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Edited by Michael Boot

Biofuels from Lignocellulosic Biomass

Innovations beyond Bioethanol

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Preface

Soot, NO_x, and low efficiency could be regarded as hallmarks of a fundamental mismatch between fossil fuels and internal combustion engines. This is not unsurprising considering the former were produced millions of years before the advent of the latter. In this respect, the emergence of ever-increasing biofuel mandates comes as a blessing in disguise; for now, we have the opportunity to blend in biofuels that might compensate for intrinsic fossil fuel deficiencies.

Governmentally imposed mandates, such as is currently the case for biofuels, are typically a testament to otherwise failed product – market combinations, suggesting that once again there might be a mismatch in what the engine would like to drink and what is on the menu. Consider, for example, ethanol. This biofuel, admittedly, has a high octane number, but the price for this benefit is high (e.g., 50% less energy per unit of volume, high heat of vaporization, hydrophilic nature). Again, a mismatch is to be expected given that fermentation of sugar to ethanol dates back as far as Neolithic times. In order to better address market demands, it might therefore prove worthwhile to first figure out what molecules the engine would actually like to drink and only then think about appropriate production processes from biomass.

Historically, however, the communication between producers and consumers of fuels has been poor to nonexistent. In fact, this book was first and foremost motivated by my astonishment that at the various biofuel conferences I attended, people who understood how an engine works were scarce to say the least. Tellingly, at engine technology conferences, few could explain how their tested biofuels were produced from biomass. This brings us to the goal of this book, which is to bridge the knowledge gap between biofuel production and biofuel combustion.

Following an introductory chapter on where future engine technology is headed, each subsequent chapter deals with a specific class of biofuels. The buildup is always the same, whereby first the choice for the fuels in question is motivated by engine experiments. The second part then goes on to discuss how the requisite molecules could be produced from biomass. Each chapter ends with a discussion on the future prospects of the fuel and a summary of the key conclusions.

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1
Fuels and Combustion

Bengt Johansson

1.1
Introduction

All internal combustion engines use fuel as the source for heat driving the thermodynamic process that will eventually yield mechanical power. The fuel properties are crucial for the combustion process. Some combustion processes require a fuel that is very prone to ignition, and some have just the opposite requirement. Often, there is a discussion on what is the optimum. This optimum can be based on the fuel or the combustion process. We can formulate two questions:

- What is the best possible fuel for combustion process x?
- What is the best possible combustion process for fuel y?

Both questions are relevant and deserve some discussion, but it is very seldom that the fuel can be selected without any considerations, and similarly, there is only a limited selection of combustion processes to choose from. This brief introduction discusses the combustion processes and the link to the fuel properties that are suitable for them. Thus, it is more in the line of the first question of the aforementioned two.

1.2
The Options

For internal combustion engines, there are three major combustion processes:

- Spark ignition (SI) with premixed flame propagation
- Compression ignition (CI) with nonpremixed (diffusion) flame
- Homogeneous charge compression ignition, HCCI with bulk autoignition of a premixed charge.

These three processes can be expressed as the corner points in a triangle according to Figure 1.1. Within this triangle, all practical concepts reside. Some are a combination of SI and HCCI, some a combination of SI and CI, and others a

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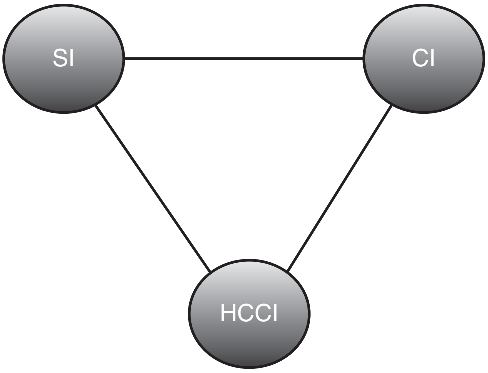

Figure 1.1 The three fundamental combustion concepts, SI, CI, and HCCI.

combination of CI and HCCI. We start by describing the basic three concepts and then move on to discuss the variations and the fuel implications that we can get with combined systems using, for instance, SI and CI at the same time.

The combined concepts to be discussed are as follows:

- Spark-assisted compression ignition (SACI)
- Partially premixed combustion (PPC)
- Reactivity controlled compression ignition (RCCI)
- Dual fuel
- Prechamber flame ignition
- Pilot-assisted compression ignition (PACI) or diesel pilot ignition.

The following section aims to give an introduction to the combustion processes and highlight the fuel requirements. Both chemical and physical properties are discussed.

