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

Michael D. Boota,*, Miao Tianb, Emiel J.M. Hensenc, S. Mani Sarathyd

Abstract
At 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.

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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 2 reviews 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.
absorption from the charge alone [7]. Accordingly, post fuel injection charge temperatures will be lower for GDI than is the case for PFI. Charge temperatures before compression were even higher before the advent of PFI, when carburetters were still the dominant fuel delivery system. To prevent icing, carburetters were heated as a matter of course, which manifested in intake air temperatures of upwards of 50 to levels as high as 150 °C vis-à-vis 30 °C for PFI [2].

2.2. Downsizing

First introduced in the 1962 Oldsmobile Cutlass, the initial purpose of turbochargers in SI engines was to boost power in US built muscle cars. Porsche had the European debut in 1975 in its 911 model. Up until the late 90s, however, turbocharged SI engines were used only in niche applications. As can be seen in Table 1, boosted SI engines became more mainstream from the 2000s onwards and had nearly a quarter of the Western European market by 2010. This sharp increase was motivated not only by continuous demand for higher power output, but increasingly also by both legislative and consumer pressure to improve fuel economy. As it happens, fuel economy benefits considerably from downsizing to smaller displacement volumes.

By means of turbocharging, the otherwise incurred drop in power is compensated by higher intake pressures, effectively mimicking a larger displacement volume. Owing to correspondingly lower throttling and other parasitic losses, engine efficiency can increase by as much as 18% when a 1.6 l naturally aspirated engine is downsized to 0.8 l and subsequently turbocharged to maintain power output [6]. In Table 1 can be seen that the increase in market share of turbocharged engines coincided with both a decrease in displacement volume and increase in power density; both being hallmarks of downsizing.

As discussed earlier, GDI reduces the charge temperature due to enhanced evaporative cooling, while leaving unaffected the charge pressure. Turbocharging an engine, conversely, increases the charge temperature by means of compression. This rise, however, is lower than adiabatic compression would predict. This discrepancy can be traced back to considerable heat losses in the intake manifold and the intercooler, the latter heat sink being the more dominant of the two [6]. In other words, for a given charge pressure, as was also seen earlier for GDI, intercooler assisted turbocharging has a cooling effect on the charge temperature.

2.3. Higher compression ratios

The compression ratio also has an influence on the unburnt charge temperature relative to pressure. As this ratio is increased, the end of compression volume reduces in size, thereby expelling a greater fraction of hot combustion gases in the exhaust stroke. Consequently, less hot residual gas is left over to mix with the cooler air during the intake stroke, effectively reducing the charge temperature relative to pressure [8,9].

Compression ratios have risen considerably over the past decade, enabled to a large extent by the previously discussed cooling effect of GDI on the unburnt gas temperature [10,11]. For a naturally aspirated engine, GDI allows increases in compression from approximately 10 to over 11.5 [11]. For a turbocharged engine, GDI has allowed for an increase from about 8.8–9.6 in recent years [11].

3. Octane booster requirements

Auto-ignition chemistry is highly dependent on the pressure/temperature history of the unburnt air/fuel mixture. The engine technologies discussed in Section 2 all result in a reduction in temperature relative to pressure, thereby reducing the knocking tendency of the engine for any given fuel. It will be made clear in this section that today’s milder engine operating conditions require new measures to determine the octane requirement of an engine. To this end, the history of octane rating methods will be discussed.

3.1. Current octane rating methods

3.1.1. Research and motor octane number

Engine knock is caused by the auto-ignition of cylinder end-gas ahead of the spark ignited flame front [12,13]. Auto-ignition chemistry of fuels in the low and intermediate temperature regime is closely related to the fuel’s anti-knock quality. Detailed chemical reaction mechanisms controlling ignition properties typically include hundreds of species and thousands of elementary reactions, especially in the low temperature regime.

Commercial fuels, like gasoline and diesel, are mixtures of different hydrocarbons types (e.g., paraffins, olefins, aromatics), each class having their own specific auto-ignition characteristics. This complexity in real fuels makes it challenging to accurately predict auto-ignition chemistry in a quantitative sense. To circumvent this, surrogate fuels, comprised of a limited number of components, are typically used to predict the ignition quality of real fuels.

Since 1932 [14], knock resistance is commonly expressed as a RON and MON. To date, both values are determined on a standardized CFR engine in accordance with ASTM protocols D-2699 and D-2700 [15], respectively. Both norms were designed to be representative of the most mild (RON) and severe (MON) operating conditions encountered in 1930s SI engines. In both tests, the highly reactive n-heptane and highly stable iso-octane are used as surrogate fuels, spanning the octane scale from 0 to 100, respectively [16].

| Year | EU-27 | Power | Displacement | Power density | W-EU | Market share |
|------|--------|-------|--------------|--------------|------|--------------|
|      | %      | kW    | cc           | kW/l         | %    |              |
| 2001 | 0      | 74    | 1709         | 43.3         | 7    |              |
| 2002 | 0      | 77    | 1723         | 44.7         | 8    |              |
| 2003 | 1      | 78    | 1731         | 45.1         | 9    |              |
| 2004 | 2      | 80    | 1735         | 46.1         | 10   |              |
| 2005 | 3      | 82    | 1732         | 47.3         | 12   |              |
| 2006 | 4      | 84    | 1730         | 48.6         | 14   |              |
| 2007 | 4      | 86    | 1729         | 49.7         | 16   |              |
| 2008 | 11     | 85    | 1696         | 50.1         | 18   |              |
| 2009 | 12     | 81    | 1619         | 50.0         | 20   |              |
| 2010 | 14     | 84    | 1633         | 51.4         | 22   |              |

Table 1

Spark ignition engine performance and market share of gasoline direct injection and turbocharging.
### 3.1.2. Road octane number

From 1947–1996, the Coordinating Research Center (CRC), a U.S.-based non-profit organization, conducted annual octane requirement surveys for the purpose of informing the automotive and oil sectors on the octane appetite of new car populations. Introduction of knock sensors on most SI engines from the early 1990s onwards reduced the efficacy and need of these surveys, ultimately leading to the termination of the program in 1996 [14].

CRC tests were conducted on chassis dynamometers at both part-load and wide-open-throttle (WOT). At both conditions, the so-called Road Octane Number is determined using full-boiling unleaded reference or FBRU fuels that have a known RON and MON. These model fuels were designed to be similar to prevailing commercial unleaded gasolines [17]. Ever-poorer octane quality FBRU fuels were burnt until the occurrence of knock at either of aforementioned operating conditions.

Based on the data from these surveys, a correlation for the Road Octane Number, measured with realistic fuels in real engines, as a function of RON and MON was introduced by Spitzer et al. in 1967 [18].

\[
\text{RoadON} = a + b \cdot \text{RON} + c \cdot \text{MON}
\]  

(1)

Least-square regression of the CRC data yielded values for the various constants. An analysis of the trends of these constants over the period 1951–1991 by Mittal and Heywood [14] reveals an ever-decreasing relative importance of MON over RON. This may be interpreted as cooler charge temperatures relative to pressure, brought about by mass adoption of the technologies outlined in Section 2, effectively reducing the Road ON to a proxy for RON.

### 3.2. New octane rating method

Knock resistance is highly sensitive to intake temperature relative to pressure [2,8,9,14,19]. RON and MON intake temperatures (Table 2), however, are notably higher than is the case for modern engines, allowing for high intake temperatures. Effective exhaust gas aftertreatment thus made possible a reversal towards lower intake temperature, for high intake temperatures. Effective exhaust gas aftertreatment and wide-open-throttle (WOT). At both conditions, the so-called Road Octane Number is determined using full-boiling unleaded reference or FBRU fuels that have a known RON and MON. These model fuels were designed to be similar to prevailing commercial unleaded gasolines [17]. Ever-poorer octane quality FBRU fuels were burnt until the occurrence of knock at either of aforementioned operating conditions.

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As exhaust gas catalysts became more efficient and were able to operate at lower light-off temperatures, there was no longer need for high intake temperatures. Effective exhaust gas aftertreatment thus made possible a reversal towards lower intake temperature, brought about, for the greater part, by the technologies outlined in Section 2.

