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Improving oil quality from waste pyrolysis using natural zeolite catalysts: towards sustainable resource recovery

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Abstract

Tyre is a polymer material that is not biodegradable. If it is not treated in the right way, it will cause considerable problems. Therefore, it is necessary to deal with waste tyre processing. One of the methods to deal with tyre waste is pyrolysis. The pyrolysis process was conducted with and without a zeolite catalyst. This study aims to determine the characterisation of natural zeolite after activation and its effect on the pyrolysis of waste tyres. The characteristics of natural zeolite were carried out using BET and EDX tests. The amount of catalyst used in this pyrolysis process is 10% of the total weight of waste tyre, which is 500 grams. Based on the results of the study, the activation process of zeolite affects the amount of surface area and Si/Al ratio of natural zeolite catalysts. The yield of liquid fuel with the catalyst tends to decrease. In the temperature range of 250°C - 350°C, the product liquid ranges from 30% - 33 wt%, but has a lower flash point. Natural zeolite from Indonesia has proven to be a promising catalyst for catalyst applications.

Keywords

Oil quality, waste pyrolysis, natural zeolite catalysts

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Introduction

Research related to the conversion of waste tires to fuel (WTDF) in the form of gas, liquid, and char has been widely investigated. Commonly used waste tyre processing methods are pyrolysis and gasification, although there is limited information regarding the application of the most efficient technology in waste tyre-to-energy processing [1]. Pyrolysis stands as an appealing technology for transforming low-cost carbon waste materials into valuable commodities such as fuel, energy, and other value-added products [2].

Several studies on waste tyre gasification have yielded various products, including syngas, high-purity hydrogen gas, activated carbon, carbon nanotubes [3], carbon monoxide, and hydrogen [4]. The waste tyre pyrolysis oil produced has a high viscosity of 4.5 cSt and a heating value of 42.5 MJ/kg, so it cannot be used directly in combustion engine operation but is suitable as a furnace fuel or boiler operation [5], but is suitable for upgrading to high-quality automotive fuel [6]. Blending tyre pyrolysis oil with diesel oil in several ratios has been able to be applied as diesel motor fuel, where there is an increase in brake thermal efficiency but CO and NO emissions increase [7].

Currently, efforts to improve the product quality from waste tyre pyrolysis have become a topic of ongoing debate. Various parameters have been identified to potentially increase both product gas yield and product gas calorific value [8], [9], [10]. These studies have explored the effects of parameters such as air equivalence ratio [10], pressure [11], temperature, steam/CO2, and catalyst on gas yield and product gas composition [12], [13], [14]. The yield and composition of pyrolysis products are significantly influenced by conversion conditions and the chemical-physical properties of the feedstock. Additionally, factors such as reactor type and residence time play crucial roles. For instance, fast pyrolysis, characterized by high heating rates and short steam residence times, is often favored to maximize oil product yield [15].

Particle size and shape determine the surface area of the raw material. Surface penetration of tyre rubber is almost impossible due to its chemical structure and physical properties [16]. Smaller particle sizes are generally desirable due to the increased contact area between solids and liquids, thus increasing the mass transfer rate. For wastes such as tyres, the processing cost to produce fine particles is prohibitive [17]. The introduction of catalysts to the pyrolysis process to enhance dehydration, decarboxylation, and decarbonylation reactions, which will ultimately improve the quality of edible oils [18]. The utilization of catalysts is anticipated to reduce reaction temperatures, accelerate decomposition rates, and enhance product quality. Various catalysts have been tested by researchers, such as zeolites, metal oxides [19], alumina silica [20], nickel, dolomite [13], and FCC Al-MCM-41 catalyst [26]. Each catalyst has a different structure and composition that affects the fuel product. However, the use of catalysts is the main cost burden for waste plastic recycling by pyrolysis.

