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Recent progress in gasoline surrogate fuels

S.Mani Sarathy^{a,*}, Aamir Farooq^a, Gautam T. Kalghatgi^b^a King Abdullah University of Science and Technology, Clean Combustion Research Center, Thuwal, Saudi Arabia^b Fuel Technology Team, Research and Development Center, Saudi Aramco, Dhahran, Saudi Arabia

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ABSTRACT

Petroleum-derived gasoline is currently the most widely used fuel for transportation propulsion. The design and operation of gasoline fuels is governed by specific physical and chemical kinetic fuel properties. These must be thoroughly understood in order to improve sustainable gasoline fuel technologies in the face of economical, technological, and societal challenges. For this reason, surrogate mixtures are formulated to emulate the thermophysical, thermochemical, and chemical kinetic properties of the real fuel, so that fundamental experiments and predictive simulations can be conducted. Early studies on gasoline combustion typically adopted single component or binary mixtures (n-heptane/isooctane) as surrogates. However, the last decade has seen rapid progress in the formulation and utilization of ternary mixtures (n-heptane/isooctane/toluene), as well as multicomponent mixtures that span the entire carbon number range of gasoline fuels (C₄–C₁₀). The increased use of oxygenated fuels (ethanol, butanol, MTBE, etc.) as blending components/additives has also motivated studies on their addition to gasoline fuels. This comprehensive review presents the available experimental and chemical kinetic studies which have been performed to better understand the combustion properties of gasoline fuels and their surrogates. Focus is on the development and use of surrogate fuels that emulate real fuel properties governing the design and operation of engines. A detailed analysis is presented for the various classes of compounds used in formulating gasoline surrogate fuels, including n-paraffins, isoparaffins, olefins, naphthenes, and aromatics. Chemical kinetic models for individual molecules and mixtures of molecules to emulate gasoline surrogate fuels are presented. Despite the recent progress in gasoline surrogate fuel combustion research, there are still major gaps remaining; these are critically discussed, as well as their implications on fuel formulation and engine design.

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* Corresponding author.

E-mail address: mani.sarathy@kaust.edu.sa (S.M. Sarathy).

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1. Introduction

Transport is an essential part of modern society, accounting for around 20% of the world's energy use [1]. Currently, about 95% of the energy used for transport is provided by liquid fuels made by refining petroleum. Nearly 40% of global transport energy is used in passenger cars, which are essentially (~80%) powered by spark ignition (SI) engines running on gasoline [2]; although in Europe diesel engines have a much larger share of the passenger car market. At around 25 million barrels of oil equivalent [3], the daily global demand for gasoline exceeds 4.8 billion liters.

The outlook for transport energy, the prime movers for change in transport technology, alternatives to conventional engines and fuels [4–6], and implications for combustion science in these developments [7,8] have been discussed. There are many forces for change in the transport sector, including increasing demand from a growing and prosperous population, concerns about local and global emissions, energy security and consumer demands and preferences. The importance of each of these varies in different countries at different times. Nevertheless, as in all energy sectors, efficiency is the primary requirement for the engines that drive transport. Engine efficiency is directly related to fuel economy and CO₂ emissions. There is also increasing pressure to minimize tailpipe emissions of unburned hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x) and particulate matter (PM). Nanoparticles are of particular concern for public health.

Reconciling these often conflicting demands for the development of future transport power systems is a tremendous challenge, one which could be better met if new fuel/engine systems are co-operatively developed. Reliable computational models that can predict engine performance and emissions will be of great benefit to development; such models will need to handle mixture formation, combustion, and abnormal combustion, such as engine knock and emissions, which limit efficiency. Fuel composition and properties can affect performance and emissions in current engines [9] and may be of greater importance in new combustion systems that use fuel properties as an additional control parameter. However, practical fuels are mixtures of hundreds of hydrocarbons, and simplified surrogate fuels are needed to represent them [10–12] in computational models. Surrogate fuels contain a limited number of pure components blended together to match a target practical fuel's combustion and emission characteristics. It is currently impossible for a single surrogate to represent all aspects of fuel behavior that are of interest in engines, and different surrogates will be needed to model different phenomena. For instance, the surrogate fuel to model vaporization and mixture formation is likely to be quite different

from a surrogate to model autoignition behavior. However, as kinetic models become available for more components and computational resources increase in speed, future surrogates could reproduce all real fuel characteristics.

