

## Nanocatalyst manganese oxide (MnO) for exhaust emissions (CO and HC) reduction

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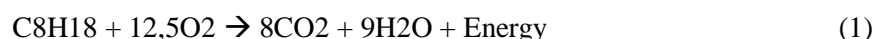
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**Abstract** The growing number of motor vehicles, particularly the exhaust gas as a result of incomplete combustion of fuels, has a very adverse impact on the environment. One effort to reduce exhaust emission levels is by applying a catalytic converter to the exhaust system. MnO is a chemical mixture that can be applied to a catalytic converter to reduce exhaust emissions because it is capable of binding CO and HC contained in motorcycle exhaust gases. This research was an experimental research aiming to investigate the difference in emission level of CO and HC between a motorcycle with and without a catalytic converter. The types of fuel used were RON 88 and RON 92. The results showed that the application of MnO as a catalyst could reduce the level of CO significantly in RON 88, i.e. 24.36%, and the level of HC in RON 88 and RON 92, i.e. 82.08% and 38.14 % respectively.

### 1. Introduction

Technological developments in various fields, particularly in the field of land transportation, have resulted in a massive increase in the number of vehicles with different types and brands. Emissions discharged from motor vehicles consist of 70.50% CO, 18.34% HC, 8.89% NO<sub>x</sub>, 0.88% SO<sub>x</sub>, and 1.33% other particles [1]. The combustion process converts fuel energy into motion. Energy transformation is derived from the combustion of fuel. According to the theory of complete combustion, a combustion reaction is represented as follows:



In real conditions, air contains  $\pm 21\%$  O<sub>2</sub> and  $\pm 79\%$  N<sub>2</sub>. On top of that, complete combustion can only occur in a laboratory. Thus, in practice, the following combustion reaction takes place:

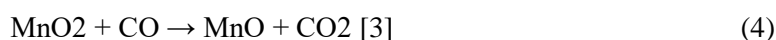


On the basis of the equation (2), one mol of fuel requires 12.5 mol of air to produce 8 mol of CO<sub>2</sub>, 9 mol of H<sub>2</sub>O, 12.5 (79/21) mol of N<sub>2</sub> and energy [2].

Emissions generated from vehicle exhaust are the result of incomplete combustion. The chemical reaction of incomplete combustion in the engine combustion chamber is as follows:



MnO used as a catalytic converter to reduce motor vehicle emissions reacts directly with the exhaust gases in the exhaust system and has the following chemical reaction:



The above reaction shows that MnO is able to reduce exhaust emissions generated by motor vehicles. In some studies, a catalytic converter is attached to a vehicle's exhaust tip. In general, the study material consists of two main parts: the inside and outside of the catalytic converter.

The use of a catalytic converter to reduce exhaust emissions produced by motor vehicles is constantly encouraged. Most catalytic converters for motor vehicles are pellet-type and monolithic-type catalysts and made of noble metal materials, such as palladium (Pd), platinum (Pt) and rhodium (Rh). These metals have high volatility (tendency to vaporize), are easily oxidized, and break easily at 500-9000°C, resulting in a reduction in catalyst activity.

Materials known as oxidation catalysts are platinum, plutonium, nickel, manganese, chromium and other metal oxides, while some metals used as reduction catalysts are iron, copper, nickel alloys and other oxide materials. In addition, several metals are oxidizable substances and reduction catalyst materials. From larger to smaller crystallite size, those metals are Pt, Pd, Ru > Mn, Cu >> Ni > Fe > Cr > Zn [4]. This type of catalytic converter can reduce exhaust emissions (CO, HC, NO<sub>x</sub>) by 16% to 80% [5]. Therefore, optimizing the ability of catalytic converters to reduce exhaust emissions is necessary [6].

The focus of this research was to determine the effect of MnO as a catalyst on RON 88 and RON 92 fuel to reduce exhaust emissions (CO and HC), since RON 88 contained of 88% of iso-octane and 12% of n-heptane. Content of 12% n-heptane caused RON 88 had low maximum boiled point, while RON 92 contained of 92% iso-octane and 8% of n-heptane. MnO selection as catalyst, due to MnO was material oxide thus decrease exhaust emission of fuel combustion [7, 8]. The others properties of MnO was greatly used as adsorbent, thus that material could be utilized as catalyst [9].

