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The effect of different zeolite based catalysts on the pyrolysis of poly butadiene rubber

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HIGHLIGHTS

- The effect of different zeolite based catalysts on the poly butadiene rubber is considered.
- The catalysts can change and decrease the pyrolysis energy and control the product size.
- The effect of heating rates on the poly butadiene rubber is considered.
- The quality and quantity of the energy can specify the pyrolysis road map especially in the unsaturated polymers.
- The degradation mechanisms changed by different heating rates in PBR pyrolysis.

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ABSTRACT

In this semi batch pyrolysis study, the effect of different zeolite catalysts containing used FCC, HZSM-5 and mordenite on the degradation of virgin poly butadiene (PBR) were considered. The liquid, gas and coke yield as well as composition of liquid product as a function of different catalysts effect in the stirred reactor were compared. Main products obtained were light hydrocarbons within the gasoline range. The formation of aromatic products depended appreciably on the catalyst type and catalyst/polymer ratio. The results showed that C6 was main component of pyrolysis product with up to 32%. The results also showed that crosslink mechanism played an important role in the rubber pyrolysis. A huge number of double bonds in the PBR chains could prepare the proper media for crosslink mechanism in slow pyrolysis while flash pyrolysis followed the chain scission mechanism in the most times of degradation.

Crosslink nets could increase the activation energy and the resistance against the chain scission degradation by difficult chain mobility and heat transfer.

1. Introduction

The fast depletion of crude oil and the environmental issues have led to an intensive search for alternate 50 fuels for internal combustion engines. Waste to energy facilities provide significant economic benefit as a partially renewable energy source [1–4].

Rubber materials (poly butadiene rubber, styrene–butadiene rubber and poly isoprene or natural rubber) are the main components of general tires. It has high volatile and fixed carbon contents with heating value greater than that of coal. This makes rubber from old tire a good raw material for thermochemical processes and proper alternative for naphtha base fuels. On the other hand, scrap tire is not a biodegradable residue and therefore it is not possible to achieve its natural degradation in landfills. As a consequence, open dumping of scrap tire not only occupies a large space, presents an eyesore and could cause potential health and environmental hazards, but also illustrates wastage of valuable energy resource [5–7].

The comparison of different disposal options available shows that pyrolysis has a promising future, as it allows valuable materials to be recovered [8].

Pyrolysis, and gasification processes are considered to be more attractive and practicable methods for recovering energy from scrap tire, plastics and biomass. Pyrolysis of carbonaceous materials can be interpreted as incomplete thermal degradation, generally in the absence of air, resulting in char, condensable liquids or tars, and trace amount of gaseous products. Gasification refers

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to pyrolysis followed by higher temperature reactions of the char, tars, and primary gases to yield mainly low molecular weight gaseous products [9–11].

The catalytic degradation of polymeric materials has been reported for a range of catalysts centered on the active components in a range of different model catalysts, such as amorphous silica–aluminas, zeolites Y, ZSM-5 and various acidic catalysts and particularly the new family of MCM materials [9–22]. However, these catalysts have been used that even if performing well, they can be unfeasible from the point of view of practical use due to the cost of manufacturing and the high sensitivity of the process to the cost of the catalyst.

A very large number of double bonds in the poly butadiene rubber have a key role in the pyrolysis of the rubber. It can help us to better understand the degradation mechanisms and effective parameters on the pyrolysis.

This paper studies the effect of zeolite based catalysts on the yield of pyrolysis, liquid composition, pyrolysis mechanism following two strategies: (i) The effect of different catalyst (catalyst/polymer: 15 w/w%) on the PBR pyrolysis, and (ii) used FCC catalyst as commercially program by reactor pyrolysis and study of the mechanism in the degradation of PBR by reactor and TGA methods.

Table 1
The specification of spent FCC catalyst used in the catalytic degradation of PBR.

