

# Properties of Nonpremixed Ammonia-substituted Hydrogen-air Flames

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## ABSTRACT

The extinction and nitrogen oxide ( $\text{NO}_x$ ) emissions of nonpremixed ammonia ( $\text{NH}_3$ )-hydrogen ( $\text{H}_2$ )-air flames were experimentally studied to evaluate the potential of partial  $\text{NH}_3$  substitution to improve the safety of  $\text{H}_2$  use and provide a database of nonpremixed  $\text{NH}_3$ -substituted  $\text{H}_2$ -air flames. Considering coflow nonpremixed  $\text{NH}_3$ - $\text{H}_2$ -air flames at normal temperature and pressure for a wide range of fuel and coflow air injection velocities and the extent of  $\text{NH}_3$  substitution, the effects of  $\text{NH}_3$  substitution and fuel and air injection velocities on the combustion stability (extinction) limits and  $\text{NO}_x$  emissions of  $\text{H}_2$ -air flames were investigated. Results show reduction of stability limits with  $\text{NH}_3$  substitution, supporting the potential of  $\text{NH}_3$  as an effective, green (i.e., carbon-free) additive in  $\text{H}_2$ -air flames. The  $\text{NO}_x$  emission index ( $EI_{\text{NO}_x}$ ) increases with enhanced  $\text{NH}_3$  substitution in general. For a given air injection velocity,  $EI_{\text{NO}_x}$  decreases and then increases with increasing fuel injection velocities.

**Keywords:** ammonia, hydrogen, nonpremixed flames, stability limits, carbon-free

## 1 INTRODUCTION

In spite of increasing interest in the use of pure hydrogen ( $\text{H}_2$ ) in combustion devices due to its unique features such as no carbon dioxide ( $\text{CO}_2$ ) emissions and wide flammability limits [1,2], the inherently high diffusivity and reactivity of  $\text{H}_2$  are responsible for the potential of explosion hazards in storage. Also, non-luminous  $\text{H}_2$  flames are difficult to be visually detected and optically monitored. Some methods to suppress hazards due to  $\text{H}_2$  usage such as the use of hydrocarbon-substituted  $\text{H}_2$  in combustion devices have been developed [3]. Recently, the use of carbon-free ammonia ( $\text{NH}_3$ )- $\text{H}_2$  mixtures in combustion devices as an alternative approach towards enabling  $\text{H}_2$  utilization and diminishing the associated safety problems have been proposed [4–6]. Similar to reaction of pure  $\text{H}_2$ -air mixtures, reaction of  $\text{NH}_3$ - $\text{H}_2$ -air mixtures does not produce  $\text{CO}_2$ , while  $\text{NH}_3$  is easily storable, which is different from  $\text{H}_2$  [7]. Although some technological challenges and public concerns are imposed by the use of  $\text{NH}_3$  [8], potentially beneficial characteristics of the combustion of  $\text{NH}_3$ - $\text{H}_2$ -air mixtures have been discussed in the previous study [4]: e.g., diminished the propensity of the mixtures to detonate due to the presence

of  $\text{NH}_3$  in  $\text{H}_2$ -air flames and enhanced the safety of  $\text{H}_2$  use due to visual detection of luminous  $\text{NH}_3$ - $\text{H}_2$  flames.