## 2. Methodology

MnO that used as adsorbent was nano powder of MnO, after synthesis process by using sol-gel method. Synthesis process passed through several steps; they were weighing, stirring, crushing, and sintering. MnO was placed between three layers of glasswool, each of which weighs 0.5 grams; 0.33 grams of MnO were filled in between layers. Overall, the amount of MnO used was one gram. As proposed by [7], 1 gram of reactant substance is used in a catalyst to absorb other substances [7].

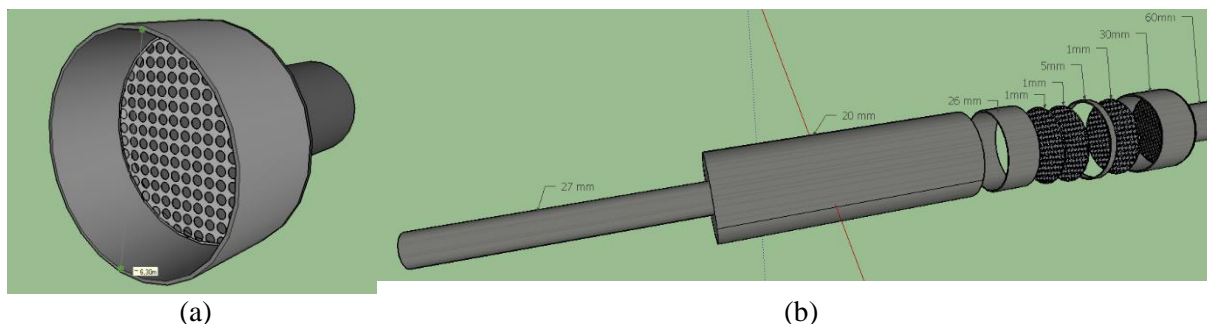
Next, the three layers of glasswool were inserted into a catalyst chimney which was connected to the motorcycle exhaust shown in Figure 1(a) which is where the catalyst is located. Then, the effect of the catalyst on the motorcycle exhaust emissions was examined.

Each layer of glasswool was flanked by two hollow sieves made of iron, a total of four. Thus, two layers of glasswool were made. On the first layer, glasswool was placed in the middle of the iron sieve, while on the second layer it was placed on the edge of the iron sieve, shown in Figure 1(b). As a result, there was no exhaust gas that could pass through the glasswool layers containing MnO.

The catalyst chimney was used to store MnO inserted in the glasswool layers as an absorbent (catalyst) for CO and HC emissions. This tube was made of galvanized iron with the design as follows:

A gas analyzer was used to examine the exhaust emissions generated from a motorcycle with and without a catalyst converter by comparing the amount of CO and HC emitted. The data result obtained

from gas analyzer that be able to analyze the result of CO which was the emission from fuel combustion [10-12].



**Figure 1.** Design of adsorption tube, (a) glasswool head place and (b) full design.

### 3. Results and discussion

#### 3.1 Phase Characterization

The phase identification was performed using the X-Ray Diffraction (XRD) aimed to compare the crystalline phases in the materials and powders, and analyze the properties of the structure (crystallite size, phase composition, crystal orientation, and crystal defect) in each phase [13, 14].

The crystallite size of MnO materials can be determined using the following Scherer Equation [15, 16]:

$$d = \frac{K \lambda}{\beta \cos \theta} \quad (5)$$

where:

- d: Crystallite Diameter
- K: Constant = 0,89-0,9
- $\lambda$ : Wavelength = 1,5406 Å
- $\beta$ : Full-Width Half Maximum (FWHM).

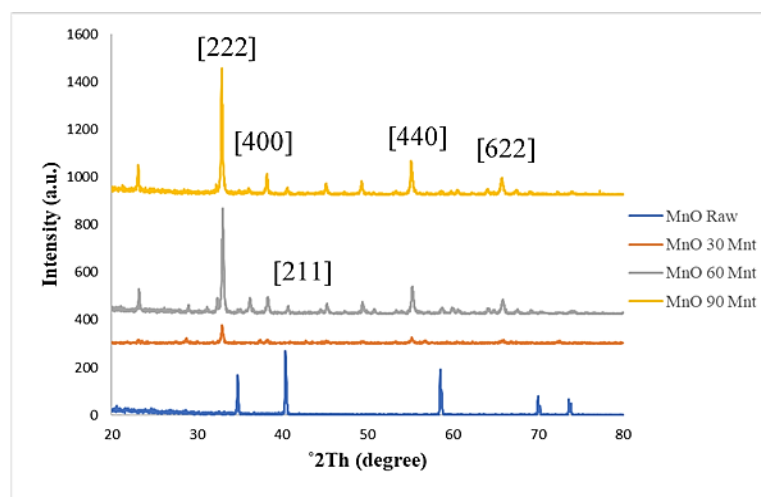
The results of calculation using the above equation are presented in Table 1. It shows that the crystallite size of the synthesized MnO powders sintered at different times (30, 60, and 90 minutes) was relatively small compared to the raw MnO powders which had the size of 143,44 nm. The comparison of all MnO samples is also shown in the graph of intensity and  $2\theta$ , is shown in Figure 2.