Zeolite catalysts are utilized in the pyrolysis of scrap tyres to produce aromatic-rich fuels. Investigating the deactivation of zeolite catalysts during the pyrolysis reaction is crucial as it significantly impacts product quality and composition [22]. In countries with small-scale applications, such as Indonesia, reducing the cost of catalysts presents an interesting challenge. Natural zeolites, abundant in various regions worldwide including Indonesia, emerge as potential candidates to address this challenge by serving as alternatives to commercial catalysts. However, natural zeolites require treatment before use as catalysts since they are initially not as effective as commercial counterparts.

Based on the literature study above, the conceptual framework that has been carried out in this research is about an experimental study on the utilization of waste tyre into fuel (WTDF) using the catalytic pyrolysis method for tyre degradation using Indonesian natural zeolite material.

Methods

Material preparation

The materials used in this study were used inner tubes. Before use, the used tyres were washed first then dried in the sun and then chopped into 1 × 1 cm sizes. The catalyst used was natural zeolite. Feedstock waste tyre show in Figure 1.

Figure 1. Feedstock waste tyre

Natural zeolite samples from the Gunungkidul area, Yogyakarta in the form of powder solids were sieved with a 100-mesh sieve. Zeolite powder was stirred with a SH-2 magnetic stirrer machine and washed with AQUA DM brand distilled water from PT Brataco. The washing capacity ratio is 1:3, where every 100 gr of zeolite powder is stirred with 300ml of distilled water for 3 hours. This washing is to remove impurity particles, so that pure zeolite can be obtained which is spared from mud and sand. Then the zeolite powder was heated at 120°C for 3 hours using an electric oven. Preparation of natural zeolite show in Figure 2.

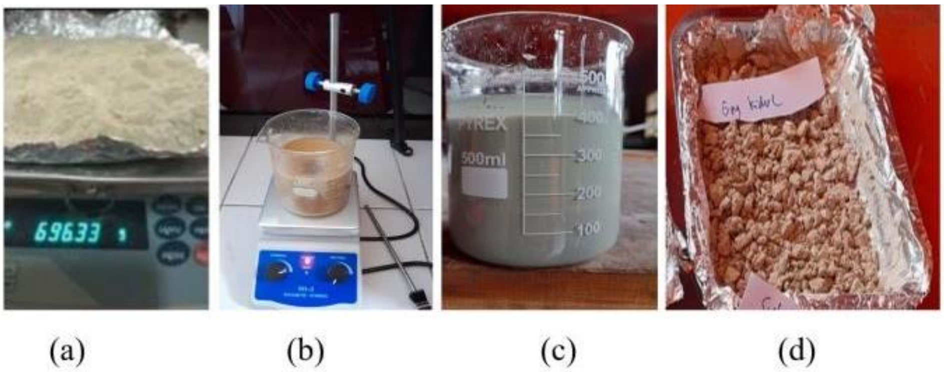

Figure 2. Preparation of natural zeolite; (a) Weighing of crushed zeolite powder, (b)Washing and stirring of zeolite+water (1:3), (c) Precipitation and separation, (d) Drying at 120°C, for 3 hours.

Fuel characterization of natural zeolite and products

This study conducted several techniques to characterize natural zeolites. Two techniques were used to characterize natural zeolites: Brunauer, Emmett and Teller Surface Area Analysis (BET), and Energy Dispersive X-Rays (EDX). BET and EDX data were used to show that the natural zeolite became ready to be a catalyst. The process of utilizing tyre waste into fuel (Figure 3) with this pyrolysis method involved preparing tyre waste types, chopping, washing, and drying. The tyre material was put into a pyrolysis reactor at 250°C, 300°C, and 350°C in a room without oxygen. The gas that came out of the reactor was then put into the condenser to obtain waste tyre oil (WTO).

