International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.08 pp 359-365, 2016

Using Oxides of Alkaline-Earth Metals as Catalysts in Used Tyres Pyrolysis

Sana Kordoghli[1,2,3]*, Maria Paraschiv[4,5], Besma Khiari[3], Fethi Zagrouba[3], Mohand Tazerout[2]

[1] EcoleNationaled'Ingénieurs de Monastir, Avenue Ibn EL Jazzar, 5019, Monastir, Tunisia
[2]Ecole des Mines de Nantes, GEPEA UMR 6144, rue Alfred Kastler, 44307, Nantes, France
[3]Institut Supérieur des Sciences et Technologies de l'Environnement de BorjCédria, HammamLif, Tunisia
[4]National Institute of R&D for Biological Sciences, 296 Spl. Independentei, 060031, Bucharest, Romania
[5]Research Center for Advanced Materials, Products and Processes (CAMPUS), University Politehnica of Bucharest, 313 Spl. Independentei, 060042, Bucharest, Romania

Abstract : This paper presents the essential features of an efficient and environmentally attractive catalytic pyrolysis for used tyres valorisation with energy recovery.

Waste used tyres were catalytically pyrolysed in a batch reactor under atmospheric pressure. The effects of oxides of alkaline-earth metals MgO and CaO uniformly plated on a single layer of graver particles of5-7mm are investigated. Through the experimental tests the variation of pyrolysis products yields, the composition of gases and the heating value of gaseous products at different thermal ranges is highlighted.

The obtained results show that, compared with thermal pyrolysis, both oxides increase significantly the amount of gases. Thus MgO generates 32.9% of gas, 27.14% of liquid, 36.8 % of solid residue while the CaO led to 35.2% of gas, 27.5% of liquid, 36.1 % of solid residue.

Also, from GC/TCD analysis is was found that, in the range of maximum degradation rate, CaO favours the formation of C_2H_4, C_2H_6 and C_3H_8, but decreases the amount of H_2. On the other hand, the use of MgO on graver particle induced a significant increasing of CH_4, from 30% to 38%(vol).

Keywords : waste tyres, pyrolysis, catalyst, oxides of alkaline, energy recovery.

Introduction

Rapid social, economic, environmental and technological changes brought human society in front of unprecedented challenges and the need for waste valorisation. Among other wastes related with the increase of economic level of societies, end of life tyres (ELTs) consist a continuously growing environmental problem with impacts to economy and health matters concerning every modern society Additionally, end of life tyres consist a high calorific waste and thus it can be used in dedicated energy-to- waste plants as fuel substitute; and as feed stock to alternative thermochemical conversion plants for both energy and carbon material production. Apart from energy and carbon material production, a wide range of materials such as steel, fibers, shredders, oils, carbon filler could be also recovered, since they are the key components of the raw material, end of life tyres.

Pyrolysis has been proposed as a viable recycling technology to treat the very large tonnages of used tyres generated each year throughout the world. Pyrolysis, the thermal degradation of the tyre in the absence of oxygen, generates oil, char, gas and residual steel wires, all of them having strong recycling potential[1-8]. The process has the advantages of producing gaseous molecules with high calorific value that can be used to provide the energy requirements of the process plant[3,4]. The steel wires may be readily recycled back into the steel industry; the oil may be burned as a substitute furnace or boiler fuel[2,3,7].

Literature papers on catalytic pyrolysis of tyres are scarcer than those dealing with the catalytic pyrolysis of other residues, such as biomass[9,10] or plastics[11-15]. An increase in the yield of BTX aromatics has been reported[16] based on results obtained by incorporating in situ zeolites in the sample container of a thermo-balance.

Previous studies mainly correspond to the reforming of the product streams, obtained by thermal pyrolysis of tyres, carried out in fixed bed[17-20] or in fluidized bed[21], and they show a significant catalyst effect on product distribution and a dependence of results on catalyst properties.

This paper studies the effect of oxides of alkaline-earth metals, MgO and CaO, used as catalysts, on the pyrolytic products and on the composition of gas, uniformly plated on two layers of graver particles of 5-7mm.

Experimental Work

Materials and Methods

The raw material is a mixture of waste tyres cut in different sizes. Sigma Aldrich analytically pure oxides, MgO and CaO, were used as catalysts. In all the experiments the ratio catalysts/waste was kept at 1/30. To ensure a good distribution of catalysts, 2-5mm particles of graver where used as single layer support.

