

Research Article

The Effects of a Sodium Carbonate Catalyst on Calorific Value, Flash Point, Cetane Index, and pH of Tire Pyrolysis Oil

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The large volume of tire waste generated globally poses a major waste disposal problem. In the natural environment, disposed of tires do not degrade easily, but they can be processed through pyrolysis, to get char, gas, and oil. In this study, tire pyrolysis was done using 0.00%, 1.50%, 2.50%, 5.00%, 7.50%, and 10.00% sodium carbonate catalyst in the feed material to produce oil. An evaluation of the effects of the catalyst on the cetane index, calorific value, pH level, and flash point of tire pyrolytic oil (TPO) was carried out since these are the essential properties in relation to safety in its handling and efficiency in engine performance and operation. There was a decrease in the calorific value by 3.09%, the flash point by 37.25%, and the cetane index by 71.2% with increasing catalyst percentage, while the pH was found to increase by 19.78% (between 0.00 and 5.00% sodium carbonate catalysts) and then decreased when more than 5.00% of the catalyst was employed. These results will provide theoretical information that will guide its handling and usage as fuel.

1. Introduction

Every year, there are over 1.5 billion motor vehicle tires produced worldwide [1, 2]. At the end of their useful lives, these tires account for a substantial proportion of the existing solid waste that ends up in landfills [3]. Waste tires pose disposal challenges in landfills since they do not degrade easily and have a high mass/volume ratio. Although used tires can also be retreaded and reused, the derived tires seem to be of poor quality and at the end of their useful lives, the retreaded tires still end up in landfills [4, 5]. Using old tires to generate renewable energy is one of the ways of solving the waste-tire disposal problem [5–7].

Tires are composed of a complex blend of components, such as different rubbers, carbon black, wire cords, as well as other minor natural and synthetic elements. Due to the various chemical and physical characteristics of their constituent components, it is difficult to reprocess the old tires. The tires' main component, a cross-linked chemical polymer, cannot be dissolved and is nonfusible, making it difficult to remold tires into other shapes without significantly

degrading the polymer [5, 6]. In nature, unlike other organic waste, tires do not easily degrade through the action of environmental microbes [8]. A sound environmental protective measure for the recovery of energy from these waste tires is thermal or chemical decomposition [9].

Pyrolysis is a thermal decomposition technique that is suitable for organic materials that allows valuable products to be recovered. The product characteristics of various pyrolysis processes have already been evaluated under varying operating conditions. For instance, time of residence, temperature, and pressure [5, 10–12]. During the pyrolysis process, the organic and volatile material in tires decomposes into other low molecular weight ingredients, liquids, and gases. The nonvolatile fractions of carbon black and other inorganic constituents are left in a solid phase and can be reprocessed into useful products. Solid char can be used to make carbon black, smokeless fuel, or used as an activated carbon precursor. The oils produced can also be used as a source of refined fuels or chemicals [3, 9, 13], while the noncondensable gases can be used as fuel [14, 15]. Pyrolysis oil generated from biomass is typically used in the

treatment of timber [16, 17]. Tire pyrolysis oil (TPO) has the potential to be used as a substitute for biomass-generated pyrolysis oil.

The calorific content of a fuel is the quantity of heat energy released per unit quantity of fuel once fully combusted. The calorific value of a substance or material defines its viability to be utilized as fuel [18, 19]. Calorific value is concerned with the quantity of energy contained in a unit fuel's mass. Lower fuel consumption corresponds to higher calorific value, and vice versa [19]. Although it has no direct impact on atomization or combustion parameters, it is among the properties of biodiesel that is important in terms of ignition fuel economy and thermal efficiency. Moreover, it is crucial for determining the energy balance, which is a ratio of the energy required to extract the fuel to its potential energy. A fuel with a high calorific value generates more energy [18].

The flash point of a fuel oil is described as the temperature at which the oil emits sufficient ignitable vapor off its surface to combust in the presence of fire [19, 20]. It does not have an impact on engine combustion, although it is an important attribute in the safe storage and handling of fuel. Fuels with a high flash point are safer to handle and store than fuels with a low flash point [21, 22]. The flash point of petroleum products is used to determine the combustibility [20].

The cetane index measures diesel engine oil's ability to ignite at a specific temperature and pressure within the cylinder [22]. The cetane index helps determine its ignitability and defines the harshness or softness of the engine as both a function of oil ignition timing and pressure increase rate [19]. The better the combustion quality, the shorter the combustion delay [19, 23]. A long combustion delay leads to more fuel being injected into the cylinder before combustion, resulting in the combustion advancing at a faster rate. A high cetane index helps streamline engine operation when starting and running in cold weather and at slow speeds [23]. A reduced cetane index causes higher particulate emissions [24].