In the previous studies in this laboratory [4–6], the potential of  $\text{NH}_3$  as a carbon-free, green additive for improving the safety of  $\text{H}_2$  use in both premixed and nonpremixed  $\text{H}_2$ -air flames was observed. The experimental and computational study on the propagation and nitrous oxide ( $\text{N}_2\text{O}$ ) and nitrogen oxide ( $\text{NO}_x$ ) emissions of spark-ignited spherical laminar premixed  $\text{NH}_3$ - $\text{H}_2$ -air flames shows substantial reduction of laminar burning velocities with  $\text{NH}_3$  substitution in  $\text{H}_2$ -air flames [4]. The potential of  $\text{NH}_3$  as a suppressant of both hydrodynamic and preferential-diffusional cellular instabilities in premixed  $\text{H}_2$ -air flames was also found. Although  $\text{NH}_3$  substitution enhances the  $\text{N}_2\text{O}$  and  $\text{NO}_x$  formation in general, the increased amount of  $\text{N}_2\text{O}$  and  $\text{NO}_x$  emissions with  $\text{NH}_3$  substitution for fuel-rich conditions is much lower than that under fuel-lean conditions. The computational study of the effects of  $\text{NH}_3$  substitution on the extinction limits and structure of counterflow nonpremixed  $\text{H}_2$ -air flames shows reduction of the blowoff limits, the concentration of light radicals and the maximum flame temperature with  $\text{NH}_3$  substitution in  $\text{H}_2$ -air flames [5]. It was found that chemical effects than thermal effects of  $\text{NH}_3$  substitution on flame structure are dominant and radiation effects on the extinction limits and flame structure are not remarkable particularly for high-stretched flames. The most recent study of burner-stabilized premixed  $\text{NH}_3$ - $\text{H}_2$ -air flames also supports the potential of  $\text{NH}_3$  as a carbon-free additive for improving the safety of  $\text{H}_2$  use, showing a reduction of stability limits with  $\text{NH}_3$  substitution and coflow [6]. It was observed that the thermal  $\text{deNO}_x$  process in the post-flame region is involved in reducing  $\text{NO}_x$  emissions for fuel-rich flames.

The aim of the present investigation is to extend previous work [4–6] on the potential of improving  $\text{H}_2$  safety by adding  $\text{NH}_3$  to  $\text{H}_2$ -air flames and provide a useful database for modeling nonpremixed  $\text{NH}_3$ - $\text{H}_2$ -air flames, with the following specific objectives. The first is to measure the combustion stability (extinction) limits of nonpremixed  $\text{NH}_3$ - $\text{H}_2$ -air flames in order to quantify the extent of stability limit reduction due to  $\text{NH}_3$  addition. The second is to measure the  $\text{NO}_x$  emissions of nonpremixed  $\text{NH}_3$ - $\text{H}_2$ -air flames in a closed chamber in order to observe the effects of  $\text{NH}_3$  substitution and fuel and coflow air injection velocities on  $\text{NO}_x$  emissions. Thus, this study has been conducted for a wide range of fuel and air injection velocities and the extent of  $\text{NH}_3$  substitution.

## 2 EXPERIMENTAL METHODS

The nonpremixed flame in a coflow using a tube type burner was adopted for the present investigation because it is the most common flame configuration for studying the combustion stability (extinction) limits and  $\text{NO}_x$  emissions of nonpremixed flames. The experimental apparatus we employed is shown schematically in Fig. 1. It consists of a fuel tube surrounded with a concentric tube to provide coflow air, a cylindrical lab-scale combustion chamber that is connected to the fuel and coflow air delivery tubes, a gas analyzer for measuring  $\text{NO}_x$  emissions, thermocouples (R-type) for measuring temperature distribution in the flame and a digital camera (Kodak Z812IS) for recording flame images.

A  $\text{NH}_3\text{-H}_2$  mixture is injected from a stainless steel (SUS316L) tube with inner and outer diameters of 3.00 and 5.26 mm, respectively, and with the passage length/diameter ratio of 150 to help insure fully-developed pipe flow at the tube exit. Coflow air is injected from a concentric stainless steel (SUS316L) tube with an inner diameter of 15.0 mm, while ambient air at low velocities is provided through the honeycomb plate that is the bottom (upstream) of the cylindrical combustion chamber (plexi-glass) with the inner diameter, height and thickness of 210, 960 and 8 mm, respectively. The coflow nonpremixed jet is spark-ignited so that a nonpremixed flame is formed and stabilized on the tube rim. Flow meters (CSM: 0–450 lpm) with accuracy  $\pm 3.0\%$  of full scale deliver the fuel mixture and air to the main and concentric tubes, respectively. Using the flow meters, fuel-mixture composition (the mole fraction of  $\text{NH}_3$  in the fuel gas  $x_a = X_{\text{NH}_3}/(X_{\text{NH}_3} + X_{\text{H}_2})$  where  $X_{\text{NH}_3}$  and  $X_{\text{H}_2}$  are the mole fractions of  $\text{NH}_3$  and  $\text{H}_2$ , respectively) and tube exit velocity  $V_{\text{fuel}}$  and coflow air tube exit velocity  $V_{\text{coflow}}$  are independently controlled. To avoid bending or melting due to hot product gases, the top cover of the combustion chamber is made of aluminum, and the exhaust port that is located on the center of the chamber top plate is connected directly to a ventilation tube.