With typical intake temperatures currently well below 50 °C, engines have moved firmly into “beyond RON” territory [20]. In order to take this effect into account, a new anti-knock quality measure, was introduced by Kalghatgi [19].

\[
\text{OI} = (1-K) \cdot \text{RON} + K \cdot \text{MON}
\]  

(2)

The octane index (OI), as formulated in Eq. (2), introduces a new parameter K, an engine condition dependent weighting factor that is a function of end-gas temperature-pressure history prior to autoignition. Note that the OI can be written as a version of the Road Octane Number when the constants of said equation are set at 0, (1– K) and K, respectively.

| Parameter                  | RON | MON |
|----------------------------|-----|-----|
| Intake air temperature     | 52°C| 149°C|
| Intake air pressure        | atmospheric | atmospheric |
| Coolant temperature        | 100°C| 100°C|
| Engine speed               | 600 rpm | 500 rpm |
| Spark timing               | 13° BTDC | 14–26° BTDC |
| Compression ratio          | 4–18 | 4–18 |

* Crank angle degrees before top dead center.

| K values reported in literature. |
|----------------------------------|
| Maximum | Minimum | Year of publication | Reference |
|---------|---------|---------------------|-----------|
| 0.28    | −0.33   | 2001                | [19]      |
| 0.21    | −1.85   | 2005                | [8]       |
| −0.13   | −1.68   | 2006                | [21]      |
| 0.25    | −0.65   | 2008                | [2]       |
| −0.5    | −4      | 2010                | [22]*     |
| −0.12   | −0.93   | 2012                | [23]      |

* GDI engine at sea-level.

By definition, K holds the value of 0 and 1 for RON and MON conditions, respectively. Traditionally, K was thought to have a positive value of 0.5, equating the OI to the anti knock index (AKI) or pump octane [20], which is still clearly labeled on gasoline fuel pumps throughout the United States.

\[
\text{AKI} = \frac{\text{RON} + \text{MON}}{2}
\]  

(3)

Based on a combination of literature, models and CRC reports, Mittal and Heywood [14] reported in 2009 that the value for K had fallen from roughly 1 in 1930, to 0.5 in 1945, and down to 0 in the early 2000s. More recent data on K shows that these authors correctly predicted K would turn negative in the near future (Table 3).

The causality of this drop may be attributed to ever-cooler unburnt gas temperatures relative to pressure effectuated by the technological developments discussed in Section 2. Accordingly, it should not come as a surprise that here is a good correlation for K with the unburnt gas temperature [e.g., at a compression pressure of 15 bar (Tcomp)15] [8,24–26]). At 15 bar, values for K were found to decrease from around 6 at 1000 K to 0 at 700–800 K, down to −2.5 at 500 K [8]. Note that for RON and MON test conditions this temperature is roughly 700 and 850 K, respectively [23]. Data on K versus Tcomp15 from various studies have been plotted in Fig. 1.

A second parameter included in the OI methodology is fuel sensitivity (S) to changing charge temperature relative to pressure. S is defined here as the difference between RON and MON (Eq. (4)) [19].

\[
S = \text{RON} - \text{MON}
\]  

(4)

The OI, as defined earlier by Eq. (2), can be rewritten as a function of both K and S (Eq. (5)) [19].

\[
\text{OI} = \text{RON} - K \cdot S
\]  

(5)

Shown in Fig. 2, the OI of iso-octane, toluene and 2-methylheptane, each having a distinct S (e.g., 0, 11 and −2.1, respectively [27,28]) are plotted against K. It can be seen that, when S > 0, the OI increases as K is decreased. As a consequence, as K moves into

![Fig. 1. K versus Tcomp15 (◊ [19], □ [23], *: RON and MON condition, × [24], ○ [26]).](image-url)
negative territory, indicative of more advanced engine technology, both a high RON and S are required to ensure adequate anti-knock quality. In other words, in modern engines at least, fuels with a high S outperform their less sensitive counterparts on the OI scale, an equal RON notwithstanding [22, 23].

Prompted by environmental concerns and associated fuel quality legislation, the relative contribution of the various hydrocarbon classes in gasoline has shifted significantly over the past two decades. Olefins (alkenes) have been linked to photochemical smog formation via exhaust born intermediate, notably 1,3-butadiene [29–31]. Aromatics have been found to increase emissions of unburnt hydrocarbons, carbon monoxide and benzene [32]. Listed by the International Agency for Research on Cancer as a Group 1 substance (i.e., agent (mixture) is carcinogenic to humans), benzene is a particularly toxic member of the aromatics family [33]. This compound has been linked to lymphatic and hematopoietic cancer [34] and leukemia [35]. Moreover, slightly higher NOx emissions have been observed for those gasolines rich in aromatic content [34].

No wonder then that olefinic and aromatic content in gasoline is subjected to increasingly stringent caps (Table 4). As a consequence, the paraffinic fraction in gasoline, notably iso-paraffins (e.g., iso-octane), has steadily risen to compensate for the otherwise drop in octane quality incurred by the removal of high octane aromatics and olefins.

Aromatics and olefins, however, tend to have S values that far surpass those of paraffins (Fig. 3). In fact, S for most paraffins is close to naught [1]. As a consequence, aforementioned paraffinic pivot will have a pronounced impact on the OI. As could be seen earlier in Fig. 2, while older engines benefit from a low S, a high value is favored in their more modern counterparts. Fortunately, this adverse impact on S has been partially offset by downstream blending of oxygenates: ethers (e.g., MTBE) since the early 80s and alcohols (e.g., ethanol) since the 2000s. These compounds have a higher RON and S than both gasoline and iso-octane (Table 5).

![Fig. 2. OI as a function of K for fuels with different S.](image)

![Fig. 3. Sensitivity plotted against paraffinic fraction for various studies.](image)

| Compounds | Octane Index | Sensitivity |
|-----------|--------------|-------------|
| Ethanol   | 109          | 90          | 128         | 19          |
| Methanol  | 109          | 89          | 129         | 20          |
| TAMEd     | 112          | 98          | 126         | 14          |
| MTBEd     | 117          | 101         | 135         | 16          |
| ETBEa     | 118          | 101         | 133         | 17          |
| TAMEb     | 112          | 98          | 126         | 14          |
| Iso-octane| 100          | 100         | 100         | 0           |
| Benzene   | 101          | 93          | 109         | 8           |
| Toluene   | 120          | 109         | 132         | 11          |
| p-xylene  | 124          | 97          | 151         | 27          |
| p-cymene  | 124          | 101         | 147         | 23          |

Table 4

| Implementation date | Directive | Olefins | Aromatics | Benzene |
|---------------------|-----------|---------|-----------|---------|
| October 1994        | Voluntary | –       | –         | 5       |
| January 2000        | 98/70/EC | 18      | 42        | 1       |
| January 2009        | 2009/30/EC | 18   | 35        | 1       |

Table 5

3.3. Blend octane numbers

By definition, linear by volume blending of primary reference fuels of n-heptane and iso-octane determine the octane number of the mixture. Recent work by Pera and Knop [42] and Kalghatgi et al. [43] have shown that linear by mole blending rules can better estimate the octane numbers and antiknock quality of toluene, n-heptane, iso-octane, mixtures. However, quantifying the octane number of mixtures comprising additional components (e.g., other hydrocarbons, oxygenates, etc.) is challenging because blending interactions are highly non-linear.

For example, Ghosh et al. [44] tested nearly 1500 gasoline fuels comprising various paraffins, iso-paraffins, olefins, naphthenics, aromatics, and oxygenates, and showed that a compositional based model for prediction RON and MON required several non-linear interaction terms. Maylin et al. [45] came to similar conclusions when studying octane numbers of various gasoline mixtures and antiknock additives. They showed that alkylates and isomerizates blend synergistically while re-formates blend antagonistically. Therefore, laws of additivity cannot be used to determine the octane numbers of complex gasoline mixtures.

There has been considerable research on ethanol addition for improving the antiknock quality of gasoline fuels. Hunwartz et al. [46]...
showed that linear by volume blending of ethanol to gasoline increased RON, but later work by Anderson et al. [47] demonstrated that octane number follows a linear by mole blending response. Anderson et al. [47] subsequently reported that ethanol addition to gasoline showed that non-linear blending regimes also existed, which was later confirmed by Foong et al. [48]. The effect of ethanol blending changes depending on the composition of the base gasoline because ethanol blends synergistically with paraffins and antagonistically with aromatics. AlRamadan et al. [49] recently showed the linear and non-linear blending regimes for ethanol addition to toluene, n-heptane, iso-octane mixtures (TPRF).

