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EFFECT OF NANO-TIO$_2$ ADDITION TO DEXLITE DIESEL FUEL ON GAS EMISSIONS

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ABSTRAK

Peningkatan jumlah kendaraan diesel di Indonesia menyebabkan peningkatan kebutuhan energi bahan bakar solar, sehingga penggunaan bahan bakar harus dikelola seefektif dan seefisien mungkin. Pada penelitian ini, penambahan aditif nanopartikel TiO2 pada Dexlite dilakukan dengan menggunakan metode ultrasonic bath. Setiap batch sintesis dilakukan dengan kapasitas 200 mL selama 20 menit, dengan variasi loading Nano-TiO2 pada Dexlite dari 0 mg/L hingga 200 mg/L. Kemudian dilakukan pengujian sifat fisik seperti densitas, viskositas, titik nyala dan nilai kalor. Selain itu juga dilakukan uji emisi. Ditemukan bahwa sifat fisik seperti densitas, viskositas, titik nyala dan nilai kalor dari Dexlite-Nano TiO2 tidak mengalami perubahan yang signifikan. Untuk uji emisi, hasil uji emisi hidrokarbon menunjukkan penurunan 74%, hasil uji emisi NOx menunjukkan penurunan 29%, hasil uji emisi CO menunjukkan penurunan 37%, hasil uji emisi CO2 menunjukkan peningkatan 24%. Penurunan NOx dicapai dengan menurunkan suhu nyala puncak setelah ditambahkan Nano-TiO2. Penurunan hidrokarbon, penurunan CO dan peningkatan emisi CO2 dicapai dengan tingkat pembakaran sempurna yang lebih tinggi, dari O2 yang disuplai oleh Nano-TiO2.

Kata Kunci: *Nano-TiO2, Dexlite, Ultrasonic Bath,* Sifat Fisik, Uji Emisi

ABSTRACT

The increase in the number of diesel vehicles in Indonesia causes an increase in diesel fuel energy demand, so that the use of fuel must be managed as effectively and efficiently as possible. In this study, the addition of TiO2 nanoparticle additives to Dexlite carried out using the ultrasonic bath method. Each batch of synthesis carried out with a capacity of 200 mL for 20 minutes, with variations in Nano-TiO2 loading on Dexlite from 0 mg/L to 200 mg/L. Then tested for physical properties such as density, viscosity, flash point and heating value. They were also tested for emission tests. It was found that the physical properties such as density, viscosity, flash point and heating value of Dexlite-Nano TiO2 did not change significantly. For the emission test, the hydrocarbon emission test results showed a 74% decrease, NOx emission test results showed a 29% decrease, CO emission test results showed a 37% decrease, CO2 emission test results showed a 24% increase. The decrease in NOx achieved by lowering the peak flame temperature after Nano-TiO2 added. The decrease in hydrocarbons, decrease in CO and increase in CO2 emissions achieved by a higher degree of complete combustion, from the O2 supplied by Nano-TiO2.

Keywords: *Nano-TiO2, Dexlite, Ultrasonic Bath, Physical Properties, Emission Test*

I. INTRODUCTIONS

According to the Central Bureau of Statistics, in Indonesia alone, there was an increase in the number of diesel vehicles at a rate of 0.5% per year from 2014 to 2018. This increase in number is associated with an increase in population that continues to climb every year. The increase in the number of diesel vehicles also leads to increased demand for diesel fuel energy. As informed by the International Energy Agency (IEA), this forecast is in line with that recorded by BPS, where the IEA said that energy consumption will increase by 28% between 2015 - 2040. The increasing demand for energy from fossil fuels contrasts with the dwindling availability of fossil fuels in nature, so the use of fossil fuels must be managed as effectively and efficiently as possible.