The concentration of  $\text{NO}_x$  was measured in the ventilation tube using the gas analyzer (Testo 350-XL) with an accuracy of 0.1–1.0 ppm, the probe of which is located on the center of the ventilation path. The combustion stability limits were measured as follows. As aforementioned,  $\text{NH}_3$ -substituted  $\text{H}_2$ -air nonpremixed flames were obtained by establishing a cold coflow jet of fuel mixture and air and then igniting the coflow jet with a spark. With and without coflow air the ambient air was always injected at 1.2 m/sec. For all experiments, the concentrations of  $\text{NH}_3$  and  $\text{H}_2$  (i.e.,  $x_a$ ) were set to fixed values in each mixture and then  $V_{\text{coflow}}$  was varied to find the combustion stability limits for a given value of  $V_{\text{fuel}}$ . Given  $V_{\text{fuel}}$  and  $x_a$ , upper combustion stability limits were observed at high  $V_{\text{coflow}}$  due to the fuel-lean mixture concentration in the flame base (blowout). In the present study, however, we have not measured lower combustion stability limits at low  $V_{\text{coflow}}$  because of the limited

capability (i.e., flow meter resolution) of the present apparatus, just focusing on the blowout limits. The blowout limits were obtained by establishing a stable flame at a relatively lower  $V_{\text{coflow}}$  and then gradually increasing  $V_{\text{coflow}}$ . Since flames were lifted off at high  $V_{\text{fuel}}$ , the liftoff limits were also measured. Final results, including the combustion stability limits and  $\text{NO}_x$  emissions of nonpremixed  $\text{NH}_3$ -substituted  $\text{H}_2$ -air flames, were obtained by averaging measurements of 4 to 6 tests at each condition. Experimental uncertainties (95% confidence) for  $V_{\text{fuel}}$ ,  $V_{\text{coflow}}$  and  $x_a$  were less than 5%. At temperature  $T = 298 \pm 3$  K and atmospheric pressure (NTP) experiments were carried out for  $x_a = 0.2\text{--}0.4$ ,  $V_{\text{fuel}} = 23.6\text{--}235.8$  m/s (Reynolds number  $\text{Re} = 619\text{--}6,193$ ) and  $V_{\text{coflow}} = 0\text{--}13.7$  m/s.

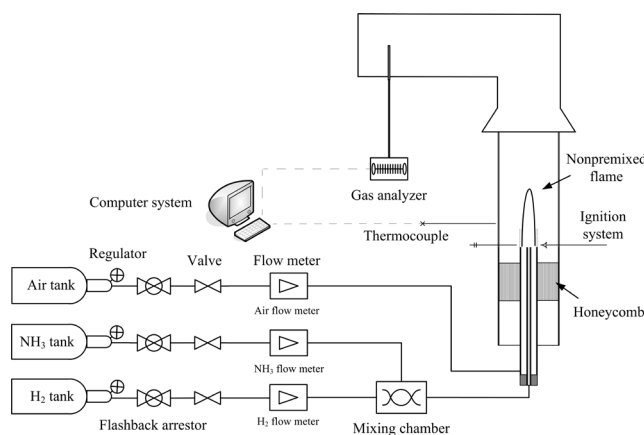


Figure 1: Schematic of experimental apparatus.

## 3 RESULTS AND DISCUSSION

### 3.1 Combustion Stability Limits

Effects of  $\text{NH}_3$  substitution on the combustion stability limits were examined to provide a database for modeling nonpremixed  $\text{NH}_3$ -substituted  $\text{H}_2$ -air flames and to quantify the extent of stability limit reduction due to  $\text{NH}_3$  addition under various fuel mixture injection conditions and thereby confirm the potential of partial  $\text{NH}_3$  substitution to improve the safety of  $\text{H}_2$  use without losing the unique feature of no  $\text{CO}_2$  emissions for pure  $\text{H}_2$  use.