1.3
Spark Ignition

The SI process is in principle very simple. Fuel and air are mixed and then the charge is compressed. Close to the piston top dead center, a spark is generated between two electrodes of a spark plug. This results in a locally very hot zone that starts exothermic reactions. Those reactions heat up the vicinity of the reaction zone and thus the reactions start there. The resulting propagating reaction zone is most often called a *flame*. The rate at which this flame propagates depends on the reactivity of the charge and how much the flame is distorted by turbulent eddies. Figure 1.2 illustrates the principle, with a spark plug to the right and a flame some 2/3 distance from the spark plug to the back wall of the combustion chamber.

The enhancement of flame speed by turbulence is not much affected by the fuel properties but by the reactivity of the charge. This reactivity is most often expressed as a laminar flame speed. Most hydrocarbon fuels exhibit a laminar

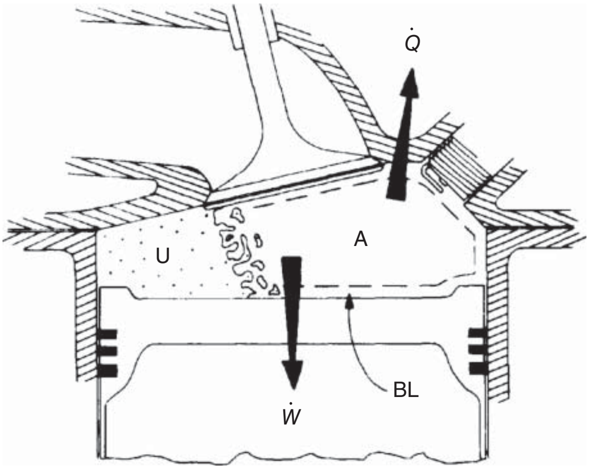

Figure 1.2 Normal flame propagation [1]. (Reproduced with permission from Heywood [1] of McGraw Hill.)

flame speed at around 0.4 m/s close to that of stoichiometric mixtures, and this then drops to very low numbers as the mixture strength approaches the lean or rich dilution limits. In fact, those *limits* are defined when the laminar flame speed is zero. The major outliner when it comes to laminar flame speed is hydrogen. The laminar flame speed of hydrogen is very much higher than that of hydrocarbons. This means that a hydrogen engine can be expected to undergo a much faster combustion than the one using conventional fuels. Also, the alcohols tend to have a slightly higher flame speed, but here the difference to regular hydrocarbons is much less (<10%).

1.3.1
Uncontrolled SI Combustion, Knock

The conventional flame propagation with SI is not that fuel-dependent; except for hydrogen, most fuel behaves the same. Instead, the major problem comes when the combustion process is not working according to plan. With SI combustion, the fuel and air are mixed to burnable proportions well before the combustion starts. This means that the reactive mixture will be heated to a rather high temperature for some time. The worst conditions are for the end gas. This is the gas that is furthest away from the spark plug in the combustion chamber. This charge is heated and pressurized during the compression stroke but also by the increased pressure resulting from the combustion of the fuel closer to the spark plug. If the end gas charge is heated too much for too long, it will autoignite. Then the combustion will be very fast and all the end gas fuel/air mixture is converted into combustion products infinitely fast, at least in terms of time scales relevant for the engine. The autoignition is sometimes called knock from the engine noise if operated with autoignition. The noise comes from the pressure fluctuations resulting from the pressure wave originating at the autoignition site in the cylinder. If a moderate amount of fuel is burned with autoignition, the pressure oscillation amplitude will be a few bars only. This can be heard but will not be directly damaging. But if the autoignition is earlier, more fuel is burned in the autoignition process and the pressure oscillations can directly destruct the engine architecture. The high-amplitude pressure oscillations will also increase heat transfer to the combustion chamber walls by breaking down the thermal boundary layer. This will reduce engine efficiency and also heat the walls. If the walls are heated too much by prolonged knocking, the wall material will eventually reach a temperature where the mechanical strength will no longer be sufficient. When the piston material melts, there will be a permanent damage or even a hole, losing all compression and hence engine performance.

1.3.2
Autoignition of SI Engine Fuel

Spark ignition knock is determined by engine parameters such as flame travel length and compression ratio and also by engine operating conditions such as engine speed, load, and spark timing. But it is also fundamentally linked to the autoignition tendency of the fuel/air mixture in the cylinder. This is given by the fuel properties as such but also the fuel/air mixture strength, the amount of hot residual gases in the cylinder, the amount of exhaust gas recirculation (EGR), and other aspects affecting the reactivity of the charge.