One effort to improve the performance of fossil fuels is the addition of TiO2 as an additive to diesel and biodiesel fuels. Some previous studies state that there is a reduction in NOx, CO, CO2 and hydrocarbon emissions. One by adding 40 ppm nano-TiO2 to Calophyllum inophyllum-based biodiesel, a 23% reduction in CO and 12% reduction in hydrocarbon emissions was obtained (Praveen, 2017). Another one by adding 250 mg/L nano-TiO2 to diesel fuel with a C.I. engine, obtained a reduction in hydrocarbon emissions by 18% and CO by 25% (D'Silva, 2015). The other one by adding 5% nano-TiO2 to diesel fuel blends with Aphanizomenon Flos-based biodiesel, obtained a 27% reduction in CO and hydrocarbon emissions (Jayabalaji, 2019).

In this study, the addition of Nano-TiO2 to Dexlite was carried out, Nano-TiO2 dispersion in Dexlite using ultrasonic waves with water media (Praveen, 2017). Then proceed with density, viscosity, flash point, calorific value, and emission test results. From this study, a synthesis method was obtained that produced Nano-TiO2 loading which gave the best emission reduction results.

II. METHODS

The type of research conducted is both quantitative and qualitative. Qualitative methods can be seen by means of visible vision of diesel fuel samples that have been given TiO2 additions (Yusof, 2021). Quantitative methods in the form of numerical characterization of calorific value, as well as analysis of exhaust gas calculation experiments. This research follows flowchart as shown in figure 1 below.

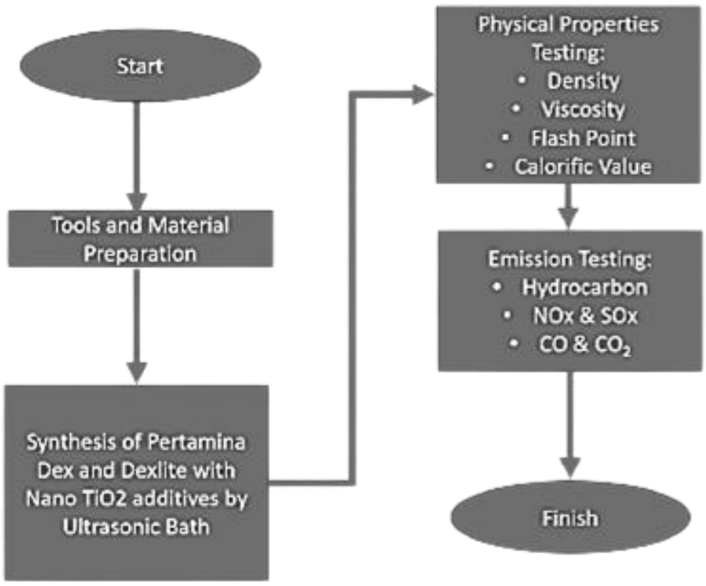

Figure 1. Research Flowchart.

The materials to be used in this research are diesel fuel produced by PT Pertamina, namely Dexlite, and Nano-TiO2 with the trademark P25 Degussa. Nano-TiO2 is a material with photocatalytic activity (Ma, 2014). The picture of the material can be seen in Figure 1 below. The tools to be used in this research are diesel flash point test device, diesel density test device, diesel calorific value test device, diesel viscosity value test device, ultrasonic bath, and glass bottles as diesel samples (Vyas, 2016). The research was carried out in 2 places, namely in the synthesis in the downstream lab of PEM AKAMIGAS and emission tests in the ALIFIA WORKSHOP in BLORA.

Figure 2. Nano-TiO2 Degussa (left) dan Dexlite (right).