**Table 1.** Intensity, FWHM, d-spacing and crystallite size of MnO.

Sample Material	X-Ray Diffraction (correspond to [222] peak)			
	Intensity (counts)	FWHM (rad)	d-spacing (Å)	Crystallite Size (nm)
Manganese Oxide (MnO) raw	264.33	1.03	2.23	143.44
Manganese Oxide (MnO) 30 minutes	72.00	0.17	2.71	47.30
Manganese Oxide (MnO) 60 minutes	436.62	2.40	2.71	68.30
Manganese Oxide (MnO) 90 minutes	516.91	1.71	2.72	84.55

The transition of MnO from grain to crystallite size is demonstrated in the graph above; there was a very significant change between the raw MnO and the synthesized MnO with various sintering times (30, 60 and 90 minutes). The transition occurred as a result of the synthesis process with variations in sintering time. The shift of crystalline intensity (as shown in Figure 2) indicated that during the sintering

process there was development in MnO nanopowders. The shifting and increasing of peak occurred in sintering process while conducting synthesis process of MnO, thus, the crystal intensity shifted (as showed at Figure 2 [17]). The crystalline intensity is a peak that indicates an increase in the purity level of MnO nanopowders. Figure 2 shows that the change or shift from the MnO peak is obvious. The peak that underwent such a shift is peak [222]. Peak [222] was like the fingerprint of MnO. MnO has several peaks, namely [111], [200], [220], [311], and [222], respectively [9, 18, 19]. Peak [222] represented the peak of MnO, since the result of XRD analysis showed the peaks at Figure 2 [9, 18]. Shifting and peak intensity containing one of the above MnO peaks indicate that the purity level of MnO is increasing. The similarity of position of the crystalline intensity indicated that the crystalline intensity was a single phase. Single phase also showed that the cubic structure centered in the MnO nanopowders already contained electrons in each atom and also a large number in the lattice. As a result, the electrons in the atoms of MnO nanopowders can be used effectively as a catalyst or as the main material in the production of batteries; in fact, the movement of the MnO atoms containing electrons reacts and spreads very quickly.



**Figure 2.** Phase identification of MnO with different sintering times.

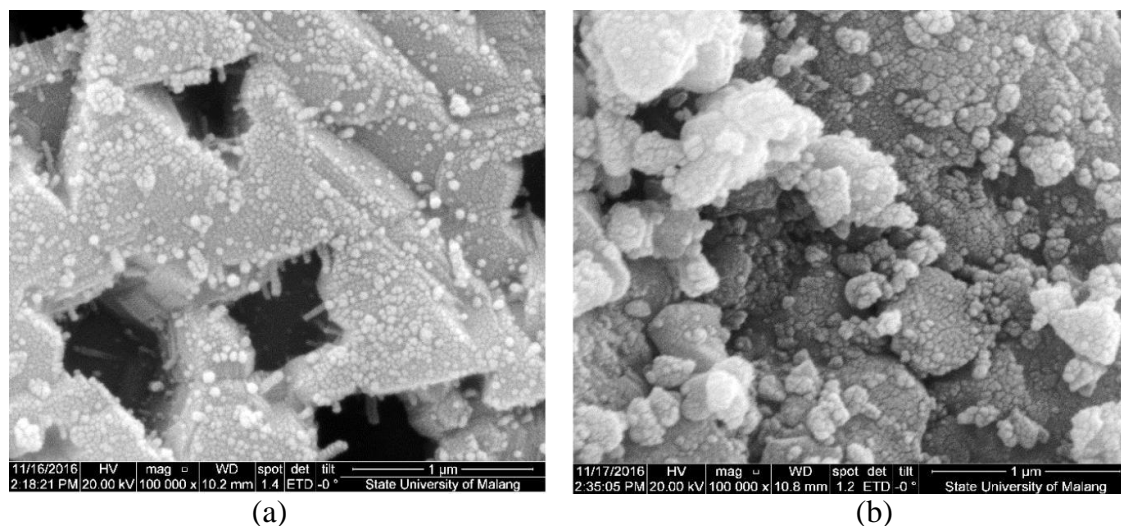
Table 1 shows that the variation in crystallite size was influenced by the duration of the crushing process, whereas the difference in crystalline purity or intensity was affected by the variations in sintering time. The longer the sintering time is carried out (according to the atomic development limit of MnO), the higher the purity level. The best purity and size of the three samples with various sintering times occurred at the sample sintered for 60 minutes the crystalline intensity or purity level was 436.62 counts, and the size was 68.30 nm. It can be concluded that the use of sol-gel method a simple method without many treatments in the synthesis process, can produce MnO nanopowders with great purity level and very small crystallite size compared to the raw MnO powder of micron size. The results of the XRD test are highly relevant because of the beam of X-ray is shot directly at the object being tested.