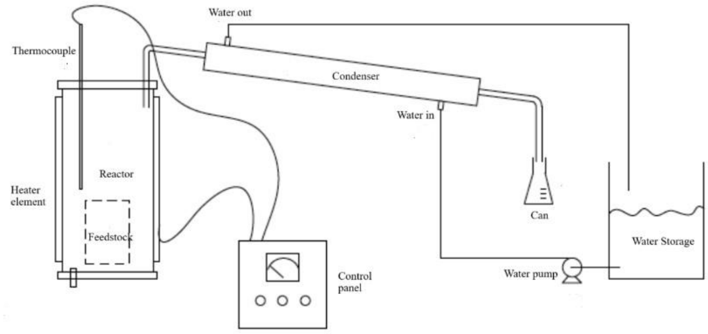

Figure 3. Schematic of waste tyre pyrolysis

The pyrolysis process of scrap tyre was conducted with and without catalyst. Prepared used tyre was then put into the reactor as much as 500 grams. Then add zeolite catalyst as much as 10% of the feedstock weight. After that, heating the waste tyre and catalyst in the reactor with a heating element for 1 hour. The result of heating the waste tyre and catalyst will produce steam that will flow into the condenser. Then cool the vapour by supplying cooling water, the temperature is kept below 20°C. Finally, collect the liquid fuel from the condenser using a container. Analyses of liquid fuel characteristics tested were density analysis (ASTM D-1298), flash point (ASTM D-93), and viscosity (ASTM D445).

Result and Discussion

Characterization of catalysts

In the pyrolysis process, catalysts are required to have a large surface area and pore volume, as noted by Ermawati (2016). Activation is one method employed to achieve these characteristics in catalysts. The catalyst activation process aims to cleanse the catalyst of impurities, thereby opening up the pores and enhancing the catalyst's activity.

1. Brauner, Emmet and Teller Surface Area (BET) Analysis

The surface area and pore volume of the catalyst can be analysed using the BrunauerEmmet-Teller (BET) method. The surface area of the catalyst can affect the activity of the catalyst. The more the surface area of the catalyst, the more active sides that are spread out so that it can increase the activity of the catalyst. A large catalyst surface area can provide a large contact area between reactant molecules and the catalyst. The magnitude of the contact area will directly affect the overall catalysis process [23]. The surface area, pore size and pore volume from BET analysis of natural zeolites that became the research sample are listed in Table 1.

Table 1. BET surface area of natural zeolite

Sample	Large Surface (m^2/g)	Pore size (nm)	Pore Volume (cm^3/g)
Natural Zeolite	45.43	5.88	0.133

This indicates that natural zeolite possesses a favorable BET surface area and pore volume. Enhanced surface area and pore volume correlate with improved catalyst activity. A larger surface area enables greater interaction between the catalyst and pyrolysis gas, facilitating the breakdown of longer chain hydrocarbons into lighter hydrocarbons. Table 1 displays the results of analysis conducted using the Brunauer-Emmett-Teller (BET) method, revealing a physical zeolite surface area of 45.43 m2/g. The relatively low surface area of natural zeolite is attributed to the absence of activation and modification treatments.

2. Energy Dispersive X-Ray Analysis (EDX)

The elemental composition analysis of natural zeolite conducted through EDX analysis is presented in Table 2. The primary elements observed are Silica (SiO2) and Alumina (Al2O3), with the combined sum indicating a Silica to Alumina ratio of 5.15 in natural zeolite. Increasing the Si/Al ratio is known to enhance the stability of the crystal framework and decrease the formation of catalyst-damaging clasts during catalytic cracking. Compositional element mapping of zeolites is depicted in Figure 4.

Table 2. Chemical composition of natural zeolite

Sample	Si/Al ratio	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO
Natural Zeolite	5.15	1,21	13,51	67,87	2,19	2,94	5,51