The addition of nano-TiO2 by ultrasonication method will follow the journal by D'Silva in 2015 entitled "Performance and emission characteristics of a C.I. engine fuelled with diesel and TiO2 nanoparticles as fuel additive". Ultrasonication was carried out in a batch capacity of 200 mL for 20 min, with variations of nano-TiO2 loading in diesel of 40 mg/L, 80 mg/L, 120 mg/L, 160 mg/L and 200 mg/L (Mahbubul, 2017). Testing of the physical properties of diesel was carried out in the downstream lab of PEM AKAMIGAS. The parameters tested were calorific value, flash point, density, and viscosity. Samples were taken in triplicate, with the average value taken. The negative control is a sample with nano TiO2 loading of 0 mg/L, other than that is a positive control. Diesel fuel emission testing was carried out at ALIFIA BLORA workshop. The parameters tested were NOx, SOx, CO, CO2 and hydrocarbon emissions (Singh, 2016). Variations of Nano-TiO2 loading in diesel were 100 mg/L and 200 mg/L. Samples were taken in triplicate, with the average value taken. The negative control is the sample with nano TiO2 loading of 0 mg/L, loading nano TiO2 above 0 mg/L is the positive control.

III. RESULTS AND DISCUSSION

3.1. Synthesis Results

The synthesis was carried out by adding Nano-TiO2 and Dexlite in a capacity of 200 mL in an ultrasonic bath for 20 minutes. With the loading variation of Nano-TiO2 in Dexlite is 40 mg/L, 80 mg/L, 120 mg/L, 160 mg/L and 200 mg/L, the results are as shown in Figure 3 and 4 below.

Figure 3. Synthesis of Dexlite – Nano TiO_2.

Figure 4. Synthesis Results of Dexlite-Nano TiO2 with loading of 40, 80, 120, 160 and 200 mg/L.

It can be seen from Figure 4 above, that the Dexlite product changes color from golden brown to more whitish brown, this happens because the white nano-TiO2 has been well dispersed into all parts of the Dexlite product. It can also be seen that the level of whiteness also increases as the amount of nano-TiO2 loading increases. This indicates that nano-TiO2 has been dissolved in diesel products. Limitation of loading above 200 mg/L is done because above loading 200 mg/L, nano-TiO2 will not dissolve (D’Silva, 2015). Table 1 below shows the calculation of the mass fraction components of each solution. From table 1 below, it can be seen that the mass fraction of TiO2 compared to Dexlite is very small, but the color change is clearly visible because TiO2 is in a very small nanoscale so that it can be dispersed well in Dexlite.

Table 1. Calculation of Mass Composition of Dexlite - Nano TiO_2.

Loading of TiO2 (mg/L)	**0**	**40**	**80**	**120**	**160**	**200**
Dexlite mass (mg)	851000	851000	851000	851000	851000	851000
TiO2 mass (mg)	0	40	80	120	160	200
Total mass	851000	851040	851080	851120	851160	851200
Dexlite mass fraction	1,00000	0,99995	0,99990	0,9998	0,9998	0,9997
TiO2 mass fraction	0,00000	0,00004	0,00009	0,0001	0,0001	0,0002

3.2. Density Testing

Density testing was carried out with a density measuring device in the form of a densitometer. The results are shown in Table 2 below.

Table 2. Density Measurement of Dexlite – Nano TiO_2.

Loading of Nano TiO_2 (mg/L)	**Data 1 (g/cm^3)**	**Data 2 (g/cm^3)**	**Data 3 (g/cm^3)**	**Data Average (g/cm^3)**
0	0,8366	0,836	0.83482	0,8366
40	0,8348	0,8348	0,8349	0,8348
80	0,8349	0,8349	0,8349	0,8349
120	0,8349	0,8349	0,8487	0,8349
160	0,8349	0,8349	0,8349	0,8349
200	0,8353	0,8349	0,8349	0,8353

As shown from table 2, there is no significant change from the addition of nano-TiO2 loading with density. This is due to the small loading of nano-TiO2 in the sample, which is on the mg/l scale. When applied to the mixture density formula as in equation (1), the density contribution of TiO2 is very small. As seen in table 1 which shows the mass fraction of nano-TiO2 to Dexlite is so small that there is no significant change in density.

$$\rho\ mixture = \sum \rho i\ .\ xi = (\rho\ dexlite.x\ dexlite) + (\rho TiO2.xTiO2) \qquad (1)$$

3.3. Viscosity Testing

Viscosity testing was carried out with a viscosity meter in the form of a viscometer. The results are shown in table 3 below. As shown from table 3, it can be seen that there is no significant change from the addition of nano-TiO2 loading with viscosity.This is due to the small loading of nano-TiO2 in the sample, which is on the mg/l scale. When applied to the mixture viscosity formula as in equation (2), the density contribution of TiO2 is very small. As seen in table 1 which shows the mass fraction of nano-TiO2 to Dexlite is so small that there is no significant change in viscosity.

