Chapter 27
Tyre Pyrolysis by Using Nano-catalyst to Improve Energy Efficiency and Fuel Quality

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Abstract Scrap tires are harmful waste because they are non-biodegradable, emit toxins, create disposable problems and produces dioxines when burnt. Technological conversion of scrap tires to fuel by pyrolysis exists. This study is about taking it one step further by using nano Calcium Oxide (CaO) catalyst derived from mineral industry waste. The nano-catalyst was synthesized from waste and characterized by XRD, FTIR, TGA, BET analysis. From the laboratory studies it was observed that this catalyst reduces the associated pollution problems and increases the energy economy. The fuel thus produced had reduced sulphur due to the formation of sulphated salts during pyrolysis. Further, it is intended towards optimizing the process to produce quality fuel. The fuel produced was recovered in three distinct product streams and characterized as per ASTM test methods. Thus, this advanced process gives an integrated solution which is environmentally and economically superior for conversion of waste tyres to fuel.

Keywords Nano-catalyst · Pyrolysis fuel · Characterization · Energy efficiency

27.1 Introduction

The disposal of solid waste is a major environmental pollution contributor across the globe. This waste mainly includes non-biodegradable high-density materials such as rubber and plastic waste, municipality solid waste, industrial waste, agriculture waste and their generation is increasing at higher rates day by day [1]. Waste management codification demands an economical and environmental system that can solve the waste disposal problem.

One of the major source of solid waste management problem is disposal of scrap tyres because they are non biodegradable, artificial long chain hydrocarbon con-

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taining polymer and can last for several decades when proper handling is not carried out. Annually, about 1.6 billion scrap tyres are generated which is attributed to the increase in global consumption of tyres for both public and commercial transportation [2, 3]. To solve this problem there are various tyre disposal options such as landfills, burning, open dumping, reclaiming, grinding, incineration, retreading etc. But these processes have their setback and serve as a potential health and environmental hazard. To curb this leading problem, it is essential to dispose it safely.

Recently, pyrolysis of waste tyres is becoming an important topic of research, because it is a technically feasible and an eco friendly way to dispose and the resultant energy recovery is an added advantage [4, 5]. Pyrolysis is a thermo chemical process in which organic materials are thermally decomposed into simpler constituent components when subjected to high heat and oxygen free atmosphere [2, 3]. The three basic products of pyrolysis are solid residue (char), liquid (crude oil) and gases. Here, the gases having a mixture of H_2, H_2S, CO, CO_2, CH_4, C_2H_4, C_3H_6 etc. have high calorific value that can be recycled in the same process. The liquid can be used as a substitute for diesel in internal combustion engine, fuel oil or petroleum refinery feedstock whereas, the solid residue can be used as a low-grade activated carbon, in cement manufacturing process and as an additive for road bitumen [6].

The main advantages of the pyrolysis process include simple equipment, ability to handle any sort of rubber material and, low pressure operation. It has negligible waste product, high energy conversion efficiency, neither toxic nor environmental hazardous [7]. However, there is an existence of some problem related to the use of liquid products due to their low quality, high sulfur content and variability of properties [8]. So, catalysts were introduced into the process to reduce sulfur content in the fuel and the extreme operating conditions. There are various catalysts used for pyrolysis process. Among them, calcium oxide is an attractive option because it produces low sulfur content liquid product when compared to other catalysts. The calcium carbonate obtained from mining industries wastes is easily available and cheaper. In this study, calcium carbonate was reduced to nano size and converted into calcium oxide nano catalyst that was investigated for catalytic pyrolysis of waste tyres.

The main objectives of this study are to solve the major environmental and economic problem related to tyre pyrolysis, and to obtain high quality and low sulfur fuel by using nano catalyst. This reduced the solid mass, sulfur content in liquid fuel and operating temperature.

27.2 Experimental Section

27.2.1 Materials Preparation

The scrap tyres used in this experiment were collected from the Chiloda waste tyre dump site, Gandhinagar district. They were cut into small pieces and the steel treads were removed manually. Further, it was washed, dried and shredded to 3–5 mm.

Calcium oxide nano catalyst was prepared by decomposing mineral rich in calcium carbonate. This waste material was obtained from mineral processing industry. Initially, it was crushed in a gyrated crusher and further it was reduced to nano size in a high rate planetary mill. These nano sized particles were calcinated at high temperature to get nano calcium oxide. The calcination temperature of the carbonate mineral was determined by TGA thermogram (TA instruments SDT Q600, German). FTIR spectrum of calcium carbonate mineral and calcium oxide were obtained from Perkin Elmer, spectrum RX I (USA) using spectroscopically pure KBr.

For the synthesis of nano calcium oxide catalyst 100 g of calcium carbonate was heated up to 800 °C and maintained for 30 min in a muffle furnace. The produced calcium oxide was cooled in desiccators and sealed in polypropylene bags to prevent from poisoning by CO_2 and H_2O.

27.2.2 Characterization

To get the desired efficiency of nano catalyst in pyrolysis process, the crystal structure, shape, size and surface area of nano catalyst are more important and must be specific. Thus nano calcium oxide catalyst was characterized by XRD, BET analysis. Crystal structure and size of the nano catalyst was characterized using Empyrean, PANalytical X-ray diffractometer. The total surface area was analyzed by HORIBA SA-9600 series surface area analyzer (Japan).

