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Design and Development of a promising Biochar-based Copper Catalyst

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Abstract

As about 70 percent of the air pollution comes from vehicles, automotive companies have always been seeking novel catalytic converters to reduce engine emissions. However, so far, a comprehensive research on the impact of copper catalytic converters on biochar has not been conducted. This research aims to study the effect of biochar-based catalytic converter on the amount of exhaust emissions in an XU7 engine. Two thicknesses of the biochar-based catalysts, 7 and 14 cm and Cu (No3)2 in two densities of 1 and 2 mmol were applied for the experiments. Five types of contaminants (i.e., CO, CO2, HC, O2 and NOx) were measured for the evaluation of exhaust emissions. In this study, the XU7 engine, which was produced in 2011, was used to perform the tests. The results showed that the levels of exhaust gases from combustion of the XU7 engine were low and acceptable in all treatments in comparison to the environmental standard. In addition, the catalyst used in the XU7 engine had a significant impact on the absorption of exhaust gas from the engine, especially for CO and the level of its concentration was significantly different in comparison with a new catalyst, biochar-based catalysts and control and also, for HC the levels of concentration were shifted applying biochar-based catalysts comparing to the new catalyst and control. Based on the results, it was observed that applying the proposed approach can be an effective step in reducing greenhouse gas emissions from combustion and increasing the life span of engines.

Keywords: XU7 Engine; Biochar;Copper catalyst;NOx;Exhaust emissions;

1. Introduction

The combustion time, in internal combustion engines, is limited by the engine's cycle to less than a second. Due to incomplete combustion of the fuel, the partial oxidation leads to emission of carbon monoxide (CO), nitrogen oxides (NOx) and a big range of volatile organic compounds (VOC), comprising hydrocarbons (HC), aromatics and oxygenated compounds. These emissions are particularly high during both stand-stills and velocity reduction, when inefficient air is taken in.

In order to decrease the harmful environmental effects of these emissions, catalytic converters are used within the car exhausts. The ordinary catalytic converters are composed of a metal guard with a ceramic honeycomb-like inside of it with protecting layers. This inner honeycomb has thin wall channels that are covered by aluminum oxide. This cover is porous and increases the surface area, letting more reactions to occur and comprising valuable metals, such as palladium, rhodium, and platinum. The amount of these metals are about 4-9 grams in a single converter. As the initial price of these metals is high and due to the expensive production of porous materials, always there has been the need to cheaper and simpler ones.

Biochar which is a residual by-product from pyrolysis of organic waste biomass, is rich in carbon, up to 50 wt%, and typically accounts for 15–40 wt% of the biomass feedstock[1]. Generally, biochar is similar to graphite that is mostly composed of the aromatic carbon rings linked together and arranged randomly and irregularly [2]. Consequently, biochar, which is an abundant and low-cost renewable carbon source, has pronounced potential to be applied as a cheap and promising catalyst. Additionally, biochar can be easily detached from catalysts by oxidation to recover the valuable metals[3].

Due to its cheap price and the easy preparation, biochar has got more attention in recent years[2-5]. Yan et al.[6]applied biochar in the synthesis of carbon-coated iron nano particles, so the catalytic activity on the conversion of synthesis gas to liquid hydrocarbons was evaluated. It was identified that a well-developed porous structure, which probably benefit the uniform dispersion of active components and stabilize these against sintering, are essential for a good catalyst support[6]. Some features of biochar assist its role as a catalytic material. For example, the incidence of inorganic, such as K and Fe in biochar

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contributes to its catalytic activity for tar cracking[7]. The functional groups of the surface in biochar could simplify the adsorption of metals, which is a necessary step for the production of biochar-supported catalysts [8]. Generally, the material is cheap and available everywhere, the methods of producing it is also applicable so the cost of making it is low and economic and it is possible to replace it with the conventional catalysts nowadays.