Table 3. Viscosity Measurement of Dexlite – Nano TiO_2.

Loading of Nano TiO_2 (mg/L)	Data 1 (mm^2/s)	Data 2 (mm^2/s)	Data 3 (mm^2/s)	Data Average (mm^2/s)
0	4,1076	4,0685	4,0489	4,0750
40	4,4499	4,4108	3,9609	4,2739
80	4,3521	3,9120	4,1076	4,1239
120	3,9609	4,4206	3,9218	4,1011
160	4,0098	3,9120	3,9902	3,9707
200	3,9218	3,9120	3,9120	3,9153

$$\mu\, mixture = \sum \mu i\, .\, xi = (\mu\, dexlite. x\, dexlite) + (\mu TiO2. xTiO2) \quad (2)$$

3.4. Flash Point Testing

Flash point testing was conducted using the ASTM D92-18 method. Results were obtained as in table 4 below.

Table 4. Flash Point Testing of Dexlite – Nano TiO_2.

Loading of Nano TiO_2 (mg/L)	Data 1 (^0C)	Data 2 (^0C)	Data 3 (^0C)	Data Average (^0C)
0	90	88	87	88,3
40	91	90	90	90,3
80	90	88	86	88,0
120	89	88	87	88,0
160	88	88	89	88,3
200	89	87	90	88,7

As shown in Table 4, there is no significant change from the addition of nano-TiO2 loading to the flash point. This is due to the small loading of nano-TiO2 in the sample. When applied to the mixture flash point formula as in equation (3), the contribution of the density of TiO2 is very small. As seen in table 1 which shows the mass fraction of nano-TiO2 to Dexlite is so small that there is no significant change in flash point.

$$LFL\, mixture = \sum \frac{xi}{LFLi} = \left(\frac{x\, Dexlite}{LFL\, Dexlite}\right) + \left(\frac{x\, TiO2}{LFL\, TiO2}\right) \quad (3)$$

3.5. Calorific Value Testing

Calorific value testing was carried out with a calorimeter device. Samples were measured with a uniform mass of 0.2 grams and a fusion length of 8 cm. Next, the sample is inserted into the device and the device will automatically analyze for approximately 5 minutes. The results of the calorific value analysis are displayed on the computer screen. The results are shown in Figure 3 below.

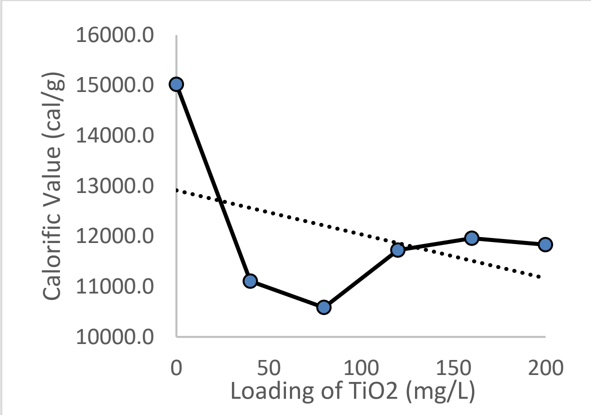

Figure 5. Results of Calorific Value of Dexlite – Nano TiO_2.

Figure 5 shows a decrease in the calorific value of the sample. This is due to the intervention of TiO2 in the Dexlite sample mixture so that it affects the calculation of the detected heating value. This decrease in calorific value affects the increase in BSFC (Brake-specific fuel consumption) in diesel engines. An increase in BSFC means a decrease in diesel fuel efficiency (Atzl, 2018).