27.2.3 Pyrolysis

Pyrolysis is the chemical decomposition of organic material at an elevated temperature in the absence of oxygen. The main reaction was carried out with 100 g of shredded scrap tyre and 1 g of nano calcium oxide as catalyst in a parr reactor up to 500 °C temperature heated at the rate of 15 °C min^{-1}. The system was maintained at this temperature for 30 min to ensure the complete conversion of tyres. To validate the positive effects of nano-catalyst pyrolysis a controlled reaction was also carried out without a catalyst under the same process condition.

27.3 Results and Discussion

27.3.1 Preparation and Characterization of Catalyst

The results of TGA showed the thermal decomposition pattern for $CaCO_3$ rich mineral in three steps. The initial decrease was observed at 80–173 °C. It was 2.3 wt% which is due to the removal of bounded and unbounded moisture. The second small decrease of 0.82 wt% at 470–546 °C was observed which is due to the removal of hydrates and the final decomposition occured at 697–792 °C this was due to the calcinations of calcium carbonate to calcium oxide. Even with a further increase in temperature, the peak remained constant indicating that the conversion was complete. According to stoichiometric proportion 56 wt% of CaO should be obtained but 61.4 wt% was obtained due to the presence of 5.4 wt% of natural impurities (Silica, Magnesium oxide etc.).

The FTIR spectrum clearly showed that the raw sample containing calcium carbonate that resembled by the peak at 721, 883, 1495, 1801, 2535, 2909 and 2995 cm^{-1}. The band at 1490 cm^{-1} is due to asymmetrical and symmetrical lengthening of the O-C-O bond whereas, inplane and outplane bending modes of carbonate anion bands were correspond to 715 and 880 cm^{-1} respectively. Absorption bands at 715, 880 and 1490 cm^{-1} were assigned to calcite phase of $CaCO_3$. After calcinations, the broad bands obtained between 250 and 600 cm^{-1} indicate calcium oxide. Peaks at 1417 and 866 cm^{-1} were ascribed to C-O bond. Thus, the FTIR spectrum conforms the formation and presence of calcium oxide.

In XRD, peaks appeared at 32.1, 37.2, 53.4, 64.8 and 67.9 associated with (111), (200), (220), (311) and (222) cubic structure of calcium oxide. The crystal sizes determined by Sherrer's equation were between 40–89 nm. Surface area was analyzed by BET. Surface area of $CaCO_3$ and CaO were 5.25 and 435.54 m^2g^{-1} respectively. The pore volume and pore diameter of CaO were 0.467 cm^3g^{-1} and 28 nm.

27.3.2 Thermal and Catalytic Pyrolysis

Pyrolysis was performed in parr reactor with 100 g of different tyre samples loaded without and with 1 wt% of nano calcium oxide catalyst. The results obtained are listed in Table 27.1. It is clear that the use of nano catalyst increased the yield of

Table 27.1 Physiochemical characterization of tyre pyrolysis product

Characteristics	Thermal pyrolysis	Catalytic pyrolysis
Weight of tyre charged	100 g	100 g
Max. temp	500 °C	500 °C
Holding time at 500 °C	30 min	30 min
95% oil recovery temp	496 °C	454 °C
Catalyst (wt%)	0%	0.5%
Liquid (wt%)	34%	46%
Residue (wt%)	38%	19%
Gas product (wt%)	28%	35%
Sulfur (Gas)	4.2%	5.1%
Sulfur (Liquid)	1.6%	0.2%
Sulfur (Solid)	1.2%	1.4%

liquid and gaseous product. The catalyst, being in nano size, it mixes thoroughly with the reactant at transition temperature of rubber to make the reaction efficient. While comparing the sulphur content, it was found that the sulfur in gaseous and solid products was high. This is due to the cracking of organic sulfur compounds into smaller non condensable gases whereas the fixing of sulfur takes place in residue to form of elemental sulfur and sulfates in solid.

27.4 Conclusion

In this study, the conversion of waste tyres into valuable liquid hydrocarbons by catalytic pyrolysis was investigated. The effects of nano catalyst on maximum recovery temperature of the product and quality of oil from catalytic pyrolysis were investigated. The main conclusions obtained by applying nano catalyst in pyrolysis are as follows:

1. The main problem preventing the use of waste tires as an alternative fuel is due to the high levels of sulfur compounds in the pyrolysis product which is solved by nano catalyst. The nano calcium oxide catalyst increases the concentration of sulfur in gaseous and solid phases to reduce the percentage of sulfur in liquid yield.
2. The process became economically viable owing to moderate temperature requirement. Reduction of above 50 °C was observed to yield maximum oil (95 wt%) was obtained in catalytic pyrolysis. The uncondensed gaseous product has high calorific value which is enough to be reused for heating purpose in the pyrolysis reaction after scrubbing.
3. Lesser amount of solid residue remained in catalytic pyrolysis than thermal pyrolysis resulting in increased quantity liquid and gas phase.

Thus, the eco-friendly technique of tyre pyrolysis was optimized and the nano catalyst solves the main problem of environment pollution by existing tyre pyrolysis plant. With further studies can result into commercially profitable business.

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