To avoid SI engine knock, a fuel with a high resistance to autoignition should be selected. The number(s) most often used to quantify the knock tendency of a fuel is called the *octane number*. To make it a bit more complex, there are two, Research Octane Number (RON) and Motor Octane Number (MON). Both are extracted by operating a standardized engine, called a *corporate fuel research (CFR)*, but with two sets of conditions. The first, RON, uses an engine speed of 600 rpm and an inlet temperature of 49 °C (150 °F) and fixed spark timing. For the MON, the engine speed is increased to 900 rpm, the inlet temperature is set to 149 °C (300 °F), and spark timing is adjusted for maximum knock.

When evaluating the octane number, the engine compression ratio is increased until a predefined level of knock is detected with a standardized microphone in the cylinder. The compression ratio is then compared to mixtures of two reference fuels: *n*-heptane, which is prone to autoignition, and *iso*-octane, which is much more resistant to autoignition. The mixture of *n*-heptane and *iso*-octane is adjusted until the same level of autoignition is reached. The *percentage of iso-octane in the reference mixture* is then defined as the tested fuel octane number. Thus, pure *n*-heptane will have an octane number of 0 by definition and pure *iso*-octane will have 100. But it should be noted that the scale between 0 and 100 is not linear. Figure 1.3 shows the compression ratio as a function of RON (and MON).

The required compression ratio as a function of fuel carbon atoms can be seen in Figure 1.4. The *iso*-octane and *n*-heptane are shown but also fuel with an octane

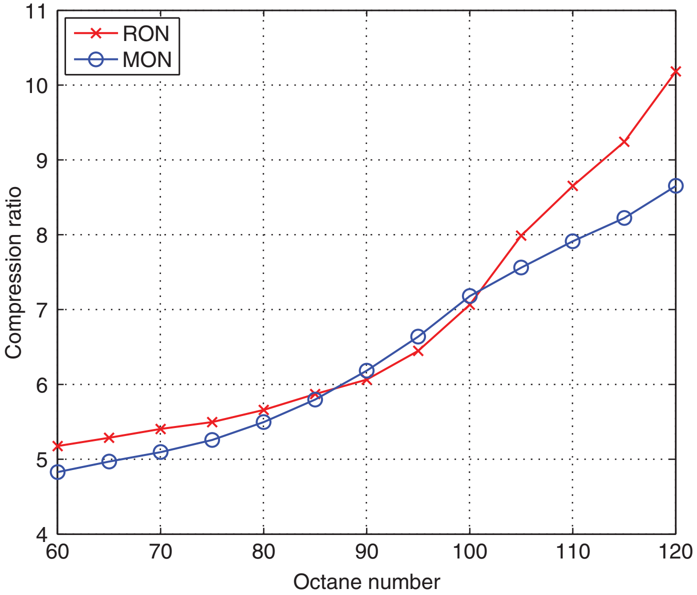

Figure 1.3 The required compression ratio for knock to be a function of RON and MON.

number higher than that of *iso*-octane. Both methane, CH_4, and benzene with the aromatic ring require higher compression ratios.

The RON test was first introduced in 1928 when the effect of fuel autoignition tendency on SI engine performance was first realized. Later, it was argued that the conditions for RON were less suitable and a more severe test was generated. This is called the Motor Octane Number. The same engine is used as with RON, but the inlet temperature is increased from 49 to 149 °C (300 °F) and the engine speed is increased to 900 rpm. There is also a significant difference in how the inlet temperature is measured. For the RON case, it is the air temperature before the fuel is added to the inlet, whereas for the MON case, it is the fuel/air mixture temperature. Thus, if a fuel would have significant heat of vaporization, leading to cooling of the charge as the fuel evaporates, a clear difference between RON and MON is expected.

For most practical hydrocarbons, the RON is higher than MON, often around 5–10 units. This has led to different definitions of octane number worldwide. In the European Union, the RON is used and there are no requirements of MON. In the United States, the average of RON and MON is used and is called *Octane Index*. As MON is most often lower, the numbers found on filling station fuel pumps are different in the European Union and the United States. A fuel rated as 87 in the United States can be equivalent to 92 in the European Union.

There has been some debate about the suitability of using both RON and MON in the United States, especially from Gautam Kalghatgi from Shell (and since a few years, Saudi Aramco) [2]. The argument is that engines of today are using a