3.6. Hydrocarbon Emission Testing

Hydrocarbon emission testing was conducted with an emission test device. Hydrocarbon emission testing was carried out at Alifia workshop, Blora. Hydrocarbon emission testing uses an emission test device that can read the amount of hydrocarbon emissions on the specified filter paper. The hydrocarbon emission test uses 1 liter of sample. The following hydrocarbon emission test results are shown in Table 5 & Figure 6.

Table 5. Hydrocarbon Emission Test of Dexlite – Nano TiO_2.

Loading of Nano TiO_2 (mg/L)	Data 1 (%)	Data 2 (%)	Data 3 (%)	Data Average (%)
0	18,7	11,4	8	12,70
100	8,9	5,5	3	5,80
200	5,9	2,1	1,9	3,30

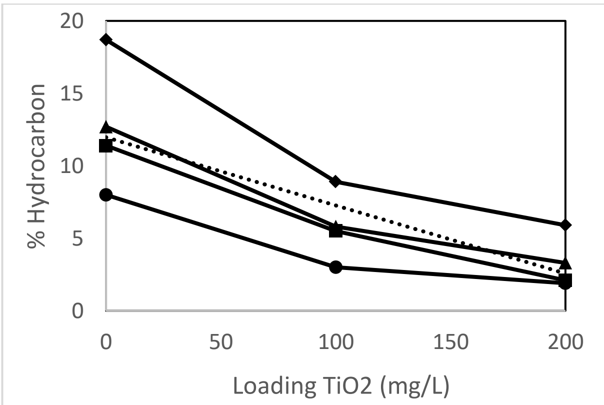

Figure 6. Hydrocarbon Emission Test of Dexlite – Nano TiO_2.

It can be seen from table 5 and figure 6 above, that there is a decrease in the percentage of hydrocarbon emissions as the loading of nano-TiO2 increases. This is due to the increasing amount of complete combustion that occurs. As is known, hydrocarbon combustion is divided into complete combustion and incomplete combustion, where perfect combustion requires more oxygen, and incomplete combustion requires less oxygen. TiO2 provides additional oxygen to the combustion process, so that complete combustion can be achieved and hydrocarbon emissions can be reduced. Equation (4), (5) and (6) below show a schematic of the relationship between the amount of O2 and complete or incomplete combustion in hydrocarbon combustion. Hydrocarbon emission testing shows a significant change with a maximum emission reduction of 80% in Dexlite products with TiO2 loading of 100 mg/L.

Complete Combustion Equation (excess of oxygen)

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad (4)$$

Incomplete Combustion Equation (lack of oxygen)

$$C_3H_8 + 7/2O_2 \rightarrow 3CO + 4H_2O \quad (5)$$

$$C_3H_8 + 2O_2 \rightarrow 3C + 4H_2O \quad (6)$$

3.7. NO_x Emission Testing

NOx emission testing was carried out with an emission test device. NOx emission testing was carried out at Alifia workshop, Blora. NOx emission testing uses an emission test device that can read the amount of hydrocarbon pollution on the specified filter paper. The hydrocarbon emission test used 1 liter of sample. The hydrocarbon emission test results are shown in Table 6 and Figure 7 below.

Tabel 6. NO_x Emission Test of Dexlite – Nano TiO_2.

Loading of Nano TiO_2 (mg/L)	**Data1 (mg/m^3)**	**Data2 (mg/m^3)**	**Data3 (mg/m^3)**	**Data Average (mg/m^3)**
0	250,0	225,0	176,0	217,0
100	147,0	187,0	203,0	179,0
200	144,0	155,0	165,0	154,7

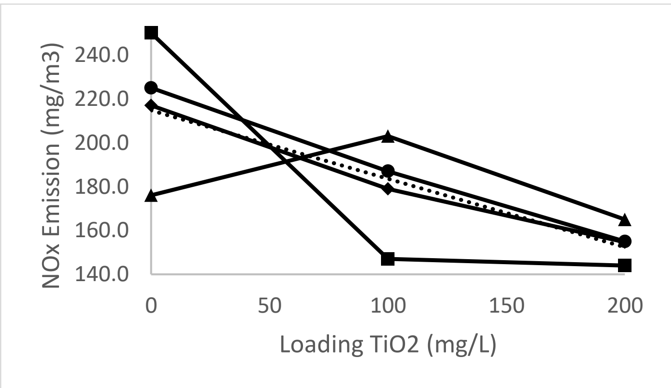

Figure 7. NO_x Emission Test Results by Dexlite - Nano TiO_2.