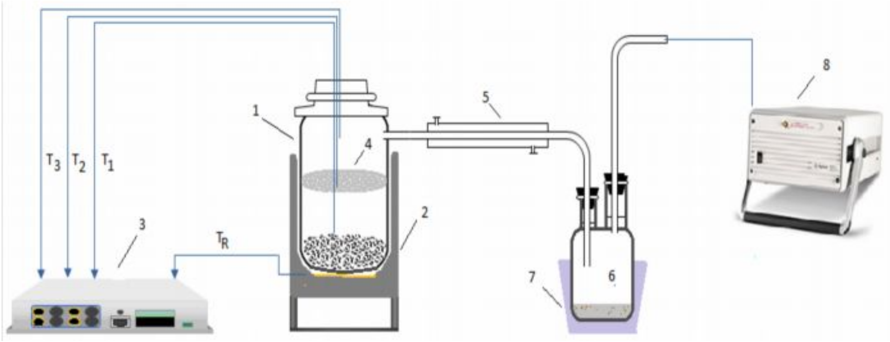
The proximate and ultimate analysis was performed on tyre rubber using a C, H, N, S – O Analyzer. It was found the following elemental composition: 0.35±0.10 %-wt of N, 84±0.20 %-wt of C, 8.4±0.15 %-wt of H, 1.35±0.25 %-wt of S, 3.52±0.2 %-wt of O. The tyres have 3.8±0.12 %-wt of ashes and the higher heating value is 35±0.40 MJ/kg.

Experimental Set-up

The experimental work was carried out into a laboratory bench scale installation using a fixed bed reaction system. The fixed bed reactor with one-stage catalytic bed has a simple design. Fixed amounts of waste tyre and supported catalyst were loaded in the reactor. Heating was controlled via an external electrical heater and temperature inside the reactor was monitored using three thermocouples.

The volatile mattersresulting from tyre decomposition are condensed and the liquid compounds are collected into a glass container, while the gases are directed to the gas-chromatograph with thermal conductivity detector (GC/TCD) for analysis. The yields of pyrolysis liquid and solid residue were determined for each experiment by weighing their amount after reaction and the gas yield was calculating by difference.

All tests have been performed at 500°C and the heating rate was keptin the range of 5-8 °C/min. The experimental assembly is outlined in the Figure 1.



1- Reactor
2- Electrical heater
3- Thermocouples
4- Catalytic bed
6- Condensable fraction collection
7- Ice bath
5- Condenser
8- GC/TCD

Figure 1. Experimental set-up

Results and Discussion

Catalytic Pyrolysis with MgO/ Support

1) Influence of MgO on pyrolysis product yield:

The main aim of testing the waste tyre pyrolysis under the conditions presented above, was to highlight the specific differences introduces by the use of catalyst supported on polydisperse sized graver particles. Figure 2 shows the yields of pyrolysis product and total conversion of tyre during pyrolysis in the absence and presence of supported MgO. It can be seen that the yield of gas was significantly improved by the presence of MgO. Since the liquid fraction is decreasing with almost the same order of magnitude, it appears that the gas fraction is growing mostly by the cracking of higher molecular weight molecules at the catalyst surface. The char yield is registering a very small reduction.

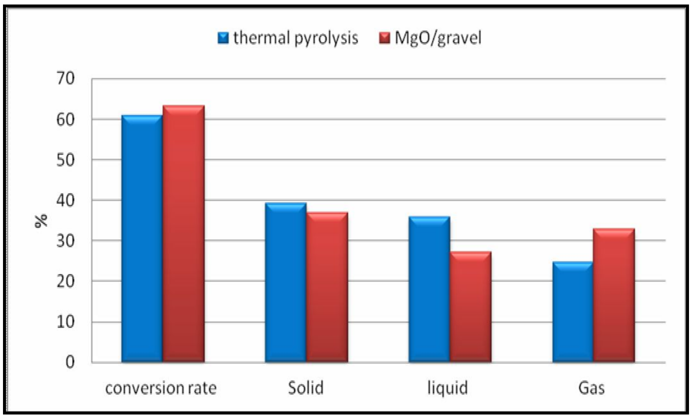


Figure 2 . Product yield from thermal and catalytic pyrolysis

Thus, the presence of MgO / graver, improve the rate of conversion (3%) and the gas yield (9%) compared to the simple pyrolysis.

