Analysis of an Extended Ionization Equilibrium in the Post-flame Gases for Spark Ignited Combustion

A. Ahmedi[1], F. Mauss[2], B. Sundén[1]
[1]Department of heat and power engineering – Lund University
[2] Division of combustion physics – Lund University

Corresponding author: Fabian.Mauss@forbrf.lth.se

INTRODUCTION

The ionization sensor is an electrical probe for combustion diagnostics. Its signal contains information on both the early phase of the combustion process due to chemical ionization in the flame front and the main combustion due to ionization equilibrium in the post-flame gases. Not all factors influencing the ion-current in spark-ignited combustion are fully understood.

The sensor signal consists of two major parts (peaks). The first peak occurs when the flame is in contact with the spark plug electrodes. It is caused by the chemical ionization in the flame, and its magnitude is related to the local equivalence ratio close to the electrode gap. The second peak is located close to the position of the maximum pressure.

Constant volume combustion is studied to analyze experimental data from reference [2]. We use a zero-dimensional model that provides an engine- or reactor-like environment in which the engine simulations allow for a variable system volume and heat transfer both to and from the system [3]. Equilibrium assumptions have been adopted for the modeling of the thermal ionization, in which Saha's equation was derived for single ionized molecules. The investigation is focused on the thermal ionization and electron attachment of 6 chemical species. The equilibrium calculation using Saha's equation is performed in a post process, using the temperature and pressure history from the constant pressure model calculation.

Existing models for the ionization current assume nitric oxide as the main electron donor in the post-flame gases [1, 8, and 9]. This is reasonable as long as NO is the species with the lowest ionization energy in the burned gas composition, and electron attachment does not influence the electron concentration. However it has been shown before that the inclusion of alkali metals (potassium and sodium) found in the environmental air, have a strong influence on the calculation of ionization current. The ionization current calculated from potassium and sodium is however much higher than found in the experiment [9]. Alkali metals are present in the atmosphere at concentration around 200 [ng/m^3 (0.1 ppb)]. In this contribution we investigate the influence of electron attachment reactions on the calculated ionization current.

IONIZATION EQUILIBRIUM

The equilibrium representing the thermal ionization of nitrogen oxide (NO), potassium (K), and sodium (Na) can be written as:

$$NO \Leftrightarrow NO^+ + e^- \qquad \text{(R1)}$$

$$K \Rightarrow K^+ + e^- \qquad \text{(R2)}$$

$$Na \Leftrightarrow Na^+ + e^- \qquad \text{(R3)}$$

The electron attachment equilibrium representing the electron attachment of Oxygen (O_2), Cyanide (CN), and Hydroxyl radical (OH) can be written as:

$$O_2^- \Leftrightarrow O_2 + e^- \qquad \text{(R4)}$$

$$CN^- \Leftrightarrow CN + e^- \qquad \text{(R5)}$$

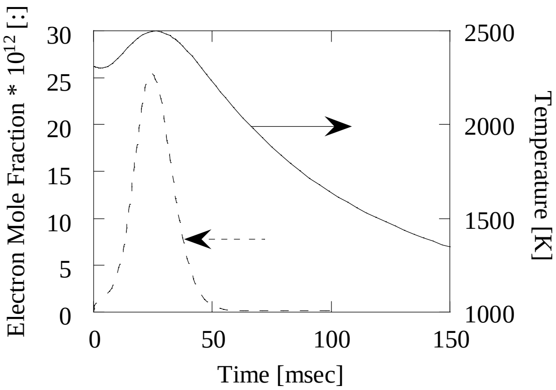
$$OH^- \Leftrightarrow OH + e^- \qquad \text{(R6)}$$

Since the equilibrium calculations are made in a post process the increase in chemical reaction rates due to the ionization is not taken into account. The balance between generation and regeneration of ions caused by thermal excitation forms the basis for the ionization and electron attachment. Both the ionization process and the electron attachment process are assumed to be fast compared to the combustion process and specifically the combustion temperature development. Therefore the electrons and ions are in thermodynamic equilibrium and the balance can be described by the Saha's equation for the thermal ionization and for the electron attachment.

RESULTS and DISCUSSION

The nitric oxide ionization is strongly dependent on temperature as shown in figure 1. Both profiles reach their maximum at the same time. The resulting calculated current (NO ionization contribution) compared the experimental measurement [2] is shown in figure 2. The calculated current peak is only 10% lower than the measured one, and one could conclude that an ionization model based on NO is sufficient to explain the ionization signal. This would allow using the ionization sensor as an NO sensor. The difference between signal and calculation was explained by: 1) - zero concentration of NO behind the flame front in the model, 2) - variation of temperature within the burned gas zone, 3) - missing heat transfer to the walls. Other possible explanations were: 1) - the simplified geometry chosen for the two electrodes in the simulation model, where the geometry of the electrodes in the experimental set up was quite complex, 2) - the fact that nitric oxide may not be the main electron donor in the combustion process [1, 9].

