Progress in Energy and Combustion Science 60 (2017) 1–25

Contents lists available at ScienceDirect

Progress in Energy and Combustion Science

journal homepage: www.elsevier.com/locate/pecs

Impact of fuel molecular structure on auto-ignition behavior – Design rules for future high performance gasolines

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ARTICLE INFO

Article History:
Received 23 May 2016
Accepted 6 December 2016

Keywords:
Octane
Knock
Auto-ignition
Gasoline
Downsizing

ABSTRACT

At a first glance, ethanol, toluene and methyl tert-butyl ether look nothing alike with respect to their molecular structures. Nevertheless, all share a similarly high octane number. A comprehensive review of the inner workings of such octane boosters has been long overdue, particularly at a time when feedstocks for transport fuels other than crude oil, such as natural gas and biomass, are enjoying a rapidly growing market share.

As high octane fuels sell at a considerable premium over gasoline, diesel and jet fuel, new entrants into the refining business should take note and gear their processes towards knock resistant compounds if they are to maximize their respective bottom lines. Starting from crude oil, the route towards this goal is well established. Starting from biomass or natural gas, however, it is less clear what dots on the horizon to aim for.

The goal of this paper is to offer insight into the chemistry behind octane boosters and to subsequently distill from this knowledge, taking into account recent advances in engine technology, multiple generic design rules that guarantee good anti-knock performance.

Careful analysis of the literature suggests that highly unsaturated (cyclic) compounds are the preferred octane boosters for modern spark-ignition engines. Additional side chains of any variety will dilute this strong performance. Multi-branched paraffins come in distant second place, owing to their negligible sensitivity. Depending on the type and location of functional oxygen groups, oxygenates can have a beneficial, neutral or detrimental impact on anti-knock quality.

Contents

Abbreviations: AKI, anti knock index; BDE, bond dissociation energy; bTDC, before top dead center; CFR, cooperative fuels research; CN, cetane number; EP, ethyl propionate; FAME, fatty acid methyl ester; FBRU, full-boilling unleaded reference fuels; GDI, gasoline direct injection; MB, methyl butanoate; MON, motor octane number; NTC, negative temperature coefficient; OI, octane index; ON, octane number; PFI, port fuel injection; RON, research octane number; SI, spark-ignition; TS, transition state; WOT, wide open throttle

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http://dx.doi.org/10.1016/j.pecs.2016.12.001

1. Introduction

Midway the 19th century, before the advent of the internal combustion engine, kerosene was long considered to be the only valuable constituent of crude oil, to be used increasingly for lighting purposes against the background of a waning supply of whale oil. What we refer to now as gasoline and diesel, are intrinsically co-produced in the refining process of crude oil to kerosene. These side streams were at the time considered either too unstable or dirty for household use, respectively. As such, these streams were either dumped in rivers or burnt on site.

With exponentially growing demand for kerosene, however, the latent value of aforementioned residual products eventually became an important catalyst for innovation and helped to spark the development of the first internal combustion engines in the late 19th century. This feedstock driven approach of designing the engine around the prevailing fuel is far from optimal, as the prevalence of engine knock, soot and noxious emissions still challenges engine designers more than a hundred years later.

In light of increasing legislative demand for biofuels and the emergence of natural gas as an alternative feedstock for fuels, the timing for a paradigm shift, whereby the fuel is designed around the engine, rather than *vice versa*, is right. Why not design bio- and natural gas refineries such that they produce biofuels that compensate for deficiencies in their crude oil counterparts? In this regard, an attractive deficiency to target is the relatively poor anti-knock quality of "raw" gasoline. Octane boosters sell at considerable premiums over this particular petrochemical cut.

The goal of this paper is to offer insight into the chemistry behind octane boosters and to subsequently distill from this knowledge multiple generic design rules that guarantee good anti-knock performance, taken into account also recent advances in engine technology.

Section 2reviews the literature on trends in spark ignition engine technology and identifies an important common denominator. Section 3 reflects on the impact of evolving engine technology on octane booster requirements. The chemistry behind octane boosting performance is subject of Section 4. Insights from Section 4 and subsequently used in Section 5 to distill generic design rules for future octane boosters. Finally, in Section 6, conclusions and recommendations will be presented.

2. Trends in engine technology

One of the most important fuel parameters for spark-ignition (SI) engines is the anti-knock quality. Knock occurs when the octane requirement of the engine exceeds the octane quality of the fuel [1]. It manifests as a metallic clanking noise due to the prevailing pressure fluctuations [2], which can ultimately lead to damage of critical engine parts such as liners, bearings and pistons.

The anti-knock quality of a fuel is normally rated by its octane number(ON), which can be determined in accordance with one of two protocols on a so-called cooperative fuel research (CFR) engine: Research Octane Number (RON) or Motor Octane Number (MON). Both standards use n-heptane and iso-octane as reference fuels, whereby both RON and MON are by definition 0 and 100, respectively.

Whether or not a fuel will auto-ignite is as much dependent on the fuel anti-knock quality as on the prevailing engine operation conditions. This section will focus on those trends in SI engine technology that have most significantly changed the conditions inside the combustion chamber. It will become evident that the common denominator of these trends, notably turbocharging, direct injection and higher compression ratios, is that all contribute to lower unburnt gas temperatures relative to pressure. This effective cooling has a favorable impact on the so-called octane appetite of the engine (i.e., minimal fuel octane number required to avoid knock). It will be demonstrated that lower gas temperatures generally result in a lower minimum octane number requirement for a given operating condition.

2.1. Direct injection

Direct fuel injection has been installed onto spark-ignition engines as early as 1902 and first featured in Antoinette aircraft, designed by Leon Levavasseur. Added benefits compared to carbureted fuel delivery included avoidance of freezing and enabling the use of less volatile, but more knock resistant alternative fuels [3]. A further refinement of the technology by Bosch fifty years later, the first gasoline direct injection (GDI) engine for an automotive application debuted in the 1952 Goliath GP700 Sport (two-stroke) and subsequently featured in the 1955 Mercedes 300SL.

After these first models were introduced, GDI was shelved, only to be reintroduced again over forty years later, this time by predominantly Japanese car makers (e.g., Mitsubishi, Nissan, Toyota) in the late 1990s. Market share for GDI in the EU-27 has since increased from a negligible level in 2001 to 14% in 2010 (Table 1).

An important benefit of GDI relative to port fuel injection (PFI) is that the improved evaporative cooling of the former injection method leads to lower charge temperatures [6]. With PFI, relatively large droplets collide with and form a liquid film on the intake valves and port wall. This results in the evaporation process being driven primarily by heat absorption from said surfaces [7]. GDI, conversely, involves injecting a well atomized spray directly into the combustion chamber, thus leading to vaporization powered chiefly by heat