It can be seen from table 6 and figure 7 above, that there is a decrease in the percentage of NOx emissions as the loading of nano-TiO2 increases. The decrease in NOx levels occurs because TiO2 reduces the peak flame temperature of combustion so as to reduce the amount of NOx formed from combustion (Vellaiyan, 2019). Hydrocarbon emission testing showed a significant change with a maximum emission reduction of 51% in Dexlite products with TiO2 loading of 200 mg/L.

3.8. SO_x Emission Testing

SOx emission testing was conducted with an emission test device. Hydrocarbon emission testing was conducted at Alifia workshop, Blora. Hydrocarbon emission testing uses an emission test device that can read the amount of SOx pollution on the specified filter paper. The SOx emission test used 1 liter of sample. The SOx emission test results are shown in Table 7 below.

Table 7. SO_x Emission Test of Dexlite – Nano TiO_2.

Loading Nano TiO_2 (mg/L)	Data 1 (mg/m^3)	Data 2 (mg/m^3)	Data 3 (mg/m^3)	Data Average (mg/m^3)
0	0	0	0	0
100	0	0	0	0
200	0	0	0	0

Table 7 shows that there are no SOx results read on the test device. This indicates that the Dexlite fuel product is free of sulfur components.

3.9. CO Emission Testing

CO emission testing was conducted with an emission test device. CO emission testing was carried out at Alifia workshop, Blora. Hydrocarbon emission testing uses an emission test device that can read the amount of CO pollution on the specified filter paper. The CO emission test used 1 liter of sample. The CO emission test results are shown in Table 8 and Figure 8 below.

Table 8. CO Emission Test of Dexlite – Nano TiO_2.

Loading Nano TiO_2 (mg/L)	Data 1 (mg/m^3)	Data 2 (mg/m^3)	Data 3 (mg/m^3)	Data Average (mg/m^3)
0	754,0	884,0	815,0	817,7
100	686,0	749,0	710,0	715,0
200	512,0	515,0	522,0	516,3

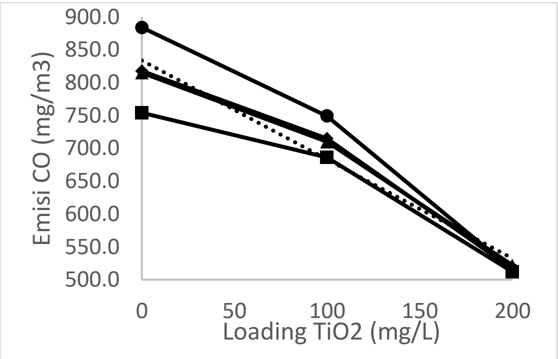

Figure 8. CO Emission Test Results by Dexlite - Nano TiO_2.

It can be seen from table 8 above and figure 8 above, that there is a decrease in the percentage of CO emissions as the loading of nano-TiO2 increases. This is due to the increasing amount of complete combustion that occurs. As is known, hydrocarbon combustion is divided into complete combustion and incomplete combustion, where perfect combustion requires more oxygen, and incomplete combustion requires less oxygen. TiO2 provides additional oxygen to the combustion process, so that complete combustion can be achieved and CO emissions can be reduced. Equation (4), (5) and (6) above show a schematic of the relationship between the amount of O2 and complete or incomplete combustion in hydrocarbon combustion. CO emission testing shows a significant change with the maximum emission reduction reaching 47% in Dexlite products with TiO2 loading of 200 mg/L.