The effect of blending on RON and MON is typically better described by a blending octane number measurement (BON). The American Petrochemical Institute [28] reported the BON for various molecules by adding 20 vol.-% to a mixture of 40 vol.-% n-heptane and 60 vol.-% iso-octane (PRF60). While this information is useful, it may not fully quantify the BON of molecules when added to real gasolines which contain other hydrocarbon components. Christensen et al. [50] measured the blending RON and MON of various oxygenates added to gasoline, and showed that some oxygenates display blending octane numbers higher than their neat fuel octane numbers while other oxygenates showed decreased blending octane numbers. These results demonstrate the complexity in determining blending effects of various antiknock additives, and suggest that significantly more research is needed to better understand interactions at the molecular level.

3.4. Classes of octane boosters

Commercial octane boosters can be divided into two main categories, organic and organometallic. The former class may contain the elements C, H, O and N, while the latter contains one or more of aforementioned elements plus a metal. Arguably, the story of organometallic additives starts in 1916, when Midgley and Kettering observed that the anti-knock quality of kerosene could be improved significantly by adding 20 vol.-% to a mixture of 40 vol.-% n-heptane and 60 vol.-% iso-octane (PRF60). While this information is useful, it may not fully quantify the BON of molecules when added to real gasolines which contain other hydrocarbon components. Christensen et al. [50] measured the blending RON and MON of various oxygenates added to gasoline, and showed that some oxygenates display blending octane numbers higher than their neat fuel octane numbers while other oxygenates showed decreased blending octane numbers. These results demonstrate the complexity in determining blending effects of various antiknock additives, and suggest that significantly more research is needed to better understand interactions at the molecular level.

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After the First World War, the same researchers, now funded by such corporations as Standard Oil and General Motors, continued their study by scanning criss-cross through the period table from arsenic to tellurium. It was found that Pb, Cu, Ni, Th, Fe and Mn containing compounds increased the octane number significantly, while Co, Zn, Bi, V, Se and Ce were slightly less effective [52]. Ultimately, tetaethyl lead (TEL) was found to be the best performing anti-knock agent, followed by tetraphenyllead, iron pentacarbonyl and nickel carbonyl [52].

Up until the 1970s, TEL was the most widely used octane booster. Owing to health concerns and incompatibility with the then recently introduced catalytic converters, organometallic compounds were gradually phased out of most markets and replaced by organic octane boosters, notably oxygenates such as MTBE and ETBE, as well as aromatics (e.g., benzene-toluene-xylene (BTX)) and iso-paraffins (e.g., iso-octane). More recently, bio-derived ethanol has become one of the most important octane boosters.

Aforementioned organic octane boosters are built up exclusively from C, H and, in some cases, also O atoms. Though far less prevalent in practice, some studies demonstrate superior anti-knock performance for octane boosters that also harbor nitrogen in their molecular structure (e.g., n-methylaniline monomethylaniline [53–55]). Although these, along with aforementioned organometallic octane boosters, fall outside the scope of this paper, it is still worthwhile to briefly review the working principles of both octane booster classes here.

The chemical mechanism behind TEL’s and other organometallics’ success involves their decomposition to metal oxide particles in the unburnt gas mixture, which tend to scavenge radicals formed as a result of low temperature fuel oxidation reactions. This, in turn, inhibits pre-flame chain branching reactions, which would have otherwise lead to autoignition and, finally, knock [56]. For example, TEL first thermally decomposes and oxidizes to lead oxide. Lead oxide, in turn, acts like a radical sink for HO2 and H2O2 by way of various surface reactions [57–59]. As will become clear in a later section, the concentration of HO2 and H2O2 is very important for intermediate temperature reactions, whereby a deficiency of said species can effectively inhibit the auto-ignition process in this specific temperature range.

The excellent anti-knock properties of organic amines were already known as early as 1919 [60]. Brown et al. [60] tested a wide range of amine additives and found that many compounds were (very) effective octane boosters, notably, 4-sec-buty1-phenylenedi-amine and n-nitrosodiphenylamine. N-methylaniline (NMA) has also been reported to be a particularly effective knock suppressant [53–55]. While no detailed amine oxidation mechanism could be found in literature, some clues are provided by Cullis et al. [61], who link amine anti-knock performance to the formation of stable...
intermediates. N-H bonds are relatively weak and therefore readily facilitate H atom abstraction [80 kcal/mol in aniline [61]]. This process competes with H atom abstraction from fuel compounds by consuming active radicals [62]. The aromatic amine radicals yielded as a result of aforementioned H atom abstraction are resonance stable [61] and thus tend to slow down the overall reaction rate.

4. Impact of molecular structure on auto-ignition chemistry

For a given set of engine operating conditions, higher octane numbers require higher ignition delays [63]. Ignition delay, in turn, for a given temperature-pressure history (and equivalence ratio), is a function mainly of fuel molecular structure. There are ten main reaction types in the auto-ignition process, which are schematically drawn in Fig. 4 and tabulated below.

(a) Unimolecular decomposition: bond cleavage at the C—C or C—H bond, which requires a lot of energy and thus occurs mainly at high temperature.

(b) Hydrogen (H) atom abstraction: a small radical or compound, such as OH, HO2, O2, CH3, reacts with the fuel molecules, removing H in the process. This reaction requires less energy and it can thus take place at both low and high temperatures.

(c) O2 addition reactions: O2 adds to the radical, producing a peroxy radical, and can initiate low temperature branching reactions. It reacts rapidly because it has a negligible activation energy. Peroxy radicals, however, are not stable at high temperature.

(d) Other addition reactions: radicals such as H, OH or HO2, attach themselves to unsaturated bond sites; a process which has a relatively low activation energy.

(e) Recombination reactions: radicals combine together to form a stable covalent bond, which also occurs at a relatively low activation energy [64].

(f) β-scission: involves a scission at the bond site in the β position to the atom (C or O) carrying the unpaired electron, yielding small olefin or aldehyde, respectively, and a radical, in the process. This reaction has a high activation energy of 15–50 kcal/mol and is therefore mainly a high temperature phenomenon.

(g) Isomerization: this refers to intra H atom transfer from one C atom to another and/or to a C—O bond moiety. The activation energy of this reaction depending on the size of the transition ring, which will be discussed later.

(h) Concerted elimination: two substituents are removed from a molecule in one step mechanism, forming an unsaturated bond.

(i) Radical cyclization: this yields cyclic products, as is the case for decomposition to a cyclic ether and an OH radical.

(j) Disproportionations: two radicals react to form two different non-radical products, typically occurring at low activation energies.

The above reactions types will now be discussed separately for each of the main carbon bond types: paraffinic, olefinic, aromatic and oxygenated. Hereby, the low to intermediate temperature range is the most interesting range as it is most representative for practical engine conditions. Detailed chemical kinetic models of various hydrocarbon classes have been well reviewed. For example, Miller et al. introduced and summarized the importance and methods to build kinetic models [65], and reviewed elementary reaction rates in a number of important reaction systems, particularly at low temperatures [66,67]. Battin–Leclerc [68] and Simmie [69] summarized kinetic models at low and high temperature, respectively, Pitz [70] reviewed various kinetic models for diesel surrogate fuels.

4.1. Paraffinic bonds

4.1.1. Negative temperature coefficient

Many studies have discussed the auto-ignition behavior of paraffins, the main constituents of commercial gasolines, and it is the most well studied group [71–84], good summary can be found in [68]. In recent years, more reactions are considered [85,86] in the mechanism to better understand the oxidation process, especially in the low temperature range. Owing to the advent of quantum chemistry calculations, revised kinetics and thermodynamics in the low temperature range can reproduce the experiments with better accuracy [87–89].

Based on the reaction mechanisms presented by Curran et al. [71,90], the main reaction pathways for long chained paraffins or alkanes can be drawn schematically as is shown in Fig. 5.

