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A new model for predicting antiknock quality of hydrocarbon fuel blends

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ABSTRACT

A procedure for predicting the Critical Compression Ratio (CCR) and the Octane Number (ON) of hydrocarbon fuel blends is presented in this work. Compositional data as well as antiknock characteristics and thermo-physical properties of the constituent hydrocarbons are taken as input parameters for this calculation. The proposed methodology was developed by considering single-step kinetics for the pre-flame reactions taking place within the combustion chamber of the CFR engine, which is the standard apparatus used in ON evaluation tests. Furthermore, a thermodynamic model was used to describe the relevant processes the in-cylinder fuel-air mixture undergoes prior to the occurrence of knock. In order to validate the proposed method, CCRs of Primary Reference Fuel (PRF) mixtures; Motor ONs (MONs) of paraffinic fuels; and Research ONs (RONs) of Liquefied Petroleum Gas (LPG) fuels were computed and compared with experimental data reported in literature. The maximal absolute error and the root mean square deviation found were, respectively, 0.084 and 0.047 for the CCR of PRF mixtures; 1.6 and 0.60 for the MONs of paraffinic fuels; and 1.45 and 0.70 for the RONs of LPG fuels.

1. Introduction

The knocking phenomenon occurs in the end-gas region of the combustion chamber of a spark-ignition engine when the temperature of the unburned fuel-air mixture surpasses a sufficiently high value during a time enough for ignition to take place before the arrival of the flame front, thus triggering spontaneous combustion in multiple spots within this region. The Octane Number (ON) is an empirical parameter used to assess the antiknock quality of a fuel on the scale devised by Dr. Graham Edgar [1], according to which the ON of n-heptane is 0 whereas that of isooctane (2,2,4-trimethylpentane) is 100. The higher the ON, the greater the fuel resistance to knock. By definition, the ON of a given fuel is the volumetric percentage of isooctane contained in a certain binary mixture of isooctane and n-heptane, which exhibits the same antiknock quality as that fuel. Such binary mixtures are called Primary Reference Fuels (PRFs).

Since the occurrence of knock is influenced by fuel and engine factors, the assessment of the fuel antiknock quality is carried out in such a way that the engine factors are kept unchanged. This is made by using a standardized apparatus – a single-cylinder, variable compression-ratio engine, known as a CFR engine – and by running this engine at fixed operating conditions, which may correspond either to Motor ON (MON) or Research ON (RON) standard test specifications [2,3].

The ON of a fuel is determined through a trial-and-error experimental procedure as described in the ASTM standards [2,3], which include as one of their many intermediate steps the determination of a compression ratio that produces standard knock intensity when the CFR is fed with the investigated fuel – this is the Critical Compression Ratio (CCR). ASTM standards [2,3] state that after the first successful assessment of the ON, the entire procedure should be completed twice again and the average of the three values so obtained is then taken as the sought ON. It is worth mentioning that although a fully automated version of the CFR engine has been available for several years, the experimental determination of ONs has been frequently carried out using previous versions of this engine, the automation level of which is very low despite their high cost, thus requiring the involvement of well-trained technicians. These aspects added to the need for using a standardized apparatus turn out the experimental ON rating a repetitive task that is time, labor and money intensive. Therefore, a methodology that would enable computing instead of measuring the fuel ON is a practical necessity, particularly in the case of an oil refinery plant, where demands for ON determination are frequent for purposes as mixing refinery streams, formulating new gasolines, and designing gasoline surrogates or special fuels [4]. Even in those cases wherein the

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Nomenclature

A	Arrhenius pre-exponential factor
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
c_1, c_2	non-dimensional parameters of the $x_b(t)$ model-functions
CCR	Critical Compression Ratio
CFR	Cooperative Fuel Research
DIR	Dial Indicator Reading, [in]
E_a	activation energy, [J/kmol]
k	CFR engine cylinder height offset, [in]
KA	knocking agent
[KA]	concentration of knocking agent, [kmol/m^3]
LPG	Liquefied Petroleum Gas
m	Mass, [kg]
M	molar mass, [kg/kmol]
MON	Motor Octane Number
n	polytropic exponent
ON	Octane Number
p	pressure, [Pa]
PRF	Primary Reference Fuel
r	engine compression ratio
RON	Research Octane Number
TRF	Toluene Reference Fuel
$\overline{R}$	universal gas constant, 8314 [J/kmol·K]
t	time, [s]
T	temperature, [K]
TDC	Top Dead Centre
u	specific internal energy (per unit mass), [J/kg]
V	volume, [m^3]
x	molar fraction in a liquid fuel blend
x_b	fuel mass fraction burned
y	molar fraction
α, β', γ	parameters of the model for the definite integral Φ
β	blending rule model parameter
λ	coefficient of air excess
ρ	density, [kg/m^3]
τ	knock start time, [s]
Φ	definite integral appearing in Eq. (13)
χ^2	coefficient of determination