The path towards cleaner burning and higher efficiency gasoline engine technologies is illustrated in Fig. 1. This review focuses on the development of surrogate fuels for gasoline, which is an integral part of achieving the aforementioned goal. SI engines operate on gasoline fuels comprising petroleum hydrocarbons obtained from fossil resources. The chemical composition of gasoline varies with time and location, so methods of characterizing important chemical and physical properties are needed. Section 2 discusses target fuel properties and strategies for the formulation of surrogate fuels. When formulating surrogates, it is important to understand the relationship between specific fuel properties and engine performance (e. g., efficiency and emissions), so these are also discussed in Section 2. Once surrogates are formulated, fundamental combustion experiments comparing them with their target gasoline fuels are useful for refining the formulation and studying relationships between fuel composition and combustion performance. Section 3 of this paper covers fundamental combustion experiments on gasoline and surrogate fuels, including measurements of ignition delay time, laminar flame speed, and product species formation. Simulating the combustion of gasoline using surrogate fuel chemical kinetic models is needed to perform computer-aided engineering and design. Therefore, Section 4 of this paper focuses on chemical kinetic models for gasoline surrogates and model validation against fundamental combustion experiments. Such models are essential for predicting various combustion phenomenon, such as knock in SI engines and combustion in homogeneous charge compression ignition (HCCI) engines. Section 5 provides concluding remarks and an outlook towards future research in gasoline surrogate fuel development.

2. Surrogate fuel formulation

2.1. Defining target properties

An appropriate surrogate fuel mixture can accurately emulate specific target properties of a gasoline fuel under investigation. A surrogate that does not fall within standard gasoline specifications would not be useful for studying fuel/engine interactions. The U.S. standard specifications for SI engine fuels are given by ASTM D4814–17, and properties vary depending on state and season [13]. Rand and Verstuyft [14] provide a good reference for various fuel specifications and their practical uses. Gasoline properties are measured following standard test methods; Table 1 provides an overview of

Fig. 1. Design process for developing optimal gasoline fuel-engine technologies with high efficiency and low environmental impact.

important ASTM methods. When formulating a surrogate, target properties are judiciously selected, with an understanding of how they impact engine combustion and operating characteristics. Because each property impacts the combustion process, the relationship between the target property and combustion performance must be considered. Target properties are classified into physical and

chemical properties. For example, physical properties, such as fuel volatility, impact spray formation, which in turn influences combustion performance; chemical target properties such as octane number impact the knock-limited operating conditions.

The selection of target properties is closely related to the engine application in which the gasoline fuel is used. Although gasoline fuels are used in both SI and CI engine applications, the combustion process in each is significantly different. Even within a specific technology, combustion processes may change, depending on specific engine operating conditions such as speed and load, or if abnormal conditions occur (e.g., pre-ignition, knock, etc.). Therefore, it is important to determine which target properties should be matched by a surrogate, and if all—or possibly only a subset—of target properties should be emulated.

This section presents a summary of important target properties and explains their role in various combustion processes. Table 2 presents typical properties of gasoline fuels from various sources, as well as the properties of some important additives (e.g., oxygenates). Both physical and chemical (thermodynamic and chemical kinetic) target properties will be discussed in the following sections. Finally, strategies for formulating surrogate mixtures by considering which targets should be emulated are discussed.

Table 1

Summary of relevant ASTM standards for gasoline fuels.

ASTM Code	Description	Reference
D4814	Standard specification for automotive spark ignition engine fuel	[13]
D2699	Research octane number (RON)	[15]
D2700	Motor octane number (MON)	[16]
D4953, D5191	Vapor pressure	[17,18]
D86	Distillation	[19]
D4052	Density	[20]
D240	Heat of combustion and lower heating value (LHV)	[21]
D6730, D1319	Detailed hydrocarbon analysis (DHA)	[22,23]
D5291	Carbon and Hydrogen content (H/C)	[24]
D4815, D5599	Oxygenate content	[25,26]
D5580	Aromatic content	[27]
D6550	Olefin content	[28]

Table 2
Typical properties of gasoline fuels.