A substance's pH is a measure of its alkalinity or acidity. The pH scale runs from 0 to 14, with 7 representing the neutral pH point [25]. The pH of tire pyrolysis oil may be increased by the use of an alkaline catalyst during pyrolysis [26].

Several experts have done catalytic pyrolysis using alkaline catalysts, metal/zeolite catalysts, metal oxides, and microporous and mesoporous zeolites [27, 28]. Catalytic pyrolysis using cordierite-platinum SCR has also been successfully employed by Salehian and Sircneshan [29] on diesel-ethanol fuel blends. During pyrolysis, a catalyst can significantly alter the reaction pathway [30]. Its application promotes the decomposition of macromolecular cross-links, as well as heavy volatiles [31]. It affects the structure, composition, and quality of the final oil [2, 6, 13].

Catalysts are used to improve the products of pyrolysis [9, 32]. The type of catalyst (acidic, alkaline, or metallic) and catalyst properties (acid site density, acid strength, and porosity) have a significant impact on product distribution and characteristics [1, 5, 29]. The primary use of catalysts in

tire pyrolysis is to reduce product distribution compared to noncatalytic thermal pyrolysis [5, 31]. The selection of a catalyst is heavily influenced by the oil's potential applications and the required product qualities. Acidic catalysts, such as those found in the zeolite family, aid in the cracking of TPO resulting in the manufacturing of useful chemicals such as aromatic compounds and light olefins. However, they increase the quantity of gaseous yield while reducing the quantity of TPO yield. Alkaline catalysts, such as NaOH, MgO, and Na₂CO₃, increase the oil yield [1, 5, 33] and reduce its sulfur content [1, 5, 34].

Following the use of catalysts, the change in pyrolysis's oil structure and composition has an effect on its calorific value, flash point, cetane index, and pH value. In this paper, tire pyrolysis was performed in a batch-type reactor using varying percentages of sodium carbonate catalyst added to the fed material. The effects of varying quantities of sodium carbonate catalyst on the calorific value, cetane index, flash point, and pH of the produced tire pyrolysis oil were then investigated.

2. Materials and Methods

2.1. Oil Extraction. Old tires were collected and cleaned to remove mud and any other impurities. The tires were subsequently dried under direct sunlight, clipped into smaller pieces of approximately 4 cm³, and then inserted into a 6 kg capacity reactor. The reactor was closed and then the heat supply unit was switched on, and heating was done at a rate of 2 C/sec, under atmospheric pressure to a temperature of 550°C [8, 35]. This temperature has been shown by İlkiç and Aydin [8] to be optimal in tire pyrolysis. This procedure was performed for the oil samples produced with 0.00%, 1.50%, 2.50%, 5.00%, 7.50%, and 10.00% catalyst weight fraction in the reactor's fed material. Figure 1 is a schematic diagram of the pyrolysis system which was utilized in the extraction of oil.

2.2. Oil Characterization

2.2.1. Calorific Value (ASTM 4809). Calorific values were determined by the use of a bomb calorimeter. This test was carried out thrice, and the average each sample was determined.

2.2.2. Flash Point. The Open Cup Exam Method was used to determine the Flash Point. The fuel was put in the examiner's cup and then gradually and steadily heated. At frequent intervals, a test flame was directed into the cup. The flash point was determined at the lowest temperature at which the vapor just above the sample ignited when the test flame was applied. This test was performed three times per sample, and the average for each sample calculated.

2.2.3. Cetane Index (ASTM D 976). Each oil sample was heated to a temperature where 50% of its volume had evaporated and then collected. For each sample, the temperature that the fuel distilled and also the specific gravity at

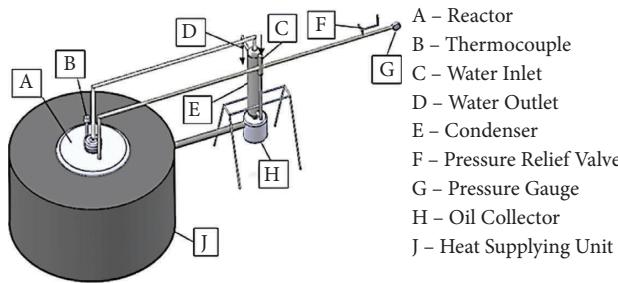


FIGURE 1: The schematic structure of the used pyrolysis system [33].

15°C could be determined. This technique was repeated three times, as well as the average data were applied to ascertain the cetane index.

The following equation was used in the calculation of cetane index [36, 37]:

$$CI = 454.74 - 1641.416D + 774.74D^2 - 0.544T_{50} + 97.803 \left[\log \left(\frac{T_{50}}{10} \right) \right]^2, \quad (1)$$

where CI—the cetane index of oil; D—the density of oil at 15°C; T₅₀—50% recovery temperature (°C).