At low temperatures, after the formation of first fuel alkyl radicals (R), H atom abstraction is the dominant initial reaction, since it requires a relatively low activation energy. The most important reaction at low temperature is the oxygen addition reaction of alkyl radicals to produce allylperoxy-radicals (RO2) (Reaction 6).

\[ R + O_2 \Rightarrow RO_2 \]  

(6)

Given an adequate pool of RO2 radicals, carbon-centered hydroperoxyalkyl radicals (QOOH) are formed by internal H atom migration via five-, six-, or seven-membered transition state (TS) rings. Fig. 6 illustrates one possible pathway of isomerization for isooctane, involving in this case a 6-membered TS ring.

QOOH radicals subsequently react further with oxygen to form peroxyhydroperoxide radicals (O2QOOH). O2QOOH radicals, in turn, tend to abstract H atoms from the C atom which attached to the OOH group, producing O(OOH)2 radicals, ultimately yielding OH radicals and Carboxyhydroperoxide species via isomerization and decomposition reactions (reaction route (a) in Fig. 7). Carboxyhydroperoxide decomposes to alkoxy and OH radicals. These reactions lead to the formation of active OH and carbonyl radicals, thereby accelerating the overall reaction rate. These chain branching reactions then lead to rapid low temperature chemistry [91]. This is the main reaction pathway of the O2QQOH, because the C–H bond adjacent to hydroperoxyl group is significantly weaker than analogous C–H bonds on a regular alkyl chain. Other sites are also possible for H atom isomerization reactions (Fig. 7) in a manner analogous to QOOH decomposition [89], which will be discussed later.

As the temperature increases, decomposition of QOOH radicals is favored over O2 addition reactions. There are three main pathways for QOOH decomposition, as is illustrated in Fig. 5. According to the different position of the abstracted H atom site, the products vary from cyclic ethers and OH radicals to olefins and HO2 or carbonyl radicals.
Tagged radicals. These are all chain propagation reactions. The HO$_2$ radical is quite stable at low temperature, so it can easily accumulate and react readily with itself to produce H$_2$O$_2$. This reaction acts as an inhibiting reaction at low to intermediate temperatures [67]. Reaction 6 is very sensitive to temperature. The temperature at which the reverse reaction becomes important is related to the so-called ceiling temperature (i.e., temperature at which [RO$_2$]/[R] = 1 [92]). This intermediate temperature, typically roughly 850 K, marks the border between NTC and low temperature chemistry.

Therefore, at intermediate temperatures, defined here as 850–1200 K [93], QOOH decomposition competes with low temperature O$_2$ addition reactions. As a result, the dominant reaction route shifts from chain branching to propagation when the temperature rises. This shift, together with the formation of stable products, slows down the overall reaction rate, manifesting as negative temperature coefficient or NTC behavior which is unique to parafins and those compounds having long paraffinic branches.

At the high end of the intermediate temperature range, NTC chemistry is gradually marginalized as Reaction 6 favors the reverse direction. When the temperature increases above 1000 K, H$_2$O$_2$ readily breaks down into two active OH radicals. These radicals accelerate the overall reaction rate, thereby releasing still more heat. Once crossing into the high temperature regime (T $>$ 1200 K), unimolecular decomposition of hydrocarbon radicals fast becomes the dominant route. Now, the reaction rate is controlled mainly by Reaction 7 and therefore fuel molecular structure becomes less important for auto-ignition chemistry [94].

\[
H + O_2 \rightarrow O + OH
\]  

(7)

Owing to low temperature branching reactions, paraffins react very fast at low temperatures, while in the intermediate range, as a result of NTC behavior, the reaction rate slows down. Said behavior is the primary reason why most paraffins have similar RON and MON values, given that both operating conditions yield reaction temperatures in the low temperature and NTC region (Fig. 8).

4.1.2. Chain length and branching

At low to intermediate temperatures, alkyl radical isomerizations (Fig. 6) are important precursors to subsequent chain branching reactions. Only transition state rings, sized within a certain range, namely five-, six-, seven-membered, have an adequately low strain energy that is needed in order for RO$_2$ to form QOOH.

Note that a hydrocarbon with a longer paraffinic chain will have more possible sites for having such isomerization reactions, which explains why longer chains are generally more reactive and have commensurately short ignition delay times. The same logic holds for highly branched paraffins, the comparatively slow reaction rates of which being the result of an intrinsic drop in average chain length for every branch.
Moreover, as will be discussed later, primary C—H bonds, located at the chain extremities are stronger than those found on C positioned within the chain. In Fig. 9, which shows the ON of different paraffins with various chain lengths, degree and location of branching, it can be seen that the ON falls dramatically for longer chains.

4.1.3. Cyclization

In general, cyclic paraffins have a lower reactivity and thus higher ON than their acyclic counterparts [63]. For example, the RON of n-hexane and cyclohexane is 24.8 and 83, respectively [28]. Cyclization results in some distinct oxidation characteristics [95]:

- Olefin yielding concerted elimination competes with low temperature branching reactions, owing to the conformational inhibition of isomerization from RO2 radicals to QOOH.
- Contrary to what is the case for acyclic paraffins, alkyl substitution of cyclic variants increases low temperature reactivity [95] by providing more H atom sites and decreasing the energy threshold for H atom isomerization, thereby facilitating chain branching reactions.

Yang et al. [95] also point out that ring strain is as a function of carbon number. Accordingly, the energy barrier for internal isomerization, along with associated reaction pathways and rates, will vary with ring size. For instance, Sirjean et al. [96] evaluated the reaction chemistry for cyclopentane and cyclohexane in the high temperature regime (e.g., 1230–1840 K) by means of shock tube experiments at elevated pressures. Their findings show cyclohexane to be far more reactive than the former compound.

Lemaire et al. observed NTC behavior for cyclohexane [97,98] and methyl-cyclohexane [99,100] in their low temperature RCM experiments. While concerted elimination competes with the cyclohexyl oxidation, the presence of NTC behavior indicates that low temperature branching reactions are dominant in the low temperature regime [98].

Yang et al. [95] observed that cyclohexanyl radicals, at low temperatures, oxidize via O2 addition, followed mainly by concerted elimination and the formation of cyclohexene. Alternatively, peroxy-cyclohexane may undergo isomerization and chain branching reactions. Pitz et al. [101] studied the oxidation behavior of methyl-cyclohexane and concluded that the ratio of chain branching to propagation is important, but not so much so as concerted HO2 elimination.

Silke et al. [102] included concerted elimination in their cyclohexane mechanisms and found that ignition delay times are quite sensitive to this reaction type. Al Rashidi et al. built a kinetic mechanism for cyclopentane (Fig. 10). The authors report that fuel radicals mainly undergo β-scission at either C—C or C—H bond sites, producing olefin in the process. Moreover, the authors observed reduced reactivity in the 850–1000 K temperature range at fuel rich conditions [103].

4.2. Olefinic bonds

Olefins have a higher RON than paraffins with the same C number. The principal olefin reaction scheme for auto-ignition is shown in Fig. 11. The divergence from the paraffinic pathway originates from the fact that olefinic C bonds provide a site for addition reactions, involving O, H, OH or HO2 radicals.

At low temperatures, H atom abstraction tends to occur on allylic sites, producing resonance stable allyl radicals in the process (pathway (d) in Fig. 11).

Resonance stable compounds, such as benzyl and allyl radicals, have a delocalized unpaired electron (Fig. 12), which increases stability that inhibits subsequent reactions and thus slows down the overall reaction rate [106,107].

The R-OH adduct formed by OH addition reactions can then undergo O2 addition reactions and, subsequently, decompose via the Waddington mechanism, forming OH radicals and aldehydes (pathway (a)).

It can also be consumed via H atom or HO2 radical addition reaction, the former followed by β-scission, producing an olefin and allyl radical (pathway (b)). The latter can then lead to the formation of an allo-ether and OH radical (pathway (c)) [108].

Alternatively, decomposition occurs via concerted HO2 elimination reactions, which results in the formation of another double bond [104] (pathway (e)). OH addition reactions (pathway (a)) are the preferred decomposition route at low temperatures, owing to the relatively lower energy barrier [109–111]. Note that pathways (a,c,e) are chain propagation reactions that produce stable radicals and compete with low temperature branching reactions (pathway (d)), slow down the reaction rate [104]. These addition reactions are more effective when the paraffinic chain lengths is short, since there are only a few paraffinic H atom sites to facilitate RO2 radical isomerization [107].