Figure 2 shows the measured combustion stability limits, including the blowout and liftoff limits, on a  $V_{\text{coflow}}\text{--}V_{\text{fuel}}$  diagram for nonpremixed  $\text{NH}_3\text{-H}_2$ -air flames with a fixed  $x_a = 0.4$  at NTP. Upper combustion stability (blowout) limits are observed at high  $V_{\text{coflow}}$  since the mixture in the flame base becomes fuel-lean and thus, the flame becomes weak and is finally extinguished with relatively high local strain rates. Up to  $V_{\text{fuel}} = 88.4$  m/sec no liftoff flame is observed, while beyond  $V_{\text{fuel}} = 88.4$  m/sec flames are lifted off at low  $V_{\text{coflow}}$  since the position where the local flow velocity matches the local burning velocity shifts downstream with enhanced  $V_{\text{fuel}}$ , i.e., the local strain rates near the burner exit are too high to match the local burning velocities [9]. A

typical extinction behavior of nonpremixed flames is observed:  $V_{\text{coflow}}$  at the extinction increases (decreases) with increasing  $V_{\text{fuel}}$  for laminar (turbulent)  $\text{NH}_3\text{-H}_2\text{-air}$  flames. Thus, with increasing  $V_{\text{fuel}}$  the range of combustion stability limits becomes extended until  $V_{\text{fuel}} = 47.2$  m/sec and then reduced.

Figure 3 shows the combustion stability limits for nonpremixed  $\text{NH}_3\text{-H}_2\text{-air}$  flames with a fixed  $x_a = 0.2$  at NTP. They can be compared with the results for  $x_a = 0.4$  in Fig. 2, showing the effects of the extent of  $\text{NH}_3$  substitution on the combustion stability limits. Similar to the results for  $x_a = 0.4$ , the blowout and liftoff limits are observed for high  $V_{\text{fuel}}$ , while only the blowout limits are observed for low-to-moderate  $V_{\text{fuel}}$ . Compared with the combustion stability limits for  $x_a = 0.4$ , they have been substantially extended, showing that  $V_{\text{coflow}}$  at the blowout limits increases. This tendency is observed because the burning intensities of  $\text{NH}_3\text{-H}_2\text{-air}$  flames, i.e., the local burning velocities of  $\text{NH}_3\text{-H}_2\text{-air}$  mixtures, have been enhanced with lower  $\text{NH}_3$  substitution. Due to the enhanced burning intensity the  $V_{\text{fuel}}$  limit has been also extended:  $V_{\text{fuel}} = 23.6\text{--}235.8$  m/sec compared with  $23.6\text{--}94.3$  m/sec for the flames of  $x_a = 0.4$  (Fig. 2).

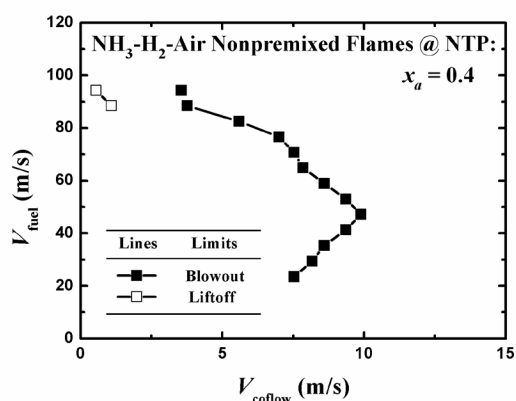


Figure 2: Stability limits of nonpremixed  $\text{NH}_3\text{-H}_2\text{-air}$  flames of  $x_a = 0.4$  at NTP.

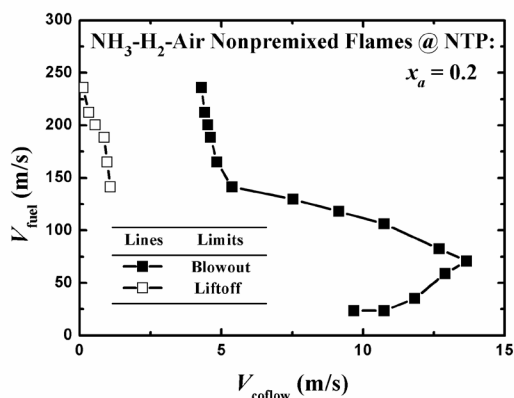


Figure 3: Stability limits of nonpremixed  $\text{NH}_3\text{-H}_2\text{-air}$  flames of  $x_a = 0.2$  at NTP.