The Biochar-based catalyst is a new and promising method to be used as it is proved that this mesoporous material is a helpful one to absorb a large variety of gases and contaminants from different media, such as water, soil and air. Therefore, it is really suitable to trap and degrade the gaseous contaminants. In order to decrease the synthesis price of the catalytic converter, copper was chosen as a catalyzer to help the conversion processes within the converter. Therefore, the present work aimed at studying the catalytic application of biochar in using as catalytic material instead of honeycomb structure of the normal catalytic converters. The objective of this study is to propose a new catalytic converter for filtering the exhaust emissions with a reasonable price.

2. Materials and methods

2.1. Copper-based biochar preparation

The biochar was produced by the pyrolysis of dried chicken manure. The pyrolysis temperature was set to 400 °C. This temperature was obtained after about 30 min of heating with the carrier gas (N_2) sweeping at 0.3 L·min^{-1}, and the porcelain crucibles were fed into the heating zone with an N_2 flow rate of 0.03 L·min^{-1}. After 2 h, the pyrolysis process was stopped. The solid yield was the biochar, sieved through a 40 mesh (0.45 mm). Copper was used to be replaced with the expensive elements such as palladium, as an oxidating agent. The results did not show a clear difference between its usage and the control one. This could be due to lower amount of it or the oxidating function was not as well as palladium or rubidium. That is why the results were not significantly sharp.

2.2. Copper stabilization on the biochar

The initial mixture including 5 g of biochar and 2.482g (2 mmol) silver nitrate was prepared in a 250 ml flask. Then, 150 ml of deionized water was added to the mixture. A magnetic stirrer was used for stirring the resulting mixture at 75 °C for 24 h. The resulting product was filtered through a filter paper and washed several times with water and placed in an oven at 80 °C for 24 hours to get dried completely. The resulting precipitate was placed in the furnace for calcination at 550 °C for 5 hours[9]. This process has been summarized in Fig. 1. In order to make uniform samples, circular tablets were prepared from the material. The pressure of 10 bar was applied to ensure a proper texture of the tablets.

2.3. Engine condition and preparation

In this study, the XU7 engine, which was produced in 2011, was used to perform the tests. The data were taken from the vehicle in the on and off mode at idle speed (860 rpm).Before performing the tests, the engine was switched on for 15 minutes to reach the optimum temperature of the engine. The temperature of the radiator water in the engine was about 85±4˚C. This is due to different function of the engine in cold condition. In this case, after the engine reached the mentioned temperature the data collection was done by placing the prop of the device into the engine, for data collection. Temperature was about 27±3˚C.Exhaust emission parameters (O_2, CO, NO_X, CO_2, HC) were measured using AGS-688 (Italy). For this reason, the initial part of the sensor (suction) of the device was placed in the designed exhaust for the car.

2.4. Catalyst mold

A molded rectangular cube was made using galvanized sheet (thickness of 1.5 mm)in two different internal lengths of 7 and 14 cm (Fig. 2).

Figure 2. Designed catalyst mold

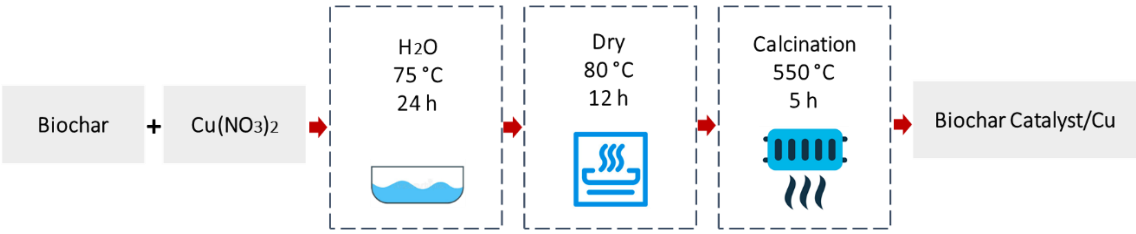

Figure 1. The preparation process of the catalyst.

2.5. Catalyst Implementation

The catalyst mold was designed and fabricated to replace the test specimens in two separate parts (door and mold case). For the catalyst die-casting, a refractory blanket was used. The test tablets were divided into four equal components and were placed in the mold (Fig.3).