This is consistent with Vanhove’s results [110], who reported that the position of the double bond has a strong impact on olefinic auto-ignition chemistry in the low to intermediate temperature regime. Long chained olefins (e.g., hexene [110]) that have the double bond on the extremity (e.g., 1-hexene) tend to display paraffinic-like NTC behavior (Fig. 5).

Conversely, when the paraffinic chains are short, as is the case for 3-hexene, NTC behavior is virtually non existent [110]. As the temperature increases, unimolecular decompositions becomes dominant (pathway (d)) and the structural impacts (e.g., position of double bond, chain length, branch level) become less pronounced.

However, because the allylic site is the weakest link, C—C bond cleavage also tends to occur at this site (Fig. 11). As the unimolecular reaction prefers to transfer along route (d), the position of the double bond will also affect the high temperature auto-ignition chemistry [104].

4.3. Benzenoid bonds

Aromatics are the second most common constituents in gasoline, comprising up to 30% of the fuel. The oxidation chemistry of aromatics, particularly of benzene and toluene, has been studied extensively [112–125]. The benzene ring that forms the core of all aromatics has a chemistry very distinct from paraffins and olefins.

For example, the ring provides a site for electrophilic substitution reactions, whereby H atom on the ring can be replaced by another radical, such as CH3 and OH radicals. This kind of reaction competes with H atom abstraction from both the ring and its side chains, when present [112,126].

![Fig. 10. Simplified scheme for cyclopentane oxidation chemistry [103] (linear products resulting from beta scission ring opening are radicals).](image-url)
Owing to the highly stable π bond in the ring (Fig. 12), it is difficult to abstract an H atom from aromatics. Accordingly, most aromatics are highly resistant to auto-ignition at low to intermediate temperatures [112]. Once the ring opens, however, bond energies change. As is shown in Fig. 13, the bond dissociation energy (BDE) of C–H bonds in benzene decrease once H atom is abstracted.

Benzene auto-ignition chemistry generally follows one of two pathways (Fig. 14):

- Unimolecular decomposition and H atom abstraction reactions, forming phenyl radicals that, when reacting with HO2 radical, O2 or O atom, produce phenoxy radicals.
- Direct oxidization to phenoxy radicals, which are also stable and go on to produce mainly phenol, which reacts back to phenoxy radicals in the low to intermediate temperature.

Phenoxy radicals, in turn, can decompose to CO and cyclopentadienyl radicals at high temperature, the latter of which being an important intermediate for later ring opening reactions that ultimately yield butadienyl radicals (C4H5).

Contrary to paraffins and long chained olefins, benzene displays neither low temperature branching reactions nor NTC behavior. Aromatic radicals, such as benzyl (Fig. 12) and phenoxy, are resonance stable and thus inhibit subsequent reactions, decelerating the overall reaction rate. The high ON of most short chained aromatics, notably toluene, 1,3,5-tri-methyl-benzene and xylene (Table 5), owes much to this stability.

For aromatics with longer side chains, initial decomposition steps are determined chiefly by side chain chemistry [59,112]. A longer side chain or multiple side chains provide more possible sites for
low temperatures branching reactions [130–135], which is why the reactivity of aromatics tends to increase with the degree of alkylation.

Toluene, a commercial octane booster, has one methyl group on the ring. Its RON and MON are 120 and 109, respectively, indicating that it has both a good anti-knock quality and a high sensitivity [27]. At low to intermediate temperatures, its main reaction scheme can be summarized by Fig. 15.

Auto-ignition commences with unimolecular decomposition and later H atom abstraction, producing either resonance stable benzyl radicals and H atom, or phenyl and methyl radicals. The C—H bond in the methyl branch is the weakest bond (88.5 kcal/mol), making it the most likely site for these initial reactions.

Subsequently, benzyl radicals may go on to react with HO2, O2, O, or OH radicals to produce benzoxy radicals. This is followed by H atom abstraction, ultimately producing phenyl and CO.

Alternatively, benzyl radicals can react with each other to form bi-benzyl [117,136,138]. At high temperature, yet another initial reaction can occur, this time O atom, thereby producing cresoxy radicals and H atom.

### 4.4. Furanic bonds

Furans, comprising a five-membered aromatic ring with four carbon atoms and one oxygen, have, like C6 aromatics, a cyclic structure of the sp² hybridization type, characterized by the sharing a π electron cloud (π bond). 2-methyl furan (2MF) and 2,5-dimethyl furan (25DMF) were both found to be promising octane boosters [139,140], having CN’s as low as 8.9 and 10.9, respectively [141].

A simplified furan reaction scheme is shown in Fig. 16 [142]. Its unique five-membered heterocyclic ring manifests in a particularly high C-H BDE. This can be traced back to the low thermodynamic stability of the radicals formed after H atom abstraction [143]. Consequently, furans have an even stronger C—H BDE than benzene (Fig. 13).

Furan auto-ignition chemistry initiates primarily via H atom or OH radical addition reactions at the C₆ position [142] (pathway (a) and (c) in Fig. 34). This leads to the formation of resonance stable dihydrofuryl-3 radicals and C₆H₄OH, respectively, followed by β–scission reactions. Other, less dominant, pathways involve H atom addition at the C₆ position (pathway (b)) or H atom abstraction (pathway (e) and (f)).

Alkylated furans, such as 2MF and 25DMF, have been subject of many studies [129,144–147]. The BDE of methyl C-H is relatively low. Accordingly, in addition to aforementioned addition reactions, H atom abstraction from the methyl group is a likely initial decomposition step.

2MF, for example, can react via H atom or OH radical addition (pathway (b) in Fig. 17), H atom abstraction (pathway (c)) or H atom ipso addition (pathway (a)) [144]. Given fuel rich conditions, decomposition via ipso addition, yielding furan, is the dominant pathway [144].

### 4.5. Oxygenated bonds

Oxygenates, including MTBE, ETBE and ethanol, are amongst the most common commercial octane boosters. The presence of fuel oxygen in these compounds has a significant influence on the autoignition chemistry:

- Reduced symmetry yields more possible reaction pathways (e.g., dehydrogenation, dehydration, decomposition). For example, intermolecular dehydration (concerted elimination) of 2-butanol (Fig. 19) produces olefins and H₂O [148].
- Reduction of the BDE of C—H bonds at the adjacent α-C site (Cα—H) or β-C site if it is a ketone, while increasing the BDE of C—H bonds at the β-C site (Cβ—H) or γ-site for ketone (Fig. 20), promotes H atom abstraction at the former site [149]. For example, in the case of isopentanol oxidation (at 800 K, 15 bar and stoichiometric mixing conditions), nearly 48% of this C—H bond type reacts by way of H atom abstraction, and produce -hydroxypentyl radicals [150].

The high activation energy required for unimolecular decomposition is readily met in the high temperatures regime. This causes the
identity of the fuel, with respect to auto-ignition chemistry, to manifest mainly in the low to intermediate temperature range. Categorized by functional oxygen group, various types of oxygenates are shown in Table 6.

### 4.5.1. Alcohols

Owing to their high knock resistance, alcohols have been considered superior alternatives to gasoline since the advent of the gasoline engine. Ethanol in particular is commercially blended to gasoline in both the US and EU.

Fig. 16. Simplified reaction scheme for furans [142].

Fig. 17. Simplified reaction scheme for 2-methyl furan [144].

Fig. 18. 5-membered concerted elimination and Waddington mechanism for propa-nol.

Fig. 19. Dehydration of 2-butanol.
ignition delays, with the other isomers displaying similar combustion behavior at high pressure (15 and 30 bar), however, tert-butanol had the longest delay [155].

iso-butanol yields the longest delay [155].

2-butanol and tert-butanol have similar ignition delays, while rapid compression machine experiments compared to other iso-

mers. 2-butanol and tert-butanol have similar ignition delays, while iso-butanol yields the longest delay [155].

The variation in reaction rates results primarily from structural effects, which favor one of various hydroxybutyl radical reaction pathways. Moreover, C–H BDE depends on the location of the OH group (Fig. 20), resulting in a unique H atom abstraction rate for each isomer.

As shown in Fig. 20, α-hydroxybutyl can react with O₂ to directly produce aldehydes and HO₂ radicals (pathway (a)). This reaction proceeds via an activated α-hydroxy peroxy adduct that can decompose rapidly to an aldehyde and an HO₂ radical. Importantly, this reaction has a very low activation energy and thus is particularly competitive in the low temperature regime [154]. An alternative route involves O₂ addition reactions, followed by concerted elimination to produce enol and HO₂ (Fig. 18).