Properties	EURO VI	CARB LEV III E10	FACE G	FACE F
RON	97.5	91.0	96.8	94.4
MON	86.6	83.4	85.8	88.8
AKI (antiknock index; [RON+MON]/2)	92.05	87.2	91.3	91.6
S	10.9	7.6	11.0	5.6
Specific gravity	0.749	0.748	0.760	0.707
Lower heating value (MJ/kg)	42.4	41.8	43.1	44.3
H/C (mole/mole)	1.78	1.98	1.83	2.13
Carbon (wt%)	85.62	82.60	86.70	84.96
Hydrogen (wt%)	12.66	13.74	13.3	15.04
Oxygen (wt%)	1.73	3.7	N/A	N/A
Ethanol (vol%)	4.7	10.0	N/A	N/A
MTBE (vol%)	N/A	N/A	N/A	N/A
Aromatics (vol%)	30.5	22.5	33.5	5.8
Olefins (vol%)	8.2	5.7	7.8	8.6
Vapor pressure (kPa)	59.8	49.6	49.6	53.8
Distillation profile				
Volume recovered (%)	T(K)	T(K)	T(K)	T(K)
10	321	332	350	346
50	373	375	411	370
90	434	431	451	391

2.2. Physical target properties

The physical properties of gasoline determine important engine-related performance measures. A typical certificate of analysis for gasoline fuel in North America and Europe provides details on specific gravity or density of the fuel at ambient conditions, vapor pressure, and distillation profile, as shown in Table 2. Other important physical properties include viscosity and surface tension, but these are not typically provided in a certificate of analysis, so they should be measured separately. Physical properties such as viscosity play a more significant role in gasoline direct injection (GDI) technology, where fuel sprays strongly impact in-cylinder combustion, as opposed to port fuel injection (PFI).

2.2.1. Overview of physical properties

The volatile characteristics of gasoline describe how easily the fuel vaporizes under various conditions. Physical properties related to volatility determine how liquid fuel droplets are converted to gas-phase species, where the combustion process occurs. Volatility characteristics strongly affect engine performance under various weather conditions: cold winter conditions require a highly volatile fuel to start the engine, while in summer lower volatility is desirable to prevent emission of volatile organic compounds (VOC). Vapor pressure and distillation profile are two important properties used to measure volatility.

Fuel vapor pressure is exerted by the vapor under thermodynamic equilibrium in the condensed liquid phase; it is an important parameter governing fuel evaporation and affecting cold start, emissions, and combustion efficiency. In the past, carbureted engines could only be started with highly volatile fuels, but modern engines with PFI or GDI do not have this requirement. The vapor pressure of market gasoline varies depending on seasonal temperature conditions. Lower volatility fuels are used at higher temperatures to minimize vapor lock and fuel vapor emissions, while higher volatility is desirable under colder conditions. Typical gasoline vapor pressure ranges from 48–103 kPa; it is measured in a closed chamber at 37.8 °C (310.95 K) and ambient pressure of one atmosphere (101.325 kPa). In the U.S., dry vapor pressure equivalent (DVPE) is typically measured by ASTM D5191 (the mini method), or ASTM D4953 (dry method) for gasoline-oxygenate blends, while in Europe the DVPE is measured by EN 13016.

The distillation profile (or distillation curve) of gasoline measures the amount of fuel distilled as the temperature varies. Hundreds of hydrocarbon and oxygenated components, of different molecular weight and molecular structure, are contained in gasoline. The boiling points of the various hydrocarbons in the mixture varies, so the gasoline mixture is distilled over a range of temperatures. Compounds with lower boiling points are distilled first, higher boiling point compounds distill later. This distillation profile impacts gasoline engine performance.