2.6. The XU7 Test Engine

In this research, a XU7 engine made in 2011 was used for the experiments. Vehicle data were taken in clear mode at idle speed of 860 rpm. Before the tests, the engine was powered on for 15 minutes until the engine temperature reached its optimum point. The temperature of the radiator water in the engine was about 85±4 °C to perform in the pollutant conditions. For data acquisition, after the engine reached the specified temperature, a data device prop was used. The air temperature was about 27±3°C. Exhaust parameters (O2, CO, CO2,NOx, HC) were measured using AGS-688 device made in Italy. For the measurements, the inlet part of the exhaust sensor was inserted into a vehicle exhaust system.

2.7. Spectroscopy measurements

To investigate the percentage of copper fixed on the surface of biochar nanocavity, EDX spectroscopy (FESEM TESCAN, MIRA III, Czech Republic) of the catalyst was taken. Also, using ICP-AES the amount of copper metal in the biochar-stabilized copper composition was determined.

2.8. Data analysis

Analysis of variance was performed using completely randomized design and mean comparisons of treatments were performed using Duncan's multiple range test. The statistical analysis was done using SAS 9.1 software.

3. Results and Discussion

3.1. EDX Spectroscopy

Based on EDX spectroscopy, it was detected that there existed C, N, O and Cu elements in the catalyst. The percentage of elemental mass for 1 mmol of these elements was6.23%, 4.48%, 49.99% and 39.29% and for 2 mmol, it was 11.41%, 2.01%, 25.08% and 61.5%, respectively.

Each of the peaks shown in Figs 4 and 5 is unique for an atom and therefore represents only one element. Peaks higher in the spectrum mean higher concentrations of the element in the sample. The results of ICP-AES test showed that the amount of copper metal in the biochar-stabilized copper composition for 1 and 2mmol was 0.043 and 0.079 mmol/g, respectively.

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Figure 3. Preparation of the catalyst mold.

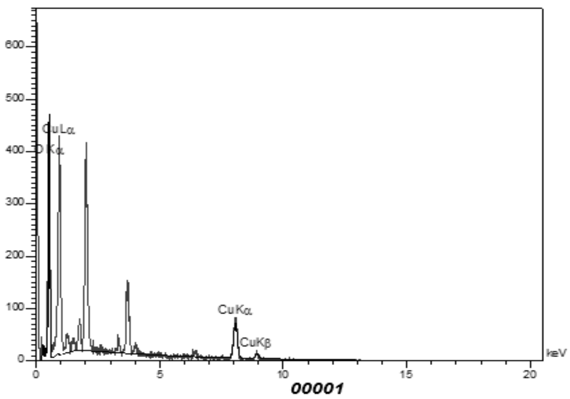

Figure 4. EDX diagram of the fixed Cu (1 mmol) on biochar.

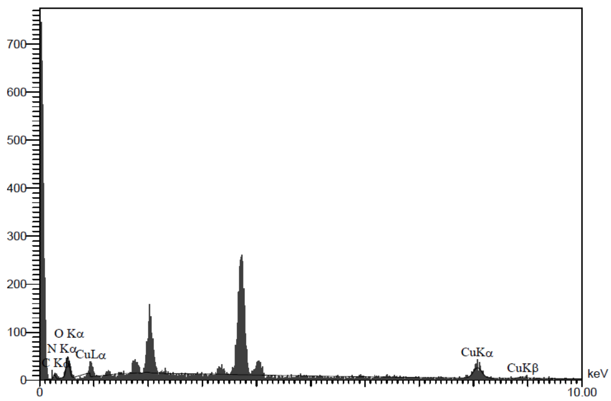

Figure 5. EDX diagram of the fixed Cu (2mmol) on biochar.

3.2. Analysis of variance

The results of the analysis for variables evaluated in XU7 engine are shown in table 1. As it is seen from the table, there were significant differences between different treatments regarding the extent of Co, HC, CO_2, and O_2, in the probability level of 1%. For λ (i.e. air to fuel ratio) there was a significant difference between catalytic treatments in the probability level of 5%. However, for the presence of NOx the difference was not significant.