2) Influence of MgO on gas quality:

Using packed column gas chromatography, it was found that the main components of the gases generated through tyre pyrolysis are carbon monoxide (CO), hydrogen sulphide (H_2S), hydrogen (H_2), methane (CH_4), ethane (C_2H_4), ethene (C_2H_4), propane (C_3H_8), propene (C_3H_6), and butane (C_4H_{10}).

Figure 3 shows the gas composition from thermal and catalytic pyrolysis at 400°C.

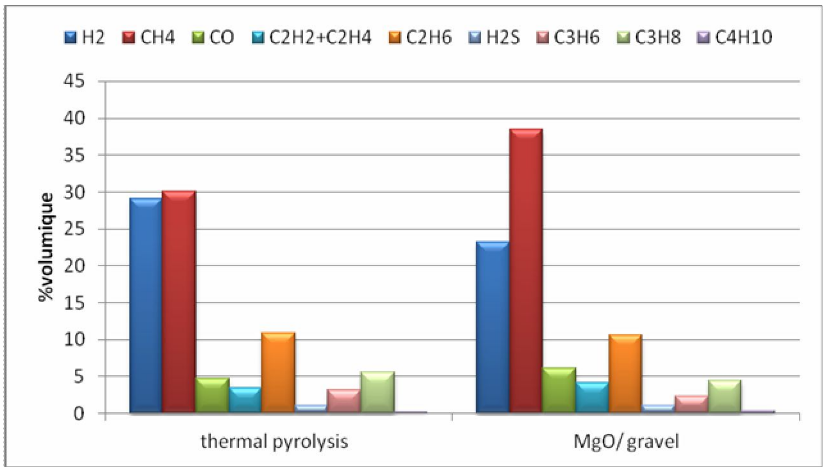


Figure 3. Gas composition in thermal and catalysed pyrolysis with MgO/gravel

The presence of MgO/gravel in the reaction system produced a large increase in gas yield, especially in CH_4. However, H_2 showed a decrease from 29 to 23.5 %-vol.

The lower heating value (LHV) of gas is calculated taking into account the volume percentages of identified gaseous species and they own calorific value. Figure 4 shows that with the presence of MgO the LHV increases, due to CH_4 concentration and also the slightly higher of fractions of CO and C_2H_4.

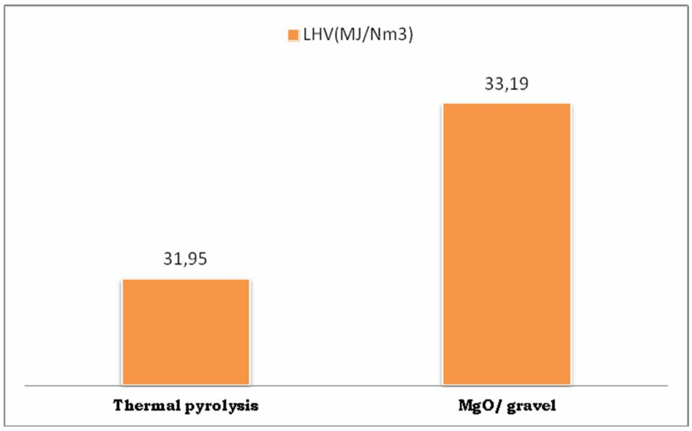


Figure 4: Lower heating values (LHV) of the pyrolysis gases

Catalytic Pyrolysis with the CaO/Support

1) Influence of CaO on pyrolysis product yield:

The total conversion and pyrolysis product yields (%-wt) obtained in the thermal and catalytic pyrolysis experiments carried out at 500°C in presence of CaO/gravel are shown in Figure 5. It can be seen that, CaO has similar influences on overall transformation of tyre. Compared to MgO, the use of CaO can improve the economic balance of the process due to the fact that it can be obtained from waste materials such as seafood shells, egg shells etc.