The front end of the distillation curve determines the initial volatility of the mixture, which impacts cold start performance and evaporative losses. Butane is typically added to gasoline under cold weather conditions to help raise front end volatility. The mid-range and tail-end of the distillation curve impacts acceleration, power output, fuel economy, and unburned hydrocarbon emissions. The distillation profile is measured by ASTM D86 methodology, in which 100 mL of fuel is heated in a flask at a controlled rate; as the fuel evaporates, the gas passes through a condenser tube and the condensate is recovered. Temperature is measured by a thermocouple placed above the sample liquid, so that it measures the gas-phase temperature. The temperature corresponding to various volumes of fuel recovered in the condensate is recorded (e.g., T at 10 vol% recovered, T50, T90, etc.).

A major drawback of the ASTM D86 methodology is that it does not measure the temperature under thermodynamically vapor–liquid equilibrium (VLE) conditions. The rate of heating and condensation, as well as the temperature measurement location, are subject to significant uncertainty. This reduces experimental precision and prevents the modeling of the experiment using thermodynamic equations of state. To resolve these issues, Bruno et al. [29–32] developed the advanced distillation curve (ADC) method, which measures true thermodynamic VLE state points with significantly improved accuracy. The ADC method's improved ability to accurately measure VLE conditions, compared to the ASTM D86 method, makes it possible to numerically predict the fuel's distillation properties using a mixture model [33].

Fig. 2 shows an example of ADC measurements for six FACE (Fuels for Advanced Combustion Engines), as measured by Burger et al. [32]. Recently, Ferris and Rothamer [34] modified an ASTM D86 distillation apparatus to determine experimental equilibrium distillation curves (EEDC). Fig. 3 from Ferris and Rothamer [34] shows typical uncertainty resulting from traditional D86 measurements of gasoline fuel, in which temperature measured in the vapor phase (D86 vapor) is much lower than the equilibrium condition. Simply measuring the liquid temperature in the sample (D86 Liquid) provides a much closer agreement to the equilibrium measurement method (i.e. EEDC). These improved distillation methods are beneficial because they make it possible to simulate complex fluid behavior using thermodynamic vapor–liquid equilibrium relations [33,35].

Fig. 2. Distillation curves for FACE gasolines measured by the ADC method of Burger et al. [32]. Reproduced with permission from The American Chemical Society.

Fig. 3. Experimentally measured equilibrium (EEDC), D86 vapor, and D86 liquid distillation curves for a certification gasoline by Ferris and Rothamer [34]. Reproduced with permission from Elsevier Publishing.

Vapor pressure and distillation profile requirements for gasoline fuels in automotive engines are specified according to ASTM D4814 in the U.S. market and EN 228 in the European market. Various categories, with their own ranges for vapor pressure and distillation profile, are provided to meet various seasonal and performance measure requirements. In the ASTM specification, vapor pressure ranges from 54 kPa for Class AA gasoline to 103 kPa for Class E gasoline. T10, T50, and T90 for Class AA gasolines are 70 °C (343 K), 77–121 °C (350–394 K), and 190 °C (463 K), respectively. For Class E gasolines, T10, T50, and T90 are 50 °C (32 K), 77–110 °C (350–383 K), and 185 °C (458 K), respectively [36]. A recent study by CONCAWE [37] showed that volatility requirements may be relaxed with the introduction of modern engine hardware, such as GDI technology, which reduces the effects of gasoline volatility on regulated emissions and driveability.

The specific gravity and viscosity of gasoline fuels are important physical properties that may impact fuel spray formation and breakup processes. Specific gravity (the ratio of fuel density to water density) is a dimensionless quantity. The density is measured by

ASTM D4052 in North America or EN 12185 in Europe. The typical range of specific gravity in the ASTM D4814 or EN 228 specifications is between 0.72 and 0.77, which is to ensure sufficient energy density. Viscosity requirements for gasoline fuels are not mentioned in ASTM D4814 and EN 228 specifications for SI fuels, and measurement and reporting of these values is not required. Gasoline viscosity has less influence on spray processes in PFI and GDI engines due to the use of hollow cone injectors with wide spray angles and relatively low injection pressures.

2.2.2. Relationship of physical properties to engine combustion processes

The previous section highlighted several important physical properties of gasoline. It is necessary to understand how these properties affect various engine combustion processes in order to know which properties are important for a surrogate fuel to emulate. This section summarizes recent literature relating various fuel physical properties with engine combustion processes and performance measures.

