Development of a Coke Index for estimating PM emissions

Steven P. Crossley[1] and Daniel E. Resasco[1]*
[1]*University of Oklahoma, Norman, Oklahoma 73019 (US)*
*resasco@ou.edu

Introduction

Particulate matter (PM) emissions are a growing concern for human health in diesel and kerosene fuels. The Environmental Protection Agency (EPA) has regulated the minimum allowable cetane number (CN) in diesel fuels [1], which will have an impact on PM emissions. It has been shown, however, that the CN of a fuel does not always correlate with PM emissions [2]. For kerosene fuels, threshold soot index (TSI) is the current indicator for how much soot will be formed, and this method is rather crude, as it involves measuring the highest flame height before the flame begins to form soot. Further, CN tests require large volumes of fuel for one test measurement, which is not very practical on a lab scale where 1-2 mL of product may be produced from a particular reaction. Even the smoke point measurement needed for TSI requires around 20 mL of fuel, which would still require days of lab reactions for one data point. For these reasons, a method was developed that gives an estimate of the amount of PM that a given fuel or specific compound may produce, while utilizing only microliters of sample.

Materials and Methods

The coke index method consists of injecting a fuel across a fixed bed of non acidic material Si_2O_3 at elevated temperatures (>800°C) in an oxygen free environment at near atmospheric pressure. PM then forms on the material via pyrolysis and the material then resembles a coked catalyst. The carbon from the "coked" sample is then burned in a temperature programmed oxidation (TPO) system in order to quantify how much carbon was deposited on the surface. Different fuels can then be compared as to how much carbon they form under the same conditions, which is an indication as to how much soot they would form when combusted, as soot formation in an engine is via pyrolysis reactions brought about by high combustion temperatures.

Results and Discussion

In order to create a reliable scale for coke index, a value of 100 was assigned to the amount of carbon that is deposited on the surface from tetralin, which is known to form PM. All other numbers were taken as the ratio of carbon formed by the compound to the amount formed by tetralin under the same conditions. As demonstrated in figure 1, it can be clearly seen that the coke index increases in the following order :
Paraffins<isoparaffins<naphthanics<aromatics, as expected.
The much higher value of tetralin is reasonable as the formation of the aromatic ring is the rate limiting step in PM formation [3].

These results show that the coke index can be a useful tool for estimating the PM that a given fuel will produce when combusted. Applications of this index include measuring the PM emissions a given fuel will produce before and after a reaction has taken place to alter the properties. Also, pure component coke index values are put in a database and a model is constructed which relates the structure of the compound to the coke index, as done by our group for CN [4] and TSI by utilizing molecular descriptors calculated from MDL® QSAR software. This approach will be used in order to predict the coke index of compounds that have not been measured, and to correlate the coke index to CN and TSI of several hundreds of predicted compounds. This provides useful information for determining which compounds are most problematic in current fuels and defining strategies in order to improve them through molecular engineering. Further applications include the estimation of PM specific biofuels may produce, as focus tends to move towards renewable energy sources.

Significance

This work provides a method for estimating the amount of PM a given fuel will produce on a laboratory scale, which could be essential motivation for molecular engineering of fuels via catalytic strategies that maximize compounds that have a lower coke index.

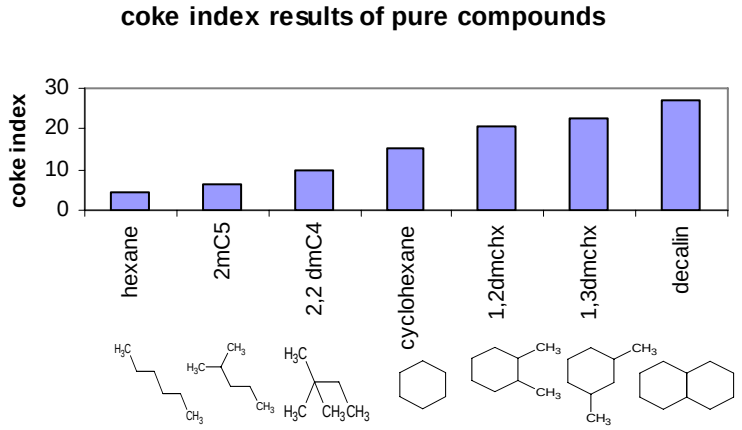

Figure 1. Coke index results of pure compounds. A value of 100 was assigned to tetralin and all other values are in reference to tetralin.

References

1. In "Summary and Analysis of Comments: Control of Emissions from on Road Diesel Engines", EPA 420-R-04-008, May 2004
2. Androulakis, I.P., Weisel, M.D., Hsu, C.S., Kuangnan, Q., Green, L.A., and Farrell, J.T., *Energy and Fuels* 19, 111 (2005).
3. McEnally, C.S. and Pfefferle, L.D., *Combustion and Flame* 143, 246 (2005).
4. Santana, R.C., Do, P.T., Santikunaporn, M., Alvarez, W.E., Taylor, J.D., Sughrue, E.L., and Resasco, D.E., *Fuel* 85,643 (2006).