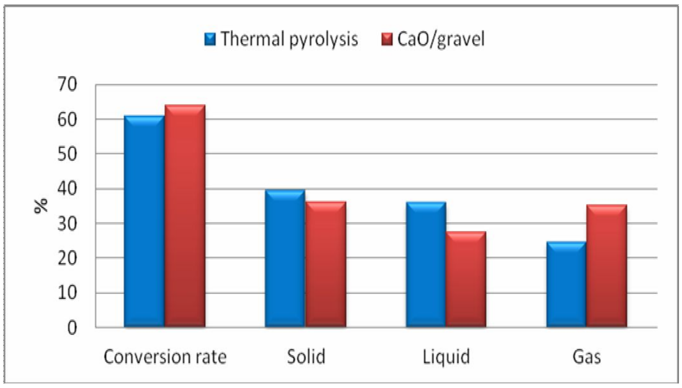


Figure 5: Product yield from thermal and catalytic pyrolysis

1) Influence of CaO on gas quality:

As far as tyre pyrolysis gases are concerned, the following gases were determined and quantified: CO, H_2S, H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_{10}. An example of gas composition determined by gas chromatography with the TCD detector is presented in Figure 6. It appears that in the used catalytic reactor CaO has negative influence on H2 and CH4 concentration. Concerning the other light hydrocarbons it can be seen that, at 400°C, C4H10 is detected only in CaO-catalysed pyrolysis.Compared to thermal pyrolysis, the presence of CaO/gravel bring a rising of C_2H_6, H_2S, C_3H_6 and C_4H_{10} concentration.

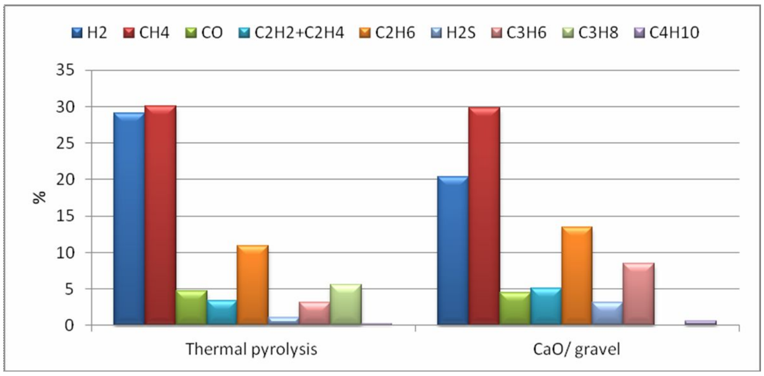


Figure 6: Gas composition for thermal and catalysed pyrolysis with CaO/gravel

The calorific values of the gases generated in thermal and catalysed pyrolysis of tyres in presence of CaO/ graver have been also calculated and the results are presented in Figure 7. It appears that the presence of CaO/gravel provided a gas with a slightly higher LHV than that determined for the gas obtained through the pyrolysis in presence of MgO/gravel.

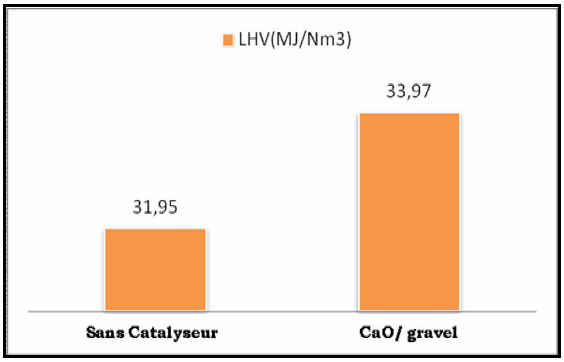


Figure 7: Lower heating values (LHV) of the pyrolysis gases

IV. Conclusions

Catalytic pyrolysis of waste tyres in presence of two oxides of alkaline-earth metals has been investigated in relation to the influence of the catalysts on the yield and composition of the gas products. The results showed that the presence of either catalyst reduced the yield of liquid fraction with a consequent increase in the gas yield.

It was found that the presence of both MgO and CaO reduced the percentage of H_2, andMgO provided a higher production of CH_4. However, the pyrolysis of tires with CaO produces a higher quantity of the other light hydrocarbon, which resulted in similar LHV of both gases.

The obtained value reveals that, even if the tyres conversion in presence of CaO/gravel and MgO/gravel is practically the same, as well as the pyrolysis products distribution, the mechanism of catalysed pyrolysis doesn't follow the same pathway for both oxides of alkaline-earth metals.

The improvement of gas fraction yield can be used in the further development of catalytic processes due to its high gross calorific values (30–40 MJ/Nm^3). This gas can provide the energy requirements of the process plant.