2.2.4. pH. A signal digital pH meter was used to measure the pH of the oil samples. The procedure was as follows:

- (1) The meter first calibrated by making a 100 standard solution of pH 7 and pH 4 with the presented tablet.
- (2) The pH meter was then calibrated by turning the calibration nobs.
- (3) The tablet was placed into the oil samples, and the pH was read from the equipment's digital readout three times for each sample. The average of the three readings was then calculated.

2.3. Error Analysis. The standard error value for all the samples in each test was determined using the following equation:

$$SE = \sqrt{\frac{\sum_{k=1}^n (x_i - \mu)^2}{n(n-1)}}, \quad (2)$$

where SE = standard error; x_i = each value from the sample; μ = the mean of the sample; n = sample size.

3. Results and Discussion

3.1. Calorific Value. Figure 2 is a graphical summary of the results, showing how the calorific value of TPO varies with the percentage of sodium carbonate.

TPO's calorific value (without sodium carbonate catalyst) was 40.431 MJ/kg (standard error 0.12167 MJ/kg), whereas that of a standard diesel fuel is 45. The calorific value of the TPO was found to be similar to that reported by Martnez et al. [35] and Hürdoan et al. [38]. From Figure 2, it can be seen that incorporation of sodium carbonate catalyst

reduced the TPO calorific value from 40.431 MJ/kg at 0% to 39.182 MJ/kg at 10%. The lowest calorific value of TPO was recorded when 10% sodium carbonate catalyst was used. The calorific value of the TPO is lower than that of diesel fuel because of more aromatic compounds (-C=C-bonds) in the TPO [19, 39]. The increase in the amount of TPO molecules with shortened chain lengths may have also resulted in a reduction in calorific value [40, 41].

3.2. Flash Point. Figure 3 shows the variation of the flash point value of TPO with increasing percentage of sodium carbonate.

The TPO had a flash point of 51°C (standard error ± 0.6650°C), while diesel fuel had a flash point of 62°C. The flash point of TPO at 50°C has also been reported by Islam and Nahian [42] to decrease with an increase in sodium carbonate catalyst from 0% to 10%. Frigo et al. [36] reported a similar decrease in TPO flash point at a temperature of 58°C. When 10% sodium carbonate was used, the TPO in the current study found to be more flammable than in TPO samples obtained at lower sodium carbonate percentages. The flash point value for TPO in the present study was significantly lower than that recommended for diesel's fuel. The TPO comprised of more branched hydrocarbons than petroleum diesel and increased branching has been shown to lower the oil's flash and boiling points [43]. The TPO's low flash point could also be attributed to an increase in the concentration of short carbon–carbon bonds as the catalyst concentration rises [19].

3.3. Cetane Index. Figure 4 is a graphical summary of the results, showing how the cetane index of TPO varies with the percentage of sodium carbonate catalyst.

The cetane index for the TPO was determined to be 12.71 (standard error ± 0.24017). These results are similar with the result reported by Williams et al. [44] of 11.35. The

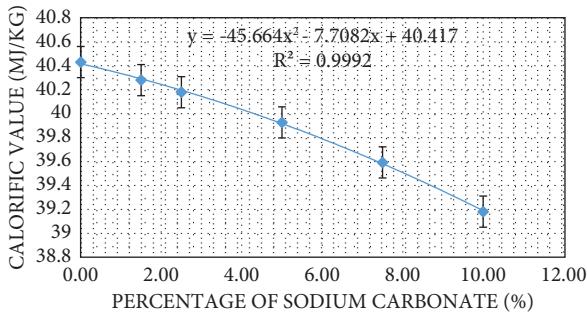


FIGURE 2: Variation in the calorific value of the TPO with increasing percentage of catalyst.

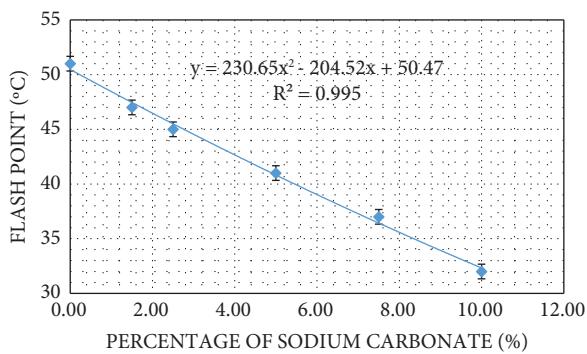


FIGURE 3: Variation of the flash point value of TPO with an increase in the percentage of catalyst.