β-hydroxybutyl can react with O₂ and subsequently decompose by way of low temperature branching (pathway (c)), propagation (pathway (b) and (d)) reactions. In the low temperature regime, however, the propagation reaction routes are the dominant ones, given the higher energy barrier in the alkyl radical isomerization needed to produce QOOH [154].

It is has been calculated that nearly all β-hydroxypropyl radicals react by way of Waddington chemistry [156]. α-hydroxybutyl radicals mainly lead to propagation reactions (pathway (a)), except in the case of tert-butanol. γ- and δ-hydroxybutyl radicals typically react via low temperature branching or termination reactions.

Given that 1-butanol has more paraffinic C bonds (i.e., γ-C and δ-C), the main sites at which branching reactions occur, it has a relatively high reaction rate.

iso-butanol, by comparison, having 6 γ-C which is located on high BDE primary sites and no δ-C, has a far slower reaction rate. This can be explained by the slower H atom abstraction rate, thereby favoring propagation reactions.

Consequently, a branched alcohol with a less paraffinic chain (less γ, δ or further C) will have longer ignition delay and therefore be the more preferred octane booster.

4.5.2. Ethers

Ethers contain two alkyl or aryl groups bonded to an oxygen atom. The presence of C–O bonds decreases the BDE of C₀ce : glyph namesbndH sites [157]. Alkyl ethers undergo similar reaction pathways as alkanes [158–161], albeit at far lower energy barriers for abstraction or isomerization at C₀ce : glyph namesbndH sites, resulting in an increased overall reaction rate. Dimethyl ether (DME), for example, has a RON of 35, while that of propane is 112.

Some ethers, conversely, including common octane boosters as MTBE, ETBE or TAME, have a remarkably high RON of 117, 118 and 112, respectively [162]). This impressive anti-knock quality can be attributed to the highly branched tertiary butyl group attached to the ether group (Fig. 22); a common denominator.

The presence of this group dramatically increases the number of primary H bonds. Moreover, this particular structure lacks any paraffinic C bonds (no γ-C). As a result, H atom abstraction and RO₂ internal isomerization reactions becomes both less prevalent and effective.

Moreover, O₂ addition, the main reaction route at low temperatures, becomes less important, as initial decomposition is more likely at the relatively weak C–O bond [163,164]. Consider for example MTBE, the auto-ignition chemistry of which takes one of the following reaction pathways (Fig. 23):

- H atom abstraction from C₀ce : glyph namesbndH sites, followed by β-scission, producing aldehydes and iso-butyl radicals (pathway (a)).
- H atom abstraction from the branched iso-butyl group, followed by β-scission, thereby forming iso-butene and CH₃O radicals (pathway (b)).
At high temperature, a four-membered elimination reaction, producing isobutene and methanol (pathway (c)).

Bond cleavage involves higher activation energies than addition reactions. Hereby, the iso-butene chemistry greatly influences the overall reactivity, as it has a strong inhibiting effect [165, 166]. Accordingly, such ethers have a high resistance towards auto-ignition [167].

Lack of low temperature branching reactions and the formation of stable intermediates (e.g., iso-butene) are the two main factors responsible for the characteristically high ON of aforementioned highly branched ethers.

Cyclic ethers are important combustion intermediates in the intermediate temperature. Interestingly, some of them have also been considered as potential alternative fuels [141]. Dagaut et al. [168], for instance, investigated the oxidation of tetrahydrofuran, arguably the most studied cyclic ether [169, 170], in the high temperature regime. NTC behavior is also apparent for tetrahydrofuran, whereby low temperature branching is the main reaction pathway, but concerted elimination, forming double bonds, is an important decomposition route as well [170].

Owing to their stable carbon ring, cyclic ethers are less reactive than their straight chained counterparts. Compared to cyclic paraffins, however, the ethers are more reactive; a distinction that can be traced back to the fact that hydrogen atom abstraction from C atoms adjacent to the ether group occurs more readily than would otherwise be the case. For example, tetrahydrofuran has a RON of 72.9 [28], whereas that of cyclopentane is far higher at 101 [171].

4.5.3. Esters

Esters harbor a C(= O)— O functionality (Fig. 24) and generally have a lower reactivity than correspondingly long alkanes. The presence of the C(= O)O group weakens adjacent C−H bonds [Fig. 24], thus making α-C the preferred site for H atom abstraction [172].

Long chained esters, notably fatty acid methyl ester or FAME (CH3(CH2)nCOOCH3) and fatty acid ethyl esters or FAEE (CH3(CH2)nCOOCH2CH3), can be produced from various plant oils and are the main constitutes found in biodiesel today [173]. Various types of short chained esters, conversely, have particularly high octane numbers. For example, methyl and ethyl valerate have a blending RON of 115 and 106, respectively [174, 175]. Methyl and
ethyl levulinate have blending octane numbers of 107 and 108, respectively [176]. Finally, alkyl acetates, too, have been reported to be potential octane boosters [177].

Less common esters proposed for use as fuel include methyl butanoate (MB) [172, 173, 178−180] and ethyl propanoate [181, 182]. Other than aforementioned esters are studied as well to better comprehend the chemistry of FAME and FAEE, such as ethyl pentanoate [183], methyl and ethyl hexanoate [184−186], methyl heptanoate [184, 187], methyl decanoate [184, 188] and a mixture of biodiesels [189, 190]. Coniglio et al. [191] reviewed the combustion kinetics of methyl and ethyl esters. Although huge progress has been made recent years, it is found that the modeling results still over-predict the reactivity compared to the experiments in the low temperature regime [192], therefore, further studies are needed to improve the accuracy of the model.

Esters display a paraffin-like reaction chemistry, however, no NTC behavior is found for short paraffinic chain esters, as is exemplified by the MB scheme, shown in Fig. 25 [180].

The paraffinic chain of MB (C4) is relatively short. This attribute, combined with the presence of an ester group, results in O2 addition reactions forming alkyperoxy radicals that tend to preferentially undergo concerted elimination, thereby yielding an unsaturated ester. Low temperature branching reactions is less important here [180]. This helps to explain the low reactivity of short chained esters in the low temperature regime.

To decelerate matters further, due the presence of a carbonyl group (C=O), the alkoxy radicals formed after H atom abstraction at β-C site are resonance stable (Fig. 26).

Esters having a paraffinic chain with more than five members are prone to NTC behavior, as has for example been observed in RCM measurements for methyl hexanoate [185]. Owing to NTC chemistry, low temperature branching reactions are important decomposition pathways for larger esters.

While the ester functionality provides an attractive site for H atom abstraction, it also enables another reaction path, involving concerted elimination through a six-membered transition state ring (Fig. 27), producing olefins, small esters or acids.

Whether or not six-membered elimination, as shown in Fig. 27, is the primary reaction pathway depends on the structure of the ester. For example, MB and ethyl propionate (EP), an equal C number notwithstanding, have distinct reactivities, which the latter being the quicker of the two.

One of the reasons for this divergence is that it is easier for EP to undergo concerted elimination reactions and produce reactive species [181], given that the activation energy for this reaction is 50 kcal/mol for EP versus 68.07 kcal/mol for MB [182].

Walton et al. [191] found that 96% of EP follows the elimination route, with only 4% reacting via H atom abstraction at 1 atm and 1200 K [181]. Elimination chemistry for MB, conversely, is rare, contributing less than 1% to decomposition.

Schwartz [193] studied five isomers of C7H16O2 esters at atmospheric pressure in a CH4/air co-flow flame and reported that six-membered elimination reactions are the dominant reaction pathway for EP, propyl acetate and isopropyl acetate. Conversely, for methyl butanoate and methyl iso-butyrate, the primary route is via simple fission (Fig. 28).

Iso-propyl acetate is the most reactive isomer because the branched C atoms allow for more H atoms to undergo six-membered elimination. This is inconsistent with the view that H atom abstraction is the dominant decomposition pathway, since there are many primary H atoms in isopropyl acetate, however consistent with aforementioned six-membered elimination observations [193].

Accordingly, six-membered elimination is the preferred decomposition route when the alkyl chain is large on the O-alkyl side of

Fig. 24. BDE of methyl butanoate (kcal/mol).