Figures 1 and 2 are repeated from our previous work for comparison purposes [9]. Figures 1 shows also the burned gas temperature profile as calculated from the two-zone model, the validation of this result was not possible in this work due to the absence of experimental data, but the shape of the temperature profile has a good agreement with the one presented in the literature [1,2,3,4 and 8].



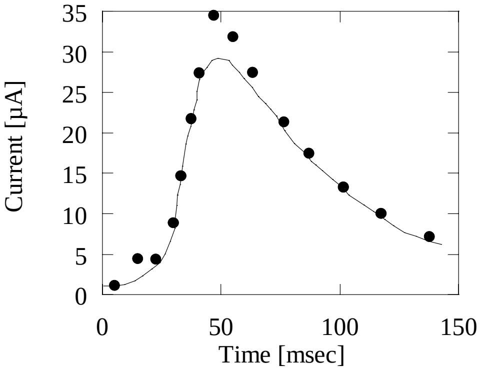


Fig. 1. Burned gas temperature and electron mole fraction produced from the ionization of NO both vs. time [9].

Fig. 2. Calculated current from NO contribution (line) vs. a measured (dots) [9].

Figure 3 shows the electron mole fraction contribution resulting from the ionization of the 6 species included in this model calculation. This calculation is referenced below as case 1. It is obvious from comparison of figure 1 and figure 3 that the electron mole fraction concentration is increased by more than one order of magnitude. We note that the electron attachment is reducing the electron concentrations in the current model. Neglecting the electron attachment increases the electron concentration by a further order of magnitude (see also comparison in reference [9]). The thermal ionization is strongly dependent on temperature. This can be seen in figure 3, where the maximum electron mole fraction, produced from the thermal ionization and the electron attachment of 6 species is reached slightly before the temperature peak.

Figure 4 shows the calculated current from the extended equilibrium compared to the experimental measurements; where one can see the excellent agreement between simulation and experiments. This underlines the importance of alkali metals found in the environmental air, and the importance of electron attachment for the interpretation of ionization signals.

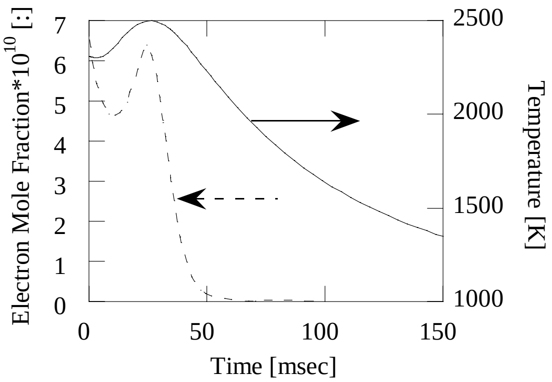


Fig. 3. Burned gas temperature and electron mole fraction produced from case 1 vs. time.

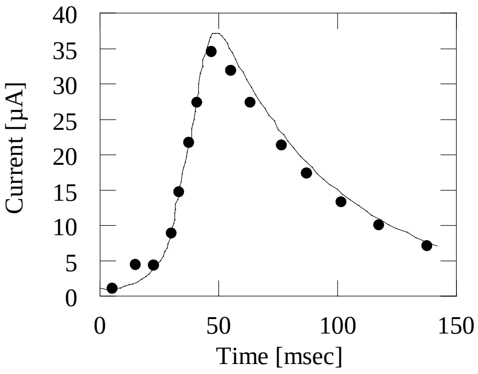


Fig. 4. Calculated current from case 1 (line) vs. a measured (dots)

Figure 5 shows the effect of the alkali metals (K and Na) on the ion current signal, where the absence of the reactions R2 and R3 from the equilibrium model (case 2) leads to a drop of about 75% of the current signal compared to the reference case where all the reactions are considered (case 1). Figure 5 shows also the importance of the electron attachment reactions in the equilibrium model (R4, R5, and R6) and the role of negative ions in the reduction of electron concentration in the combustion chamber. Thus the electrons produced by the thermal ionization of NO (R1) are directly consumed by electron attachment reactions (R4, R5, and R6).