### 3.2 Morphological characterization

SEM was used to analyze and compare the morphology of MnO materials [20, 21]. The analysis aimed to examine whether there was a change in the morphology of MnO after undergoing different synthesis processes. Morphological changes that occurred in the synthesized MnO with variations in sintering time as the results of SEM are shown in Figure 3.

The different morphologies of MnO can be seen from the results of SEM at a magnification of 100k. The results showed morphological changes in MnO due to variations in sintering time. The changes may be caused by the temperature of 600 °C, as stated by [17] that drying and shrinkage occur due to

the sintering process. Drying and shrinkage occurred due to molecular reactions occurring at room temperature, gel formation and drying solution. Under these conditions the mixed materials have many characteristics morphologies and manganese oxide (MnO) which corresponds to the sintering temperature range, starting from 600 °C to 1000 °C.



**Figure 3.** Morphology of manganese oxide (MnO), (a) without synthesis and (b) synthesis with 60-minute sintering.

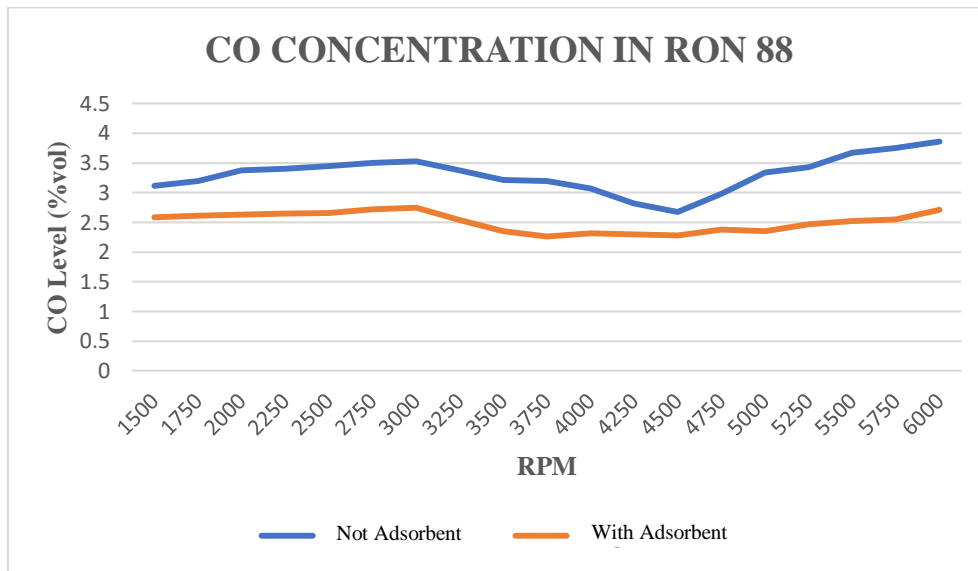
Figure 3 shows the raw MnO morphology-which is not synthesized. SEM is used to check the MnO standard morphology at 100k magnification. The results show that the raw MnO is triangular in shape. The difference in grain shape on the surface shows that agglomeration occurs when particles are deposited on the membrane of the MnO grains. MnO powders were tested using SEM to determine the initial form of MnO powder prior to synthesis. The different things occur in MnO synthesized with various sintering times (30, 60, dan 90 minutes), the initial shape of MnO (triangular with little dots) turned into spheres with agglomeration (grouping of granules in some places). This was influenced by the sintering temperature (600 °C) and time (30 minutes), and the duration of the crushing process. The transition of MnO from micro to nano indicates that the synthesis had been successfully done.