3.2.1. Carbon monoxide

A comparison of the average volumetric CO concentration of the exhaust emitted by the XU7 engine with respect to the types of catalysts is given in Fig.6. As it can be observed, the average amount of CO emissions was lower than the standard limit(i.e. less than 2.5%). It is also notable that carbon monoxide is produced when the combustion is rich in fuel and air but the oxygen is insufficient. The results of the experimental treatments were significantly reduced for CO emissions of all treatments (in the probability level of 1%). The results showed that there was a significant difference between the proposed and non-catalyst treatments. However, there was no significant difference between experimental treatments.

3.2.2. HC

A comparison of the average concentration of unburned HC hydrocarbons in the exhaust of the XU7 engine with respect to the types of catalysts, biochar, proposed catalysts and no catalyst is shown in Fig. 7. As the figure shows, in the XU7 engine the average HC pollutant was below the standard limit (i.e. less than 250 ppm). This might be due to lack of several factors involved in the production of hydrocarbons, of which the most important are the non-stoichiometric fuel ratio, incomplete combustion, leakage and leakage volumes, leakage through outlet valve, simultaneous open valves, sediment, and oil on the combustion chamber wall. The results indicated that the effect of HC on engine exhaust gas level was significant and a significant difference between various treatments was observed (p>0.01).

According to the researches, HC and CO in vehicle exhaust oxidize and produce water and carbon dioxide. Catalytic engineering applied to automobiles is actually able to reduce CO and HC emissions up to ninety percentage [10] and particulate matter about fifty percentages is dipped down [11].

Table 1. The results of ANOVA test.

Sources of variation	Degree of freedom	Mean Squares					
		Co(%vol)	HC (ppm)	NOx (ppm)	CO_2(%vol)	O_2(%vol)	λ
Treatments	7	0.181**	5864.17**	0.0219ns	0.849**	0.259**	0.000131*
Errors	16	0.0014	159.417	0.389	0.0275	0.0155	0.0000375
CV (%)	-	5.865	11.539	4.118	1.2	10.209	0.592

**significance level p>0.01, *significance level p>0.05, ns not significant

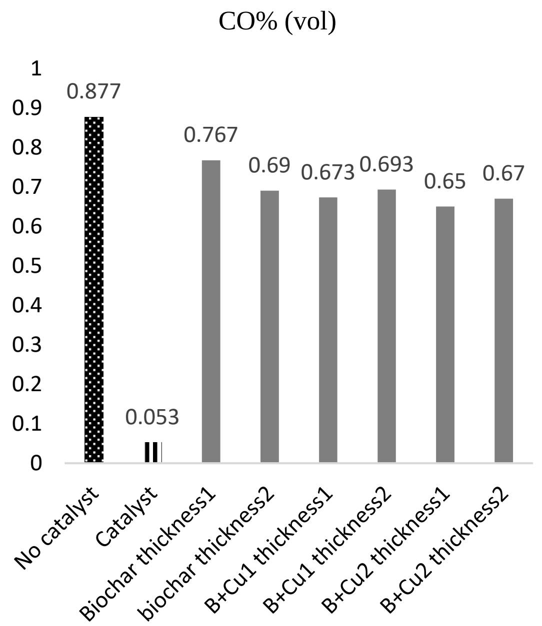

Figure 6. The amount of Co emissions in XU7 engine.

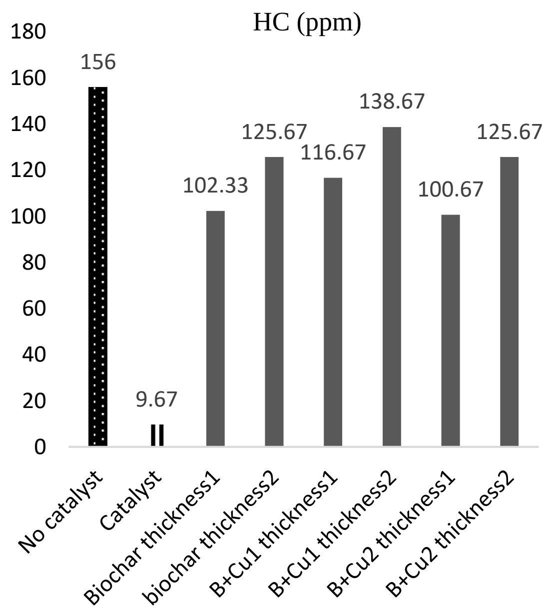

Figure 7. The amount of HC for XU7 engine.