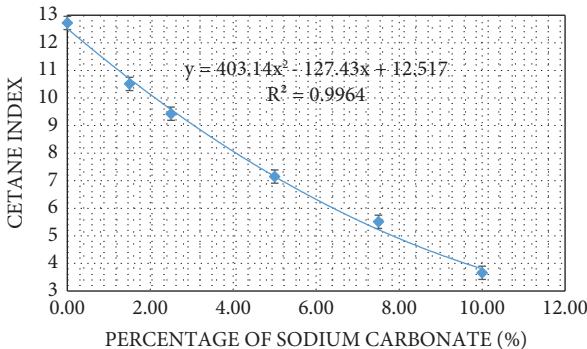


FIGURE 4: TPO cetane index variation with increasing percentage mass of catalyst.

recommended cetane index for diesel fuel is 47. As shown in Figure 4, the TPO's cetane index decreased with increasing sodium carbonate in the feed material. TPO contained unsaturated and branched hydrocarbons. The concentration of these branched and unsaturated hydrocarbons increased as more catalyst was incorporated in the feed material resulting in a reduction in the oil's cetane number and, consequently, poor ignition [45]. Increased branching has been shown to result in a reduction in TPO's recovery temperature, as well as increasing the oil's specific gravity and lowering its cetane index [43].

Thus, employing pure TPO to power an internal combustion engine can present a challenge. This is because of the oil's low cetane index which will lead to an ignition time

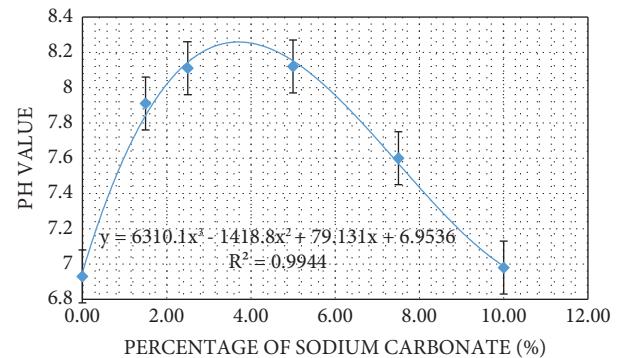


FIGURE 5: pH variation with increasing percentage of sodium carbonate.

delay when the oil is injected into the cylinder [46]. As a result, the TPO might have to be mixed with diesel fuel to meet the required cetane index. Suitable additives might also be added to the TPO to improve the oil's cetane index.

3.4. pH. Figure 5 is a graphical summary of the results, showing how the pH level of TPO varies with percentage of sodium carbonate.

The pH of TPO produced with 0.00% Sodium carbonate catalyst was found to be 6.93 (standard error ± 0.14867) and that of diesel fuel was found to be 4.44. This shows that the pH of the TPO was neutral while that of diesel was acidic. The pH number increased as the amount of catalyst in the feed material increased to 4%, and then decreased with any further addition of the sodium carbonate catalyst. All the TPO samples had pH values that bordered on neutral. Whereas Martnez et al. [35] realized that TPO has an alkaline pH of 7.5; Islam et al. [47] reported an acidic pH of 4.3.

The oil samples that had pH numbers of 6.93 and 6.98 at 0 and 10% sodium carbonate, respectively, indicated that oil had low concentrations of hydrogen ions. pH values above 7 generally indicate the presence of hydroxide ions in the oil. The pH increased with increasing sodium carbonate in the feed material and beyond 4% sodium carbonate catalyst, the pH gradually decreased. If the TPO samples were to come in contact with a metallic surface, they would be less corrosive compared to diesel fuel.

4. Conclusions

In the study, we investigated the effects of a sodium carbonate catalyst which increases oil yield during tire pyrolysis but also causes branching, unsaturation, and reduction of the carbon chain length of the oil, affecting its structure and composition. The structure and the composition of tire pyrolytic oil affected its calorific value, flash point, cetane index, and pH. The following conclusions were drawn from this study:

- (1) The TPO's calorific value was found to be equal 40.431 MJ/kg. It was lower when compared to diesel fuel and it decreased with an increase in sodium carbonate catalyst.

- (2) The TPO's flash point was found to be equal 51°C while for diesel fuel was 62°C. The TPO's flash point decreased with increasing catalyst concentration, reaching 32°C when 10% of the catalyst was used.
- (3) The cetane index of TPO was found to equal 12.71 and it gradually decreased to 3.66 with 10% sodium carbonate catalyst.
- (4) The TPO's pH value was found to be averagely neutral value since it was fluctuating between 6.93 and 8.12, whereas that of diesel fuel was found to be 4.44 which was slightly acidic.
- (5) Although previous studies have shown that the use of alkaline catalysts increases TPO yield, these catalysts seem to have an overall negative effect on the flash point, calorific value, and cetane index of the TPO.

In spite of the low calorific value, flash point, and cetane index, the sodium carbonate catalyst produced can be used as a preservative in wood treatment. Hydrogenation and distillation of the TPO can also be done and the resulting oil's properties can be determined.

Data Availability

The datasets used during the current study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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