3.10. CO_2 Emission Testing

CO2 emission testing was carried out with an emission test device. CO2 emission testing was carried out at the Alifia workshop, Blora. Hydrocarbon emission testing uses an emission test device that can read the amount of CO2 pollution on the specified filter paper. CO2 emission testing uses 1 liter of sample. The CO2 emission test results are shown in Table 9 and Figure 9 below.

It can be seen from table 9 above and figure 9 below, that there is an increase in the percentage of CO2 emissions as the loading of nano-TiO2 increases. This is due to the increasing amount of complete combustion that occurs. As is known, hydrocarbon combustion is divided into complete combustion and incomplete combustion, where perfect combustion requires more oxygen, and incomplete combustion requires less oxygen. TiO2 provides additional oxygen to the combustion process, so that complete combustion can be achieved accompanied by additional CO2 gas emissions. Equation (4), (5) and (6) above show a schematic of the relationship between the amount of O2 and complete or incomplete combustion in hydrocarbon combustion. CO2 emission testing shows significant changes with the maximum emission increase reaching 29% in Dexlite products with TiO2 loading of 200 mg/L.

Table 9. CO_2 Emission Test of Dexlite – Nano TiO_2.

Loading Nano TiO_2 (mg/L)	Data 1 (%)	Data 2 (%)	Data 3 (%)	Data Average (%)
0	2,0	2,1	2,1	2,1
100	2,2	2,5	2,6	2,4
200	2,3	2,7	2,7	2,6

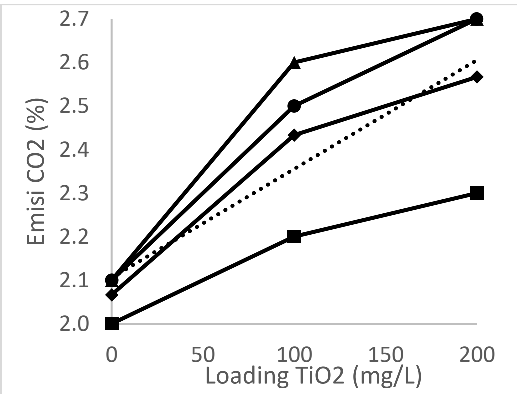

Figure 9. CO_2 Emission Test Results by Dexlite - Nano TiO_2.

IV. CONCLUSION

The following conclusions can be drawn from the implementation of this research: Testing of physical properties such as density, viscosity and flash point did not show any significant changes due to the small loading of TiO2 so that the contribution of its mass fraction is small. The results of the calorific value characterization with a bomb calorimeter showed that there was a decrease in the calorific value of the Dexlite-TiO2 sample in all variations of nano-TiO2 loading. This is due to an increase in BSFC which results in a decrease in diesel fuel efficiency. Hydrocarbon emission testing shows a significant change due to the role of TiO2 in providing oxygen which serves to increase the rate of complete combustion. The maximum emission reduction reached 74% in Dexlite diesel products with 200 mg/L TiO2 loading. The results of the NOx emission test showed a decrease in NOx content, the best results were shown by samples with a variation of nano-TiO_2 loading of 200 mg/L, which amounted to 29%. This is supported by a decrease in peak flame temperature in combustion so that the NOx value also drops. SOx emission test results show the absence of sulfur content in the sample so it can be concluded that Dexlite diesel fuel is sulfur-free. The results of the CO emission test show a decrease in CO content, the best results are shown by samples with a loading variation of nano-TiO_2 as much as 200 mg/L, which is 37% for the Dexlite-TiO_2 sample. This is supported by increasing the perfect combustion rate so that the CO value decreases. CO_2 emission test results show a decrease in CO_2 content, the best results are shown by samples with a loading variation of nano-TiO_2 as much as 200 mg/L, which is 24% for the Dexlite-TiO_2 sample. This is supported by increasing the perfect combustion rate so that the CO_2 value increases.

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