Unburned hydrocarbons produced at the gasoline burning stage are converted to carbon dioxide and water vapor according to the oxidation process of Equation (1) [12]:

$$C_xH_{2x+2} + [(3x+1)/2]\ O_2 \rightarrow xCO_2 + (x+1)\ H_2O \quad (1)$$

The results indicated that the removal rate by the proposed catalyst was 0.1626 g per catalyst, and the adsorption by the metal catalyst fixed on biochar was 1.2296 g per catalyst. The results showed that reduction of HC for the thickness of 2 mm and density of 1 mmol had a significant difference with thickness of 2 mm and density of 2 mmol, thickness of 2 mm and density of 1 mmol.

3.2.3. CO_2

The results for the percentage of CO_2 emissions for all treatments have been presented in Fig. 8. It was observed that carbon dioxide produced in the XU7 was below the standard limit (more than 14%) with the exception of the catalyst-free case. This is a remarkable achievement for the proposed catalyst as the excessive carbon dioxide emissions worsens the global warming crisis.

In addition, the above results showed that in case of the proposed catalyst, the value of 0.0019 g per catalyst, gas increase was obtained, while the increased value of gas by the copper catalyst stabilized on biochar was achieved as 0.0041 g per g catalyst [13].

3.2.4. NOx

The results showed that the NOx produced in the XU7 was below the standard limit (i.e. < 50 ppm)(Fig. 9). The results showed that the effect of NOx on the gas output from the engine was not significant. For the proposed catalyst, the amount of gas absorption was 0.0003 g per catalyst. For the designed catalyst of copper fixed on biochar, the amount of gas absorption was 0.0018 g per catalyst. The results showed that there is no profound difference between the proposed catalyst and the other treatments.

3.2.5. O_2

Fig. 10 provides the results for the comparison of presence of O_2in the XU7 engine exhaust. The results showed that the amount of oxygen produced in the XU7 engine was below the standard limit (i.e. < 3%). The results showed that the effect of O_2 on engine exhaust level was significant ($p>0.01$).

According to the proposed catalyst, the amount of O_2 increased by 0.001 g per catalyst. However, the amount of gas released compared to the designed sample is 0.0028 g per catalyst. This is because of the decomposition of the water vapor produced in the gasoline combustion stage and due to the involvement of O_2 in the CO_2 and HC oxidation reaction of O_2.Installing the catalyst on the motor prevents the gas from releasing, which causes the exhaust gases to condense behind the catalyst to the smoke valve. This causes choking and impedes airflow into the engine.

The results showed that there was a significant difference between the proposed catalyst with other treatments. The highest mean value was obtained for catalyst-free combustion, indicating the highest amount of O_2 emission. In the proposed catalyst, the $O_2$was absorbed to a greater extent, indicating that the gas was involved in the catalytic reaction.