The SEM results at 100k magnification (as shown in Figure 3) show that MnO morphological changes also occur as a result of 60-minute sintering. There were no significant changes in grain form compared to 30 min sintered MnO. However, morphological differences are indicated by the number of spheres in which large agglomerations occur. Due to sintering process and duration of crushing thus the agglomeration enlarge but the diameter of powder became smaller [22]. It can be concluded that the transition of MnO from micro to nano was successful. This could occur due to the duration of sintering, the uneven crushing, and the duration of crushing.

### 3.3 The addition of MnO as a catalyst could reduce carbon monoxide (CO) emissions in RON 88

Data on the concentration of CO in RON 88 are presented in Figure 4. It shows, the use of MnO catalyst resulted in lower CO emission levels than that without a catalyst. In principle, the maximum adsorption process occurs only in catalysts having nanoparticle size. As proposed by [8], the smaller the nanoparticle size, the wider the contact, hence a high absorbency [8]. Rami Nader, *et al.* (2014) also explained that in the form of nanoparticles, atoms have the ability to make direct contact with other substances better than larger particles [23]. The application of MnO to RON 88 showed quite significant results. Without the use of MnO catalysts, RON 88 produced high CO emissions, i.e. 3.86% vol, while with MnO catalysts, the highest CO concentration reached only 2.735% vol.



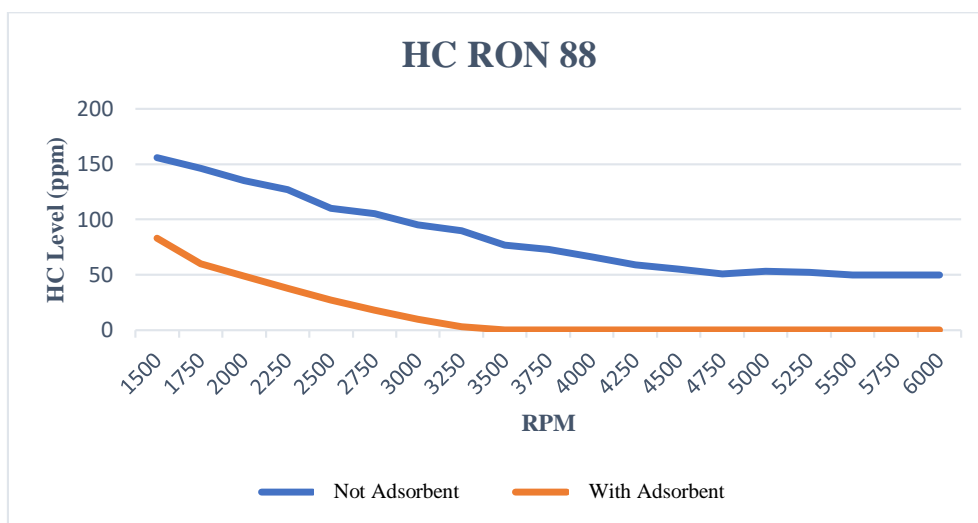


**Figure 4.** Comparison graph of CO level with and without a catalytic converter in RON 88.

Based on the mean value, the level of CO in the treatment with the addition of MnO catalyst was lower than that in the non-catalyst treatment, and both treatments had a significant difference. Thus, it can be concluded that the addition of MnO as a catalyst in RON 88 results in lower CO emission levels. This demonstrates that MnO as a catalyst affects vehicles with RON 88 fuel positively it can significantly reduce CO emissions.

