Painting a clear picture of how nitrogen oxides are formed

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Nitrogen oxides (NOx) are some of the most significant pollutants in our atmosphere—they contribute to the formation of smog, acid rain and ground-level ozone. Because of this, combustion researchers and engine companies have been working since the 1980s to understand how these gases are produced during combustion so that they can find ways to reduce them.

In a new review paper published in *Progress in Energy and Combustion Science*, researchers from the U.S. Department of Energy's Argonne National Laboratory and the Technical University of Denmark explain how they synthesized more than a decade's worth of combustion studies to create a new overarching model of how nitrogen oxides are produced.

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"NOx production is one of the main concerns for engine companies," said Argonne chemist Stephen Klippenstein, an author of the paper. "Our understanding of how these pollutants are produced in different engine environments has deepened dramatically."

A wide array of different chemical interactions occur within the mixture of fuel and air in an engine, and the new model identifies several different routes to NOx formation.

In one pathway, called prompt NO (nitrogen monoxide), atmospheric nitrogen combines with carbon to form an intermediary of one carbon and two nitrogen atoms, which eventually combine with oxygen to form nitrogen monoxide. In another pathway, called thermal NO, nitrogen monoxide is produced directly from nitrogen and oxygen. In a third, called fuel NO, a compound of nitrogen, carbon and oxygen forms the intermediary step on the way to nitrogen monoxide.

"Trying to put together these pathways to create a model that accurately reproduces experimental observations has always been a bit of a guessing game," said Argonne chemist Branko Ruscic, another author of the study. "However, because so many scientists from around the world are contributing information about different segments of the larger picture, we're closer than ever before to a model that truly represents reality."

According to Klippenstein, one of the main characteristics of the combustion process—temperature—makes a big difference in the quantity of NOx produced. "The temperature affects the lifetimes of the molecules in the mix," he said. "Being able to accurately model and predict the behavior of some extremely short-lived molecules is crucially important to determining the pathways of the reaction."

"If you can run your engine at a lower temperature, you can avoid the formation of much of the NOx," he added.

Another factor in the combustion process that dramatically affects NOx production involves what researchers call the richness of the fuel mixture—that is, the proportion of fuel to air as combustion takes place in the engine. Engines that run richer will have molecules with more methyl groups, Ruscic said, which tend to promote the formation of NOx.

"We're getting to a place where we understand NOx production pretty well," said Ruscic. "It's really a good example of the triumph of community science."

"It's like putting together a jigsaw puzzle where some of the pieces might seem to fit but haven't yet been painted," said Klippenstein. "It's our role to figure out how to paint a few more pieces so that our collaborators can put together the picture better."

The study, "Modeling nitrogen chemistry in combustion," appeared on

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More information: Peter Glarborg et al, Modeling nitrogen chemistry in combustion, *Progress in Energy and Combustion Science* (2018). DOI: 10.1016/j.pecs.2018.01.002

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