Surface area (BET)	235 m^2/g
SiO_2	80.10%
Al_2O_3	13.40%
Na	0.30%
Ca	1.54%
Si/Al	6
Fe	0.20%
V (ppm)	450
Ni (ppm)	180

Table 2
The specification of HZSM-5 and mordenite catalysts used in the catalytic degradation of PBR.

Specification	HZSM-5	Mordenite
Si/Al	20	20
Surface area (m^2/gr)	381.3	449.1
Porosity (ml/gr)	432.68	367.92
Porosity radius (Å)	22.69	14.39

2. Experimental

2.1. Material

PBR 1220 grade is supplied by Arak petrochemical company (Arak, Iran). Nitrogen gas (purity 99.99%) is supplied by Roham Co. Equilibrium FCC catalyst is supplied by Abadan FCC Refinery-regenerated at 750 °C, mild steaming – and its composition/properties are given in Table 1.

HZSM-5 and mordenite catalysts are supplied by Sudchemi Company and Table 2 shows the specification.

2.2. Instruments

2.2.1. Analyzer instruments

Identification of varied compounds in the condensed was carried out by a gas chromatograph mass spectrometer of model GC–MS-QP5000. The analysis was performed on a 60 m $*$ 0.32 mm capillary column coated with a 1 μm film of DB^{-1}. The oven temperature was programmed, 40 °C hold for 10 min to 300 °C at 5 °C/min hold for 10 min. Compounds were identified by means of the NIST12 and NIST62 library of mass spectra and subsets HP G1033A.

The thermo gravimetric analysis was performed with a Netzsch TG 209 thermo balance. The PBR samples were studied at various heating rates between 15 and 45 °C/min. The initial mass of the sample was 12.0–15.0 mg. The experiments were carried out in a nitrogen atmosphere (99.99% minimum purity) with a flow rate of 30 ml/min.

2.2.2. Pyrolysis process

Pyrolysis experiments were carried out in a 1 L stirred semi-batch reactor (bucchi pilot plant with a 120 custom built reactor) under atmospheric pressure and the schematic diagram is shown in Fig. 1. The fixed experimental conditions are as follows: The mixture of PBR rubber and catalyst in the reactor, carrier gas stream (300 ml/min), agitator speed (50 rpm) and heating rate (25 °C/min) up to the final temperature. The non-condensable products were vented after cooling through three condensers.

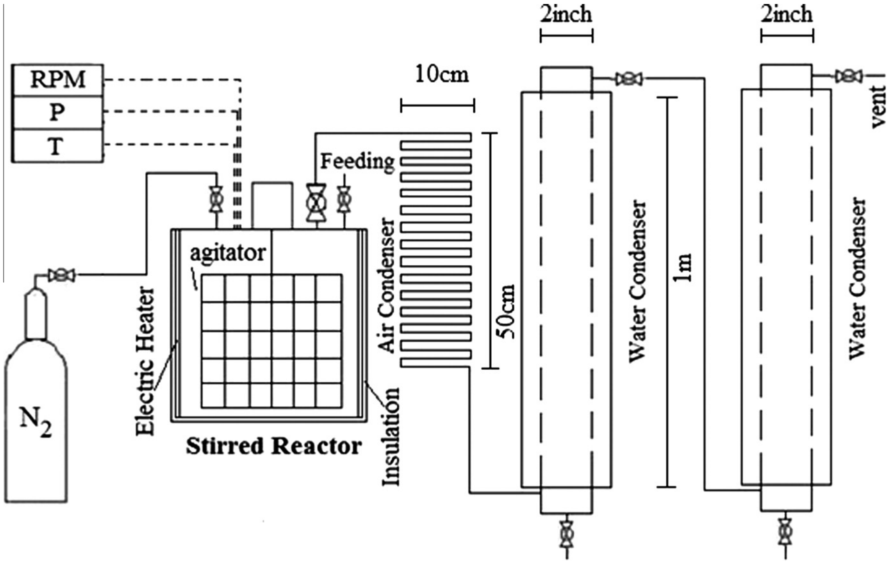

Fig. 1. Flow scheme of the laboratory stirred reactor.