Fig. 25. Simplified reaction scheme for methyl butanoate at low temperature [180].

Fig. 26. Resonance stable structure of methyl butanoate radicals [173].
the ester. What is more, the branching effect reduces the activation energy needed for the six-membered transition state ring [194].

4.5.4. Aldehydes/ketones

Aldehydes and ketones are important intermediates and end-products in hydrocarbon combustion [195,196]. Given their prevalence as intermediates, it is no wonder that aldehydes and ketones tend to be unstable and therefore not particularly well suited for fuel use. Nevertheless, a short discussion of these classes will be provided here as an understanding of their oxidation characteristics could be of interest to researchers working on auto-ignition phenomena.

Both oxygenate types are characterized by the presence of a carbonyl group in their respective molecular structures. In the event said group involves C bonded to at least one H atom, the resulting compound is classified as an aldehyde, else, as a ketone. Ketones (e.g., 4-heptanone) are potential biofuel candidates, which have been reported to be produced via endophytic fungal biomass conversion or by other methods [197].

Aldehydes can be important diesel engine emissions, particularly from those engines operating in premixed auto-ignition combustion modes. These modes include Premixed Charge Compression Ignition (PCCI) and Homogeneous Charge Compression Ignition (HCCI), both of which are regarded as High Efficiency Clean Combustion (HECC) strategies [196,198,199].

Alternatively, aldehydes emissions arise when burning gasoline that contain alcohols in conventional SI engines. Fortunately, the majority of which decompose readily in modern three-way catalysts [200,201].

At high temperature, as shown in Fig. 29, the main reaction pathways for small ketones is H atom abstraction or unimolecular decomposition, followed by β-scission, producing small hydrocarbon radicals [202–204].

At low temperatures, fuel radicals can react via O₂ addition, leading to the formation of hydroperoxyl radicals [195] and another O₂.
addition to form OOQOOH. Subsequent isomerization for H atom transfer, however, is inhibited by the modest low temperature reaction rate [206].

Aldehydes such as propanal and butanal are very reactive compared to other compounds with similarly sized carbon chains. Their main decomposition pathway in the low temperature regime is similar to that observed for paraffins [196] (Fig. 30).

The main differences for aldehydes versus paraffins, with respect to auto-ignition chemistry, are itemized below for the n-butanal case.

- The primary H atom abstraction site is at the C1,ce: glyphsizes bond: the weakest C−H bond (Fig. 31).
- O2 addition and subsequent low temperature branching is not the dominant decomposition pathway for Cα radicals. Rather, α-scission is the preferred route.
- α-scission of n−C3H7CO radicals yields propyl radicals and CO (pathway (a)) in Fig. 30) and has a negative effect on the overall reactivity, as it does not lead to paraffinic-like low temperature branching reactions [196].

Both propanal and n-butanal display NTC behavior. Iso-butanal, conversely, does not, owing to its short, highly branched chain that instead favors beta-scission over O2 addition.

At high temperature, pathway (a) (Fig. 30) becomes the dominant route. For example, 100% of n−C3H7CO radicals decompose this way at 1320 K and 3 atm in shock tube experiments [207].

4.5.5. Carbonates
Carbonates, characterized by a R−O−C(=O)−O−R molecular structure, have been also been proposed as fuel additives. For example, both dimethyl and diethyl carbonate (DMC and DEC) were found to reduce soot emissions in diesel engines [208–210]. DMC, DEC and dipropyl carbonate have high RON’s of 125, 110 and 110, respectively [209] and are therefore interesting octane booster candidates. Glaude et al. built a kinetic model of DMC oxidation and validated it in an diffusion flame [211]. Nakamura et al. studied the oxidation kinetics of DEC and validated the model by means of ignition delay measurements in a jet stirred reactor [212]. The three oxygen atoms native to the carbonate class manifest in some distinctive oxidation characteristics. Shown in Fig. 32, DEC can oxidize via three pathways.

Pathway a) involves H atom abstraction at Cα sites, which is followed by O2 addition. The peroxy radicals, like esters, can then undergo concerted elimination, thereby forming a double bond and an HO2 radical. Alternatively, these radicals can decompose via isomerization reactions, involving 5-, 8- or 9-membered transition rings, followed by low temperature branching. RCM experiments revealed NTC-like behavior of DEC in the low temperature regime at elevated pressures [212].

Importantly, aforementioned transition state rings have a higher energy barrier than the 6− variant common to paraffins, making it more difficult to form OOQOOH radicals. Moreover, at low temperature, most of the peroxy radicals tend to react back to α-fuel radicals [212]. The formation of stable intermediates (e.g., double bonds) and high transition state ring energy barriers are two probable reasons for the high ON of aforementioned carbonates. In pathway b), DEC reacts to β-fuel radicals and then undergoes O2 addition reactions. Finally, DEC can decompose to ethylene and ethyl formic acid in pathway c).

4.5.6. Benzenoids
A recent book by Boot et al. [174], on the performance of various types of oxygenates in both compression ignition and SI engines, found that all reviewed aromatic oxygenates shared a low CN and commensurately high RON. Moreover, their aromatic oxygen-laden benzene base structure lends itself well for production from lignin, a phenolic polymer found in residual streams of paper pulping and cellulosic ethanol plants [174].

As was the case for the foregoing oxygenates, adding O atoms to aromatic branches will decrease the BDE of side chain C−H bonds. Oxygenation, though, will severely affect the BDE of aromatic C−H bonds. The initiation of auto-ignition chemistry, given the stable benzene base central to all aromatics, typically occurs on the side chains when present.

When O atom connects to the phenyl group, the strong phenyllic C−O bond weakens the C bond on the alkyl side. Anisole, a phenyl methyl ether, has an ether group attached to the benzene ring. Herein, the Oce : glyphsizes bondCH3 bond is the weakest link and...
thus the most likely site for initial reaction chemistry, producing phenoxy and methyl radicals [213].

Alternatively, H atom abstraction can occur from the methyl group, producing C6H5OCH2 radicals (Fig. 33 [213]).

For aromatic oxygenates that do not have O atom bonded directly to benzene ring, the impact of the phenyl group on overall reactivity is dependent on the length of the side chain.

When the side chain is short, as is the case for benzaldehyde, the CαC bond is weak and the dominant pathway is H atom abstraction, producing C6H5CO. This is followed up by CO elimination at high temperature, leading to phenyl.

Therefore, as mentioned earlier, more or longer side chains will have an acceleratory effect on the overall reaction rate. Consider guaiacol for example. Here, the presence of a hydroxy group weakens the BDE of the OCe bond (Fig. 33 [213]) and also provides possible site to proceed the reaction.

5. Design rules for future octane boosters

Auto-ignition chemistry can be divided into three consecutive categories of reactions [214]:

- Initial → formation of the first radicals.
- Intermediate → maintaining and/or increasing radical pool by propagation and/or chain branching reactions.
- Terminal → recombination of radicals to stable compounds.

The overall reaction rate is controlled primarily by chain branching, which can rapidly accelerate the reaction by filling the radical pool. The rate of chain branching, in turn, is a function of many factors, including molecule structure, reaction temperature, pressure, equivalent ratio and initial concentration of fuel and air. A sufficiently large radical pool is the critical factor that determines whether or not a fuel will auto-ignite. When the initial conditions in the combustion chamber are fixed, the overall reaction rate is determined by fuel molecular structure:

- Initial → type, location and number of C—H bonds
- Intermediate → hydroperoxyl radical (RO2) chemistry (propagation and branching).
- Terminal → number and reactivity of intermediate species (termination).

![Fig. 32. Simplified reaction scheme for diethyl carbonate at low temperature [212].](image)

![Fig. 33. Anisole reaction scheme [213].](image)

![Fig. 34. Bond dissociation energies for toluene, anisole and guaiacol [127,213] (kcal/mol).](image)

![Fig. 35. C—H bond dissociation energy (BDE) (in kcal/mol) for various hydrocarbon types (red: primary C—H bonds; blue: secondary C—H bonds; green: tertiary C—H bonds). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)
5.2. Short chain length

$RO_2$ radicals produced by Reaction 6 are very important intermediates at low temperature [67]. Both alkyl and peroxy radicals can undergo intra H atom transfer via a transition state ring to produce $QOOH$, which dominates low temperature chain branching.