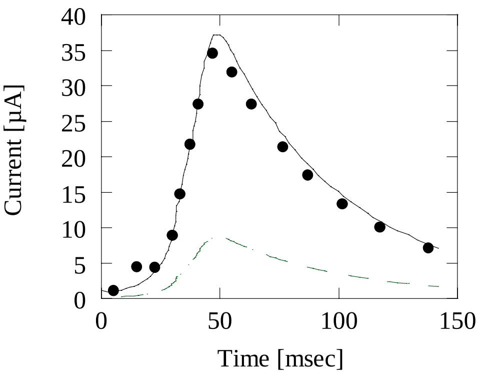


Fig. 5. Calculated current from case 1 (line) and case 2 (dashed line) vs. measurements (dots)

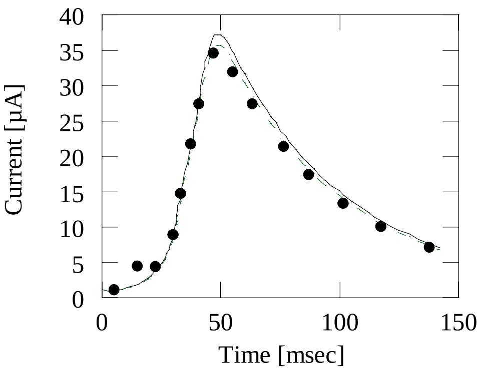


Fig. 6. Calculated current from case 1 (line) and case 3 (dashed line) vs. measurements (dots)

The results from the ion current signal calculation with the absence of the thermal ionization of NO (reaction R1) from the equilibrium model (case 3) are shown in figure 6. It shows a good agreement between the calculated current signal in both cases (case 1 and case 3) and the experimental results. But the most important information we can have from this figure is the fact that in spite the absence of NO as an electron donor we still have a good match between simulation and experiment. Which lead us to say that NO was not found to be a very important electron donor in these calculations.

It follows that the ionization sensor provides information on temperature and pressure only, because in combustion processes alkali metals are just impurities and not combustion products. Any impurities having low ionization energy such as alkali metals (K, Na) will contribute to ionization, at both low and high temperature. Since only trace quantities are required this source must be carefully considered.

The assumption that nitric oxide is the main electron donor, as stated in the models available for the ionization sensor [1, 8] does no longer hold because of the existence of species with a lower ionization energy and electron affinity e.g. alkali metals, which might make a significant contributions to ionization as seen for potassium, sodium, and other species which undergo electron attachment process.

CONCLUSION

In this study we investigated the second peak of the ion sensor signal in a constant volume combustion chamber. Species concentrations in the burned gas have been calculated with a simple two-zone model. The electron concentration in the burned gas was calculated by assuming thermal equilibrium. Different from prior studies we included environmental trace elements with low ionization energy, i.e. the alkali metals potassium and sodium, and electron attachment reactions in our analysis.

It is found that the alkali metals, appearing in low concentration in the environmental air, have a stronger influence on the ion signal than nitrogen oxide. It is further found that electron attachment reactions have a strong influence on the calculated electron concentration. We conclude that the ion sensor can be used to gain information on temperature and pressure in the combustion chamber. However, it is not possible to gain information on concentrations of electron donors, such as nitrogen oxide.

REFERENCES

1. Saitzkoff, A., Reinmann, R., Berglind, T. and Glavmo, M. “An ionization equilibrium analysis of the spark plug as an ionization sensor”, SAE paper 960337, 1996.
2. Franke, A. “Characterization of an Electrical Sensor for Combustion Diagnostics”, Doctoral thesis, Lund University, 2002.
3. Hajireza, S., Mauss, F. and Sundén, B., “Investigation of End-Gas Temperature and Pressure Increases in Gasoline Engines and Relevance for Knock Occurrence,” SAE Paper No. 971671, 1997.
4. Heywood, J.B., Internal Combustion Engine Funda-mentals, McGraw-Hill, New York, 1989.
5. Mitchner, M. and Kruger, C.H. Jr., “Partially Ionized Gases” a Wiley-interscience Publication, John Wiley & Sons. 1973.
6. Franke, A., Reinmann, R. and Larsson, A. “Analysis of the Ionization Equilibrium in the Post-Flame zone”. SAE 2003-01-0715, 2003.
7. Sweitlicki, E., Puri, S., Hansson, H. C., Edner. ”Urban air pollution source apportionment using a combination of aerosol and gas monitoring techniques”. Atmosph. Environ., 30:2795-2809, 1996.
8. Naoumov, V., Demin, A., Sokolov, A., Andersson, I., ”Modeling of combustion and nonequilibrium ionization in spark ignition engines”. SAE, 2002-01-0009, 2002.
9. Ahmedi, A., Franke, A., Soyhan, H.S., Mauss, F., Sundén, B., ”Prediction Tool for the Ion Current in SI-Combustion ” SAE, 2003-01-3136, 2003.