The results in Figs. 2 and 3, showing reduction of the combustion stability limits with  $\text{NH}_3$  substitution in  $\text{H}_2\text{-air}$  flames, support the potential of  $\text{NH}_3$  as a carbon-free, green additive for improving the safety of  $\text{H}_2$  use in nonpremixed  $\text{H}_2\text{-air}$  flames in addition to the previous results from premixed and counterflow nonpremixed  $\text{NH}_3\text{-substituted}$   $\text{H}_2\text{-air}$  flames at NTP [4–6].

### 3.2 $\text{NO}_x$ Formation

Effects of  $\text{NH}_3$  substitution,  $V_{\text{fuel}}$  and  $V_{\text{coflow}}$  on the  $\text{NO}_x$  emissions of nonpremixed  $\text{NH}_3\text{-H}_2\text{-air}$  flames were examined to evaluate the performance of combustion devices using  $\text{NH}_3\text{-H}_2$  mixtures and the results are given in Figs. 4 and 5. The  $\text{NO}_x$  emission index  $EI_{\text{NO}_x}$  that is defined as the fraction of the mass (g) of the produced  $\text{NO}_x$  per the mass (kg) of the provided  $\text{NH}_3$  and  $\text{H}_2$  is used as a performance parameter. In addition to the  $\text{NO}_x$  emission data, the  $\text{NO}$  data are separately provided.

Figure 4 shows  $EI_{\text{NO}_x}$  for nonpremixed  $\text{NH}_3\text{-H}_2\text{-air}$  flames with  $x_a = 0.4$  and  $V_{\text{coflow}} = 0$  and  $2.2$  m/s at NTP. It is observed that for  $V_{\text{coflow}} = 0$  (only with the ambient air)  $EI_{\text{NO}_x}$  decreases up to  $V_{\text{fuel}} = 70.7$  m/s and then increases with increasing  $V_{\text{fuel}}$ , though the absolute value of  $\text{NO}_x$  emissions monotonically increases with increasing  $V_{\text{fuel}}$  (not shown here). The tendency of  $EI_{\text{NO}_x}$  decrease with increasing  $V_{\text{fuel}}$  for low  $V_{\text{fuel}}$  is observed since the effects of recirculation of burned gas in the combustion chamber that encloses the coflow burner dilute unburned mixtures for low  $V_{\text{fuel}}$  where flame is relatively small [10]. Meanwhile, the tendency of  $EI_{\text{NO}_x}$  increase with increasing  $V_{\text{fuel}}$  for high  $V_{\text{fuel}}$  is observed since the reduced flame length (residence time) due to the liftoff behavior and thereby the reduced radiant heat losses enhance  $\text{NO}_x$  emissions for high  $V_{\text{fuel}}$  where flame is relatively large and thus the effects of recirculation of burned gas are not enhanced any more. When coflow air is injected ( $V_{\text{coflow}} = 2.2$  m/s),  $EI_{\text{NO}_x}$  has been somewhat reduced due to the dilution effects of added coflow air.

Figure 5 shows  $EI_{\text{NO}_x}$  for nonpremixed  $\text{NH}_3\text{-H}_2\text{-air}$  flames with  $x_a = 0.2$  and  $V_{\text{coflow}} = 0$  and  $2.2$  m/s at NTP. They can be compared with the results for  $x_a = 0.4$  in Fig. 4, showing the effects of the extent of  $\text{NH}_3$  substitution on the  $\text{NO}_x$  emissions. Similar to the results for  $x_a = 0.4$ ,  $EI_{\text{NO}_x}$  decreases up to a certain value of  $V_{\text{fuel}}$  ( $= 94.3$  m/s) and then increases with increasing  $V_{\text{fuel}}$  for no coflow condition (only with the ambient air), while  $EI_{\text{NO}_x}$  is reduced with coflow air. Compared with  $EI_{\text{NO}_x}$  for  $x_a = 0.4$ , it has been somewhat reduced, showing that  $EI_{\text{NO}_x}$  increases with enhanced  $\text{NH}_3$  substitution, though it is not remarkable. Meanwhile, the flame temperature decreased with increasing  $\text{NH}_3$  substitution (though data is not provided). Thus, this result indicates that the thermal  $\text{NO}_x$  mechanism does not play the main role in enhancing  $\text{NO}_x$  emissions with increasing  $\text{NH}_3$  substitution for the nonpremixed  $\text{NH}_3\text{-H}_2\text{-air}$  flames.