References

1. Williams, P.T., Waste Treatment and Disposal, Second Edition, Wiley, 1998.
2. Cunliffe, A.M., Williams, P.T. Influence of process conditions on the rate of activation of chars derived from pyrolysis of used tires. Journal of Energy Fuels, 1999, 13,166-175.
3. Cunliffe, A.M., Williams, P.T. Properties of chars and activated carbons derived from the pyrolysis of used tyres. Environmental Technology, 1998, 19, 1177-1190.
4. Williams, P.T., Besler, S., Taylor, D.T. The batch pyrolysis of tyre waste—Fuel properties of the derived pyrolyticoil and overall plant economics. The Proceedings of the Institution of Mechanical Engineers, 1993, 207, 55-63.
5. Cunliffe, A., Williams, P.T. Composition of oils derived from the batch pyrolysis of tyres. Journal of Analytical and Applied Pyrolysis, 1998, 44,131-152.
6. Benallal, B., Pakdel, H., Chabot, S., Roy, C. Characterization of pyrolytic light naphtha from vacuum pyrolysis of used tyres comparison with petroleum naphtha. Fuel, 1995, 74, 1589-1596.
7. Williams, P.T., Bottrill, R.P., Cunliffe, A.M. Combustion of tyre pyrolysis oil. Transactions of the Institution of Chemical Engineers, Part B, 1998, 76, 291-301.
8. Pakdel, H., Roy, C., Aubin, H., Jean, G., Coulombe, S.Formation of dl-limonene in used tire vacuum pyrolysis oils.Environmental Science and Technology, 1991,25,1646-1649.
9. Olazar,M., Aguado, R., Barona, A., Bilbao, J. Pyrolysis of sawdust in a conical spouted-bed reactor with a HZSM-5 catalyst.AIChE Journal, 2000,46,1025-1033.
10. Elordi, G., Olazar, M., Aguado, R., Lopez, G., Arabiourrutia, M., Bilbao, J. Catalytic pyrolysis of high density polyethylene in a conical spouted bed reactor. Journal of Analytical and Applied Pyrolysis, 79, 2007, 450-455.
11. Elordi, G., Lopez, G., Olazar, M., Aguado, R., Bilbao, J. Product distribution modelling in the thermal pyrolysis of high density polyethylene. Journal of Hazardous Materials, 2007,144, 708-714.
12. Marcilla, A., Gomez-Siurana, A., Berenguer, D.Study of the influence of the characteristics of different acid solids in the catalytic pyrolysis of different polymers. Applied Catalysis A: General, 2006, 301,222-231.
13. Hernandez, M.R., Gomez, A., Garcia, A.N., Agullo, J., Marcilla, A.Effect of the temperature in the nature and extension of the primary and secondary reactions in the thermal and HZSM-5 catalytic pyrolysis of HDPE, Journal of Applied Catalysis A: General, 2007, 317,183-194.
14. Hernandez, M.R., Garcia, A.N., Marcilla, A.Catalytic flash pyrolysis of HDPE in a fluidized bed reactor for recovery of fuel-like hydrocarbons. Journal of Analytical and Applied Pyrolysis, 2007, 78,272-281.
15. Marcilla, A., Gomez-Siurana, A., Valdes, F. Catalytic pyrolysis of LDPE over H-beta and HZSM-5 zeolites in dynamic conditions: Study of the evolution of the process. Journal of Analytical and Applied Pyrolysis 2007, 79, 433-442.

16. San Miguel, G., Aguado, J., Serrano, D.P., Escola, J.M.Thermal and catalytic conversion of used tyre rubber and its polymeric constituents using Py-GC/MS. Journal of Applied Catalysis B: Environmental, 2006, 64,209-219.
17. Williams, P.T., Brindle, A.J. Catalytic pyrolysis of tyres: influence of catalyst temperature. Fuel 2002, 81, 2425-2434.
18. Shen, B., Wu, C., Wang, R., Guo, B., Liang, C.Pyrolysis of scrap tyres with zeolite USY. Journal of Hazardous Materials, 2006, 137, 1065-1073.
19. Shen, B., Wu, C., Guo, B., Wang, R., Liang, C.Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts. Journal of Applied Catalysis B: Environmental, 2007, 73, 150-157.
20. Shen, B., Wu, C., Liang, C., Guo, B., Wang, R.Pyrolysis of waste tyres: The influence of USY catalyst/tyre ratio on products. Journal of Analytical and Applied Pyrolysis, 2007, 78, 243-249.
21. Williams, P.T., Brindle, A.J.Fluidised bed catalytic pyrolysis of scrap tyres: influence of catalyst: tyre ratio and catalyst temperature. Journal of Waste Management and Research, 2002, 20 546-555.

*****