature. Fuel 81 (18), 2425–2434.
- Williams, P.T., Brindle, A.J., 2002b. Fluidised bed catalytic pyrolysis of scrap tyres: influence of catalyst: tyre ratio and catalyst temperature. Waste Manage. Res. 20 (6), 546–555.
- Williams, P.T., Elbaba, I.F., Wu, C., Onwudili, J.A., 2010. High yield hydrogen from the pyrolysis-catalytic gasification of scrap tyres. In: Third International Symposium on Energy from Biomass and Waste, Venice, Italy.
- Zhang, X., Wang, T., Ma, L., Chang, J., 2008. Vacuum pyrolysis of waste tyres with basic additives. Waste Manage. 28 (11), 2301–2310.