Addition agents effects on hydrocarbon fuels burning

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Abstract. Literature review on addition agents effects on hydrocarbon fuels burning has been conducted. The impact results in flame pattern and burning velocity change, energy efficiency increase, environmentally harmful NO\textsubscript{x} and CO emission reduction and damping of self-oscillations in flow. An assumption about water molecules dissociation phenomenon existing in a number of practical applications and being neglected in most explanations for physical-chemical processes taking place in case of injection of water/steam into combustion zone has been noted. The hypothesis about necessity of water dissociation account has been proposed. It can be useful for low temperature combustion process control and NO\textsubscript{x} emission reduction.

1. Introduction
Hydrocarbon fuels combustion technologies are widely spread and rapidly developing recently. Development is specified by energy market competition and toughening environmental requirements. Using of different fuel additives significantly affecting combustion processes is a way to satisfy it.

Water and steam injection is challenging technology for power systems based on gas-turbine engines [1]. This method is promising for low and average power engineering where use of high performance combined-cycle plants is unreasonable and implies long payback period.

Injection takes place into different air-gas channel areas: compressor inlet, combustion chamber or turbine cooling system. Increasing water/steam temperature by gaining burnt gases heat by means of recovery boiler is reasonable.

2. Review and discussion
Numerous computational simulations and experimental measurements devoted to addition agents effect on hydrocarbon fuels burning were conducted. Water, steam, hydrogen, ammonia etc. diluting fluid and gaseous fuels (black oil, kerosene, methane and different gas mixtures) were investigated [2-7]. Injection was implemented separately as well as being premixed with fuel (fine-dispersed emulsified fuels). Experimental setups complexity varies from simple atmospheric burners up to full-scale sophisticated combustors.

It was determined that addition agents could increase thermal efficiency and power, improve environmental aspect decreasing significantly NO\textsubscript{x} and CO emissions and decrease combustion instabilities.

Accepted explanation for these effects are based on additive heat release corresponding components calorific values in case of efficiency improving injection and decreased temperatures of lean flame in areas of NO\textsubscript{x} formation in case of emission improving injection. However, these models are not proper for explaining hydrocarbon and carbon monoxide CO burning as well as NO\textsubscript{x}...
neutralization that take place at low (<900K) temperatures in presence of water steam without any catalyst. Kalashnikov A.P. [8] described method for limiting NO\textsubscript{x} emission by mixing CO\textsubscript{2} with hot combustion products containing water steam and passing through finely porous carbonaceous substance.

It can be explained by following assumption for most combustion processes taking place in presence of steam. Molecules of water dissociate into OH\textsuperscript{−} and H\textsuperscript{+} ions that react with NO\textsubscript{x}. Its oxidation state gets decreased to the lowest (NO).

\[
\begin{align*}
\text{NO}_3 + H^+ &\rightarrow \text{NO}_2 + OH \\
\text{NO}_3 + OH^- &\rightarrow \text{NO}_2 + HO_2 \\
\text{NO}_2 + O^+ &\rightarrow \text{NO} + O_2 \\
\text{NO}_2 + H^+ &\rightarrow \text{NO} + OH \\
\end{align*}
\]

Then nitrogen monoxide gets neutralized with CH and NH radicals:

\[
\begin{align*}
\text{NO} + CH &\rightarrow CO + NH \\
\text{NO} + NH &\rightarrow N_2 + OH \\
\end{align*}
\]

Intensive NO\textsubscript{x} neutralization requires significant inflow of CH that is the final substance of hydrocarbons decomposition that takes place with OH\textsuperscript{−}, O\textsuperscript{+} and H\textsuperscript{−} participation. These radicals can be contained in fuel components or appear due to water dissociation.

\[
\begin{align*}
\text{CH}_4 + OH^- &\rightarrow \text{CH}_3 + H_2O \\
\text{CH}_4 + H^+ &\rightarrow \text{CH}_3 + H_2 \\
\text{CH}_4 + O^+ &\rightarrow \text{CH}_3 + OH^- \\
\text{CH}_2 + OH^- &\rightarrow \text{CH}_2 + H_2O \\
\text{CH}_2 + H^+ &\rightarrow \text{CH} + H_2 \\
\text{CH}_2 + O^+ &\rightarrow \text{CH} + OH^- \\
\end{align*}
\]

Burning of generated hydrogen yields fuel calorific value increase.

Water dissociation can be caused not only by thermal effect but also by water molecules vibrational excitation in case of different impacts – rapid fuel and oxidizer molecular-level mixing process, solid catalyst presence, electromagnetic pulse impact, etc. In such cases energy consumed by dissociation is significantly less than energy released from hydrogen burning.

Technologies for neutralization of NO\textsubscript{x} contained in post-combustion gas that use ammonia (NH\textsubscript{3}) are linked to forementioned processes. Due to Muzio and Arand experimental data [9] shows that NO\textsubscript{x} emission decreases with temperature increase, reaches its minimum in the range of 1200-1250K and then tends to raise again (Figure 1).

![Figure 1. Effect NH\textsubscript{3} injection on NO\textsubscript{x} reduction, $\chi = [\text{NH}_3]/[\text{NO}]$](image-url)
According to usual burning theory main reactions rate coefficients are in monotonic dependence of temperature and give no explanation about pronounced minimum of NO\textsubscript{x} concentration. Thus, it happens due to other reasons. Reaction mechanism proposed by Miller and Bowman [10] considers NO\textsubscript{x} reduction with help of self-generated OH\textsuperscript{-} radicals and NH\textsubscript{3} molecules:

\[
\text{NH}_3 + \text{OH} \leftrightarrow \text{NH}_2 + \text{H}_2\text{O} \\
\text{NH}_2 + \text{NO} \leftrightarrow \text{N}_2 + \text{H}_2\text{O}
\]

Gaining certain temperature value major part of ammonia gets dissociated and NO\textsubscript{x} reduction begins to go down.

3. Conclusion
Effects of water and steam injection on hydrocarbon fuels combustion including methane-air burning are well investigated but effects of probable water dissociation usually are not taken into consideration. In spite of separate researches there is no clear ultimate model taking account of dissociation yet. Relying on available experimental results analysis an assumption about ability to manage combustion processes via water dissociation at different temperatures has been proposed.

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