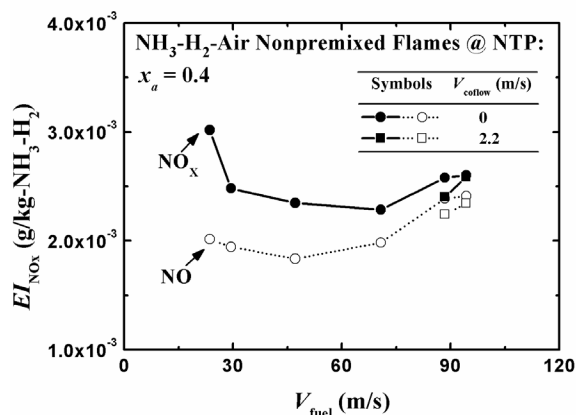


Figure 4: Effects of  $V_{\text{fuel}}$  and  $V_{\text{coflow}}$  on  $\text{NO}_x$  emission index of nonpremixed  $\text{NH}_3$ -substituted  $\text{H}_2$ -air flames of  $x_a = 0.4$  at NTP.

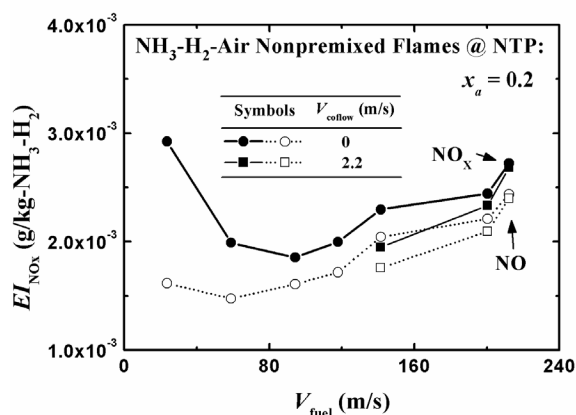


Figure 5: Effects of  $V_{\text{fuel}}$  and  $V_{\text{coflow}}$  on  $\text{NO}_x$  emission index of nonpremixed  $\text{NH}_3$ -substituted  $\text{H}_2$ -air flames of  $x_a = 0.2$  at NTP.

## 4 CONCLUSIONS

The effects of  $\text{NH}_3$  substitution on the combustion stability (extinction) limits and  $\text{NO}_x$  emissions of nonpremixed  $\text{H}_2$ -air flames at normal temperature and pressure were experimentally studied to evaluate the potential of partial  $\text{NH}_3$  substitution to improve the safety of  $\text{H}_2$  use and provide a database of nonpremixed  $\text{NH}_3$ -substituted  $\text{H}_2$ -air flames. The major observations and conclusions of the study are as follows. A typical extinction behavior of nonpremixed flames is observed: the blowout limits at high coflow air tube exit velocity  $V_{\text{coflow}}$  due to the fuel-lean mixture concentration in the flame base and the liftoff limits at low  $V_{\text{coflow}}$  due to the high local strain rates near the burner exit compared with the local burning velocities. The coflow air tube exit velocity at the extinction increases (decreases) with increasing fuel tube exit velocity  $V_{\text{fuel}}$  for laminar (turbulent)  $\text{NH}_3$ - $\text{H}_2$ -air flames.

Ammonia substitution substantially reduces the blowout limits. The  $\text{NO}_x$  emission index  $EI_{\text{NO}_x}$  increases with enhanced  $\text{NH}_3$  substitution, though it is not remarkable. For given  $V_{\text{coflow}}$   $EI_{\text{NO}_x}$  decreases and then increases with increasing fuel tube exit velocity, though the absolute value of  $\text{NO}_x$  emissions monotonically increases. The effects of recirculation of burned gas in the combustion chamber that encloses the coflow burner reduce  $EI_{\text{NO}_x}$  for low  $V_{\text{fuel}}$ , while the reduced flame length due to the liftoff behavior and thereby the reduced radiant heat losses enhance  $EI_{\text{NO}_x}$  for high  $V_{\text{fuel}}$ . The present observations support the potential of  $\text{NH}_3$  as a carbon-free, green additive for improving the safety of  $\text{H}_2$  use with reasonable levels of  $\text{NO}_x$  emissions.

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