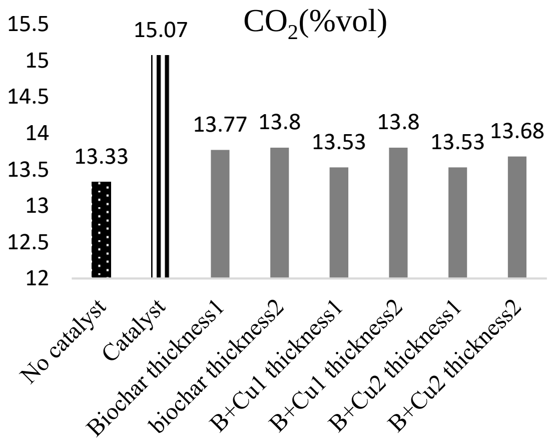

Figure 8. The amount of CO_2 gas for XU7 engine

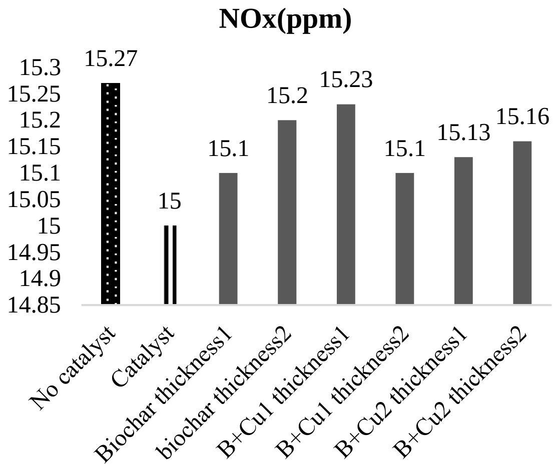

Figure 9. The amount of NOx gas for XU7 engine

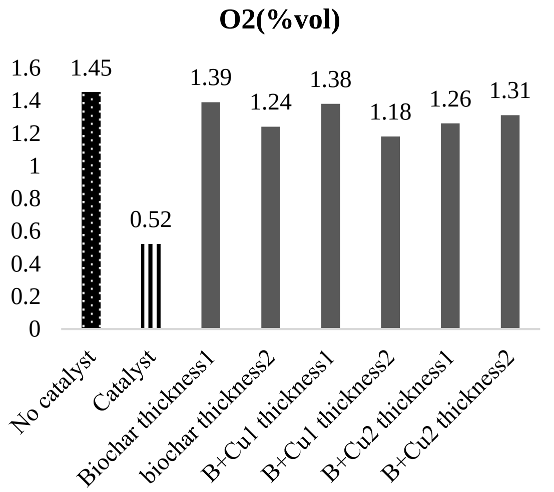

Figure 10. The amount of O_2 in XU7 engine exhaust.

3.2.6. Coefficient of λ

The results showed that the coefficient of λ in the XU7 engine was below the standard limit (i.e. < 3%)(Fig.11).The ratio of coefficient of λ increased with respect to the proposed catalyst sample. However, due to the catalyst-free state of approximately 0.0002 g/L, the reduction of λ was carried out using a catalyst-based converter based on the activated carbon (present in biochar substrate). This is because of the decomposition of the water vapor produced in the gasoline burning stage as well as the involvement of O_2 in the CO_2 and HC oxidation reaction of O_2. The less the O_2, the less the coefficient of λ of the inlet airflow to the engine.

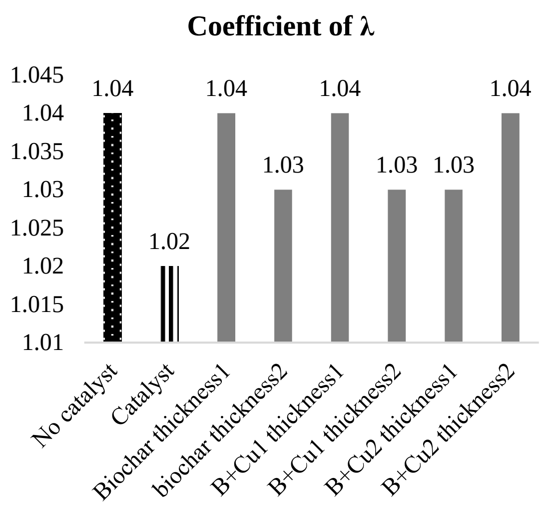

Figure 1. Coefficient of λ in XU7 engine**.**

4. **Conclusion**

The study presented a promising and cheap catalyst for the reduction of engine emissions. A copper catalyst supported on biochar was used as a catalytic converter in XU7 engine. The results showed that the proposed catalyst lowered all the measured contaminants (i.e. CO, CO_2, HC, O2 and NOx) to below the standard level. The proposed catalyst increased the ratio of air to fuel (λ) significantly in comparison to other treatments. According to the results, it is suggested that the usage of the proposed catalyst can be an effective step in reducing greenhouse gas emissions combustion and increasing the life span of engines.

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