Competition between isomerization and decomposition of $RO_2$ or $QOOH$ affects the reaction route, as well as the reaction rate. Competition between decomposition and $O_2$ addition reactions has a negative and active impact on increasing the whole reaction rate, respectively. The main factor driving the branching ratio is temperature.

$O_2$ addition reactions are important because of their negligible energy barriers. However, as temperature increases, $RO_2$ radicals become thermally unstable and readily decompose back to fuel radicals.

The formation of the transition state ring that produces $QOOH$ is integral to low temperature chemistry, because from here it can undergo another $O_2$ addition reaction, followed by chain branching reaction, thus increasing the whole reaction rate. Alternatively, it can undergo decomposition reactions, producing ethers, ketones or other species via propagation reactions, which has no acceleration effect.

The activation energy for isomerization reactions is defined as [90]:

$$E_a = \Delta H_{rxn} + \text{ringstrain} + E_{abst} \quad (8)$$

In this equation, $\Delta H_{rxn}$ is the enthalpy of the endothermic reaction and $E_{abst}$ is the nascent barrier to abstraction. This equation is used both for alkyl radical ($R$) isomerization and hydroperoxyl radical ($RO_2$) isomerization. The ring strain energy is highly dependent on its size, with lower energies seen for larger rings (Table 7). From Fig. 36, it can be seen that a minimum chain length of two and five C is required to form a 5-membered or 8-membered transition state ring, respectively. This implies that hydrocarbons, as they grow longer average chain lengths, have more options for low energy barrier isomerization reactions and therefore higher overall reaction rates.

Recently, quantum chemistry models have been used to calculate $RO_2$, concerted elimination and isomerization reaction rates [215–218]. The results also show a decrease in activation energy as the transition ring size increases or the C–H bond type changes from primary to tertiary. The lowest activation energy is observed for a seven-membered ring size comprising mainly tertiary C–H sites.

The presence of functionalities such as double bonds and oxygen groups affects the possible reaction pathways and preference thereof as a result of their impact of BDE. Moreover, these groups may interfere with radical isomerization reactions.

Concerning oxygenates, the BDE most affected by the presence of oxygen functionalities is felt by carbon atoms adjacent to oxygen atom in question. Owing to the tendency of most oxygen functional groups to attract electrons from neighboring atoms, adjacent C-H bonds are commensurately weakened, thereby promoting initiation

| Number of ring members | Ring strain energy (kcal/mol) |
|------------------------|------------------------------|
|                        | Curran [90]               | Battin-Leclerc [83]  |
| 5                      | 8.6                        | 15.5                 |
| 6                      | 2.8                        | 8                    |
| 7                      | 0                          | 5                    |
| 8                      | 2.8                        | 4                    |

Table 7. Impact of transition ring size on strain energy.

Fig. 36. Paraffin $RO_2$ isomerization involving a 5–8 membered transition state ring.
reactions and subsequent metathesis (i.e., H atom abstraction) chemistry.

For example, the BDE of the $C_a-H$ bond found in methyl butanoate (MB) is 93.6 kcal/mol. This is noticeably lower than the 98.5 kcal/mol seen for $C_b-H$ bonds. Accordingly, the former will be the preferred site for H atom abstraction. The ensuing O$_2$ addition reaction will also prefer to take place here. However, the energy barrier for the formation of the transition state ring for isomerization will also be affected, resulting in isomerization and branching no longer being dominant later on. Rather, concerted elimination or $\beta$-scission, both chain propagation reactions, are the main consumption pathways. Both of which tend to slow down the overall reaction rate.

For esters, shifting an H atom involves a higher strain energy than seen for paraffins (Fig. 37) [184]. Moreover, other propagation reactions now compete with chain branching. In ethers, the presence of $C-O$ will decrease the energy barrier when the O atom is connected to straight chained paraffins. This will facilitate subsequent chain branching reactions. However, in the event the carbon chains are highly branched, as is the case for MTBE (Fig. 25), the presence of many primary H atoms, along with the branched structure itself, will make it more difficult for the transition state ring to form, thereby rendering the compound quite stable.

In the presence of an olefinic bond, the $C_b-H$ bond adjacent to the double bond will have a lower BDE (83.8 kcal/mol). Once broken, this will result in the formation of resonance stable allyl radicals (Fig. 11). H atom transfer from C atom adjacent to the double bond will decrease the isomerization reaction rate, because of the additional strain energy seen for transition rings constructed from allylic radicals [107,219]. Moreover, RO$_2$ at an allylic site decomposes readily back to O$_2$ and an R radical, in effect inhibiting the chain branching process [109].

Both effects contribute to the high ON of olefins relative to paraffins (Fig. 38). Besides H atom abstraction and unimolecular decompositions, there is another initial reaction path for double bonds at low temperature: the addition reaction. It competes with the low-temperature branching ones [104]. For example, the addition of OH radicals at the double bond site allows for Waddington type
reactions (Fig. 11), which becomes the dominant reaction pathway. This results in the formation of more stable double carbon and vinylic C-H bonds, suppressing low temperature internal H atom migration.

From Fig. 38, it can further be seen that olefin sensitivity decreases with carbon number as it becomes of an increasingly saturated nature.

5.3. Strong carbon-carbon bonds

As discussed earlier, resonance stable intermediates may accumulate to high concentrations readily at low temperature and may even go on to produce even less reactive dimers or/and lead to subsequent termination reactions [220,221]. Resonance stability increases the activation energy towards further decomposition, thereby depressing the overall reaction rate.

Resonance stable intermediates, including allyl, benzyl, benzoxy and cyclopentadienyl radicals share one apparent common denominator: the presence one or more unsaturated C bonds. A second frequent, though not omnipresent common denominator is cyclicity. C atoms in benzene is linked together by means of super r bonds, the electrons of which being delocalized and shared amongst its six C members, creating stable structure, particularly at low temperatures.

Benzyl radicals are also resonance stable and will, in an oxidative environment, lead to radical-radical reactions, such as the production of even more stable bi-benzyl. This proclivity lies at the heart of both the low propensity for aromatics to decompose further and the formation of soot [117]. Benzoxy radicals, the main intermediate for ring opening reactions, is also resonance stable. Ring opening is preceded by the formation of cyclopentadienyl radicals irrespective of the nature of side chains [222].

6. Conclusions

The generic design rules for octane boosters as outlined in Section 5 can be condensed as follows:

- A strong weakest link → Strong C-H bonds inhibit initial radical formation (Section 5.1). For a given carbon structure, addition of an aldehyde or ether functionality is not desirable, as these groups tend to lower C-H bond strength in adjacent carbon (Section 4.5).
- A short average chain length → Short chains have a lower propensity to form transition state rings (Section 5.2). For a given carbon structure, a well placed ether group can be beneficial here, as the associated relatively weak C-O bonds tend to break up the fuel into shorter fragments (e.g., MTBE; Section 4.5).
- Strong and/or cyclic carbon skeleton → Unsaturated and/or cyclic carbon bonds promote the formation of stable intermediates (Section 5.3). For a given carbon structure, the presence of an alcohol, ester or ketone group has a positive effect, given that these functionalities can facilitate indirect routes towards unsaturated carbon bonds (Section 4.5).

It should be noted here that abiding by the second rule automatically leads to satisfaction of the first, seeing as shorter chains are laden with more primary C-H bonds. These bonds are stronger than the secondary sort that eventually become dominant for long chains (Section 4.1). The latter rule should therefore take priority over the former.

While abiding by these rules will certainly yield a high RON, this exercise will not automatically also lead to a high sensitivity S (Section 3). SI engines have over time become considerably more powerful and fuel efficient. This progress owes much to technological achievements, notably in the fields of direct injection and turbocharging (Section 2).

Common denominators herein, with respect to prevailing temperature-pressure histories in the combustion chamber, are not only a higher absolute value for pressure and temperature, but also higher values for the former relative to the latter. To accommodate a changing combustion chamber environment, future octane boosters, as suggested by Octane Index (ID) theory (Section 3), should have both a high RON and sensitivity S.

S arises from the absence of NTC behavior (Section 3.2). As NTC chemistry is unique to paraffins and other hydrocarbon types with large paraffinic side chains, the recipe for high S coincides with the unsaturation component of design rule 3. Accordingly, the third rule should take priority over the other two.

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

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