### 3.4 The addition of MnO as a catalyst could reduce hydrocarbon (HC) emissions in RON 88

Data on the concentration of HC in RON 88 are presented in Figure 5. The motorcycle-generated hydrocarbons come from fuels that break down due to a heat reaction which then turns into other HC



**Figure 5.** Comparison graph of HC level with and without a catalytic converter in RON 88.

clusters emitted along with the exhaust gas:



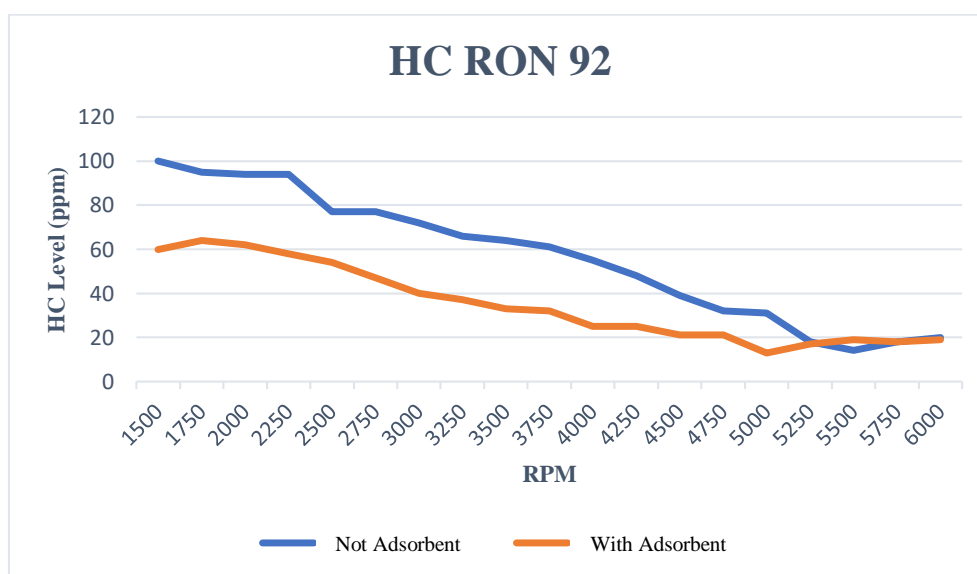
Hydrocarbons are crude fuels which are unburned during combustion processes in a combustion chamber. They are the crude fuels left on the cylindrical wall after combustion and emitted. They are also unburned gas in the combustion chamber after misfiring when the engine is accelerated or decelerated [24].

The maximum adsorption process occurs only in nanoparticle-sized catalyst materials. The microparticle-MnO catalyst used in the treatment in this study was fairly capable of showing significant differences compared with the treatment without using a catalyst. In fact, the HC emissions in the treatment without a catalyst were high with the highest HC of 156 ppm, whereas that with the use of MnO catalyst had the highest HC of only 83 ppm.

In sum, it is known that the addition of MnO as a catalyst in RON 88 results in lower HC emission levels. This shows that the use of MnO as a catalyst in vehicles with RON 88 fuel can significantly reduce HC emissions.

### 3.5 The addition of MnO as a catalyst could reduce hydrocarbon (HC) emissions in RON 92

Data on the concentration of HC in RON 92 are presented in Figure 6. At a high rotation rate (5750 RPM), the HC produced by both treatments had the same level of concentration *i.e.* 18 ppm. It happened due to the fact that the higher the temperature, the lower the level of HC.



**Figure 6.** Comparison graph of HC level with and without a catalytic converter in RON 92.

Based on the mean value, the level of HC in the treatment with the addition of MnO catalyst was lower than that in the non-catalyst treatment, and both treatments had a significant difference. Thus, it is known that the addition of MnO as a catalyst in RON 92 results in lower HC emission levels. This indicates that MnO as a catalyst could significantly reduce the HC emissions from vehicles with RON 92 fuel.

## 4. Conclusion

Based on the research and discussion on the application of manganese oxide (MnO) as a catalyst in RON 88 and RON 92 fuel to reduce exhaust emissions (CO and HC), we conclude that:

1. Using MnO as a catalyst is only effective to reduce CO emissions from motor vehicles using RON 88 fuel (24.36%), not those using RON 92 fuel since they used microparticle-sized MnO—the most effective size is catalysts in nanoparticles. Also, since RON 88 fuel has a low maximum boiling point, MnO could react faster to bind the exhaust emissions.

2. Using MnO as a catalyst is only effective to reduce HC emissions from motor vehicles using RON 88 (82.08%) and RON 92 fuel (38.14%), not those using RON 90 and RON 98 fuel. MnO could react well in RON 88 and RON 92 because they produced high HC levels and had a low maximum boiling point

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