It has been noted that volatility and distillation profile characteristics affect engine cold-start performance and emissions. Volatility primarily affects fuel evaporation rate, and thus, the air/fuel ratio in the combustion chamber. The main processes affecting mixture preparation in PFI SI engines are shown in Fig. 4 [38]. The processes are extremely complex and include both droplet evaporation prior to entering the combustion chambers and the entrainment of liquid droplets into the bulk flow. Wall wetting by larger droplets impinging on the inlet port or intake valve is also important. The dynamics and evolution of these processes are controlled by their fuel volatility characteristics, temperature, engine design and operating conditions. Skippon and Norton [38] investigated many of the effects of gasoline volatility on engine performance. They showed that when the engine is fully warmed up, all fuels are completely vaporized in the inlet port, regardless of their T50 or T90. However, under cold start conditions, only 20–30% of the fuel is vaporized in the inlet port, making wall wetting significant. T50 has a significant impact on how much fuel is vaporized under cold-start conditions, while the T90 is less relevant. However, as the engine warms up, T90 impacts vapor phase composition.

Fig. 4. Important processes affecting in-cylinder mixture formation in PFI SI engines. Reproduced from Skippon and Norton [38] with permission from SAE International.

A detailed study of PFI engines by Takei et al. [39] showed that fuel volatility has a significant impact on HC emissions. Gasoline fuels with a high T50 result in leaner air/fuel ratios in the cylinder due to poor vaporization of the fuel, causing lean misfiring and increasing HC emissions. If the T50 is too low however, the air/fuel ratio becomes rich and results in rich misfire and increased HC emissions. Ryan and Matheaus [40], performed HCCI engine measurements with gasolines of different volatilities. They showed that less volatile fuels inhibit the fuel/air mixing process, so that perfectly—or even partially mixed—fuel/air mixtures did not occur before the start of reaction. Incomplete fuel evaporation in HCCI engines results in fuel droplets that undergo diffusion combustion in the cylinder, increasing both soot and NO_x emissions. In principle, the high volatility of gasoline-like fuels are desirable in HCCI and other compression ignition engine concepts, where sufficient premixing of fuel and air is required prior to combustion [41–47].

In GDI engines, the distribution of the fuel spray has a significant impact on the in-cylinder combustion process due to the short time available for fuel/air mixing. The effects of fuel volatility and engine operating conditions on GDI fuel spray were investigated by VanDerWege and Hochgreb [48]. Their experiments used planar laser-induced fluorescence to image sprays ensuing from a pressure-swirl fuel injector in an optically-accessible direct injection spark ignition (DISI) engine. They showed that the higher volatility components in multi-component fuel mixtures evaporate quickly when fuel temperature is high, resulting in disruption of the spray structure and formation of a vapor core within the spray core. Fuel volatility also impacted spray penetration length and spray width.

Using Schlieren and Mie scattering techniques, Li et al. [49] also studied the effects of fuel volatility on GDI spray characteristics at high pressures and high temperatures. They tested two surrogate fuel mixtures comprising various amounts of n-pentane, isooctane, and n-decane, as well as a fully formulated gasoline fuel [49]. Their results showed that higher fuel temperature increased evaporation and decreased liquid and vapor penetration distances. Furthermore, fuel mixtures with a larger fraction of heavier components had lower volatility, and therefore lowered evaporation and increased liquid and vapor penetration.

Davy et al. [50] and Zigan et al. [51] showed that flash boiling influenced by fuel composition and volatility characteristics affects mean droplet diameter and mixture formation in DISI engines, thereby affecting combustion and emissions. The volatility of gasoline alters with the addition of ethanol due to non-ideal mixing behavior. Ethanol blending is known to cause higher volatility in gasoline-ethanol mixtures, while also introducing discontinuities in the distillation profile. Changes in T50 and T90 due to ethanol blending often motivate researchers to modify the gasoline blendstock by adding higher boiling point hydrocarbons in order to remain within ASTM D4814 limits. However, a recent study by Anderson et al. [52] showed that studies which evaluate the effects of ethanol blending on engine performance and emissions obscure the results, due to the mixing of higher hydrocarbons; for this reason, such modifications to the gasoline blendstock should be avoided.