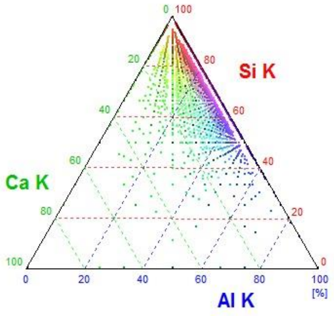

Figure 4. Compositional element mapping on zeolites

Characteristics of waste tyre oil

The test results of used tyre materials and used tyre catalysts provide the best fluid results based on temperature variations. The higher the temperature obtained, the more oil products are produced, especially in the temperature range of 250°C to 350°C. Based on Figure 5 and Figure 6, it can be explained that temperature and time play an important role in the pyrolysis process. Also shown is a comparison of oil yield from pure waste tyre and waste tyre mixed with catalyst. Catalysts generally reduce oil and residue content and increase gas content, so waste tyre material mixed with catalysts produces less oil. This is because the oil fraction resulting from thermal degradation is broken down using the catalyst and the long hydrocarbon chains are cut into shorter chains [23].

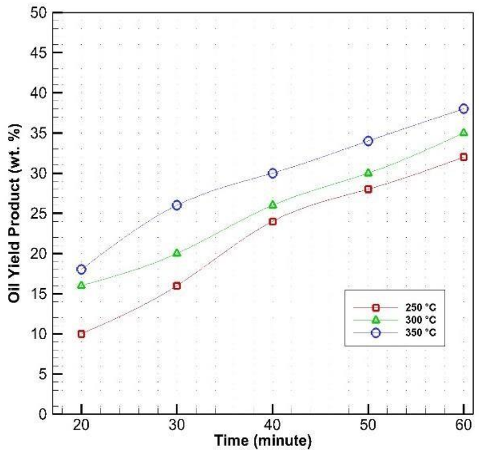

Figure 5. Comparison of tyre pyrolysis product oil yields

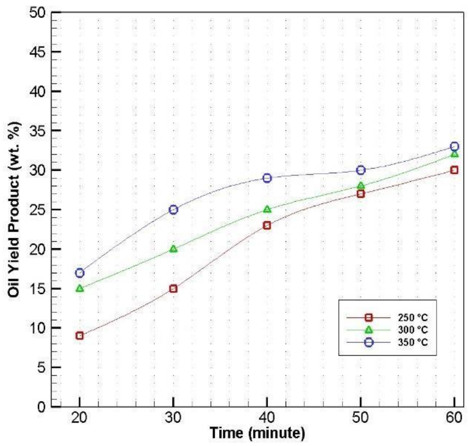

Figure 6. Comparison of oil yield of tyre pyrolysis product with natural zeolite

Liquid fuels produced through the pyrolysis process of waste tyres with and without zeolite catalyst were subjected to properties tests such as density, flash point, and viscosity tests. The use of natural zeolite catalyst decreased the yield of liquid products, but the flash point was lower. Temperature affects the viscosity value; the higher the temperature, the lower the viscosity. Temperature is inversely proportional to the density value, the higher the temperature used, the lower the density value. This is caused by thermal decomposition, which is the cutting of long hydrocarbon chains into shorter chains [24]. A comparison of liquid fuel properties for the pyrolysis process of waste tyres is shown in Table 3.

Table 3. Characterisation of liquid fuels with and without catalysts

Temperature	Natural Zeolite Catalyst			Without Catalyst		
	Density (g/ml)	Kinematic Viscosity (mm^2/s)	Flash Point (°C)	Density (g/ml)	Kinematic Viscosity (mm^2/s)	Flash Point (°C)
250° C	0.814	1.9	30	0.831	3.2	43
300° C	0.790	1.8	27	0.826	3.0	43
350° C	0.754	1.8	27	0.814	2.9	42

Conclusion

The characterization data presented for various natural zeolite suggests their potential use as catalysts in pyrolysis treatment. Acidification followed by calcination enhances the BET surface area, achieving an optimal Si/Al ratio. Given environmental and economic considerations, there exists significant potential for the advancement of waste tyre rubber pyrolysis technology. The use of zeolite catalysts expedites the decomposition of waste tyres and enhances the quality of pyrolytic oil, albeit at the expense of reduced product yield. Further research is warranted to investigate the impact of catalyst weight variation, cracking time, and temperature on product yield percentage during the catalytic cracking process.

Acknowledgments

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