Subscripts

1z	related to the single-zone combustion model
approx	approximation
b	burned zone
cr	critical value
dur	duration
eoc	end of combustion
i	related to the *i*-th component
*iC*8	related to isooctane
lin	related to the linear $x_b(t)$ model-function
*nC*7	related to n-heptane
soc	start of combustion
u	unburned fuel-air mixture

experimental determination of the fuel ON is mandatory, the utilization of such a computing methodology can be helpful in guiding the trial-and-error measurement procedure, thus reducing the workload.

A number of models for predicting antiknock quality of hydrocarbon blends are reported in literature. Such models are referred as blending rules, as they are functions of the fuel composition and some properties of its individual constituents. A straightforward example of a blending rule is provided by the Graham Edgar's scale definition, according to which the ON of a PRF is obtained as a linear weighting of its component ONs by their respective liquid volume fractions. However, this simple rule is accurate only for PRFs and has limited usefulness for other fuels, as these typically exhibit a non-linear mixing behavior, the description of which demands additional compensatory parameters. Some of the blending rules reported in literature will be considered in the following paragraphs.

Starting from a set of assumptions related to the cause of fuel knock, Sanders [5] derived an equation that allows calculating the CCR of a fuel blend as a function of its composition, the CCRs of its constituents and the respective (so called) blending constants. Sanders compared calculated and experimental CCR values, thus concluding that these are in close agreement. Twu and Coon [6] proposed an interaction-based empiric correlation for predicting RON and MON of gasoline blends containing saturates, olefins and aromatics. Nikolaou et al. [7] presented a correlation for calculating RON values, and validated it by comparing predicted and measured RONs for 20 isomerisation gasolines containing mainly paraffins and cycloparaffins. Pasadakis et al. [8] developed artificial neural network models to determine gasoline blend RONs. Predicted and measured values were compared for a series of synthetic blends and it was found that the model accuracy is comparable to that of the standard ASTM method.

Several chemometric models can be found in literature, as that by Guan et al. [9] who studied the determination of RON and MON by dielectric spectroscopy coupled with partial least squares multivariate calibration method. To this group of models belongs also that developed by Mendes et al. [10], who explored the usage of distillation curves associated with partial least squares multivariate calibration.

Knop et al. [4] reviewed several octane blending rules reported in literature and proposed a linear correlation on molar basis, which allows predicting the ONs of ternary mixtures of isooctane, n-heptane and toluene (called Toluene Reference Fuels – TRFs). The proposed correlation was compared to alternative formulations from the literature thus evidencing its high accuracy. Based on the work by Morganti et al. [11], AlRamadan et al. [12] proposed a blending rule to predict ONs of ethanol-PRF and ethanol-TRF blends. Predicted and measured ONs were in close agreement, exhibiting a maximum error of 2.7 ON-units but with most of predictions being within the reproducibility limits of the ASTM methods. Yuan et al. [13] proposed a model that combines linear regression and optimal fitting of Scheffé polynomials for correlating ONs of fuel mixtures. These authors also applied their model to the study of ethanol-TRF blends and found maximal absolute errors less than 2 ON-units for mixtures with RON between 80 and 120. Naser et al. [14] presented a methodology to estimate RON and MON from homogeneous gas-phase ignition delay time data, and concluded that predicted values agree satisfactorily with measurements.

A thorough review of the antiknock quality blending rules reported in literature may show that all of them share at least one of the following two characteristics: (*i*) the rule targets straightly the calculation of ON, treating this characteristic as the natural parameter to assess the fuel antiknock quality; (*ii*) the rule is essentially empirical and does not draw upon the underlying physics of the knocking phenomenon. Although being recurrent, these characteristics may impact, respectively, the accuracy and the applicability range of the blending rule. In order to realize how the accuracy is affected, it is worth recalling that while the Graham Edgar's scale allows defining ON ratings up to 100, a different scale definition is necessary for values exceeding this limit. The ASTM adopted one based on the knocking behavior of mixtures containing isooctane and tetraethyl lead. Therefore, considering that the ON rating involves two different approaches, it is expected that the mathematical description of an ON blending rule will also be accomplished with different mathematical expressions, each accounting for