Low speed pre-ignition (LSPI) and superknock phenomena in GDI engines has also been shown to be related to fuel volatility. One common hypothesis is that LSPI is caused by fuel impinging on combustion chamber walls, which interacts with oil on the liner and results in oil–fuel droplets detaching from the surface. These oil–fuel droplets serve as reactive hot spots that result in pre-ignition. Mayer et al. [53] showed that increasing fuel volatility significantly reduces the tendency for pre-ignition. They explained that less volatile fuels increase wall wetting and enter the piston crevice volume, thereby enhancing the detachment of oil droplets by local fuel dilution. Their experiments were further confirmed by proving that HC emissions increase with decreasing fuel volatility, which also correlated with the pre-ignition tendency.

2.3. Chemical target properties

Chemical properties of gasoline affect the combustion process because fuel/air oxidation is controlled by the fuel's molecular structure. As mentioned previously, gasoline is a complex mixture of hundreds of hydrocarbons, as well as oxygenated additives. A gasoline certificate of analysis typically provides information on fuel octane numbers, carbon content, hydrogen content, oxygen content, H/C ratio, aromatic content, olefinic content, and lower heating value (LHV), all of which are determined by various ASTM or EN standard methods. In addition to these typical chemical properties, more detailed information on gasoline chemical composition can be obtained by detailed hydrocarbon analysis (DHA), including the distribution of PIONA (**p**araffins, **i**soparaffins, **o**lefins, **n**aphthenes, **a**romatics), and even individual hydrocarbon structures. Laminar flame speed is another chemically-related target property that is not typically reported for market fuels, but may be measured using various methods.

The chemical composition of the fuel ultimately affects combustion related target properties such as RON, MON, laminar flame speed, and LHV. However, it is currently difficult to include the full spectrum of hydrocarbons in a gasoline surrogate mixture, primarily due to the present lack of chemical kinetic models for most species (as discussed in Section 4). Nevertheless, it is plausible that as kinetic models become available for hundreds of hydrocarbons, future gasoline surrogate mixtures would include a large number of components that accurately emulate all properties of the target gasoline.

2.3.1. Lower heating value

The LHV of gasoline is a gauge of its energy content, which is measured as the heat produced by combusting a prescribed amount of fuel in stoichiometric proportions with air under certain initial temperature and pressure conditions. For this reason, LHV is also commonly referred to as *heat of combustion*, and is directly related to the chemical composition of the gasoline fuel. LHV is measured by ASTM D240, using a bomb calorimeter, and is typically reported on a mass basis, according to SI units (MJ/kg). On a mass basis, the LHV is similar for fuels with similar molecular structure. For example, all paraffinic hydrocarbons from C₅ to C₁₆ have LHV in the range of ~44–46 MJ/kg, while aromatics have LHV near 40–41 MJ/kg. This relationship between molecular structure and LHV is shown in Fig. 5 [54], in which the LHV is linearly proportional to the H/C ratio of a complex real fuel mixture.

Gasoline fuels are typically sold on a per unit volume basis, so it is often useful to understand the amount of energy per unit volume (e. g., MJ/L). This has an impact on vehicle fuel economy, which is

Fig. 5. Correlation between LHV and H/C ratio. Reproduced from Narayanaswamy et al. [54], with permission from Elsevier Publishing.

measured in units of L/100 km (or miles per gallon), because distance travelled per unit of fuel is directly related to the volumetric energy density of the fuel. Converting LHV to volumetric energy density requires multiplying by the liquid density of the fuel, which varies greatly with its molecular structure. Low molecular weight hydrocarbons have lower liquid density, therefore their volumetric energy density is notably lower than higher molecular weight hydrocarbons. The addition of oxygenates (e.g., ethanol) to gasoline decreases LHV (mass basis) because fuel-bound oxygen does not burn to generate heat (i.e., oxygen has no heating value). Therefore, the volumetric energy density of oxygenated fuels is also lower than pure hydrocarbon fuels, lowering oxygenated fuel economy. In general, the reduction in LHV is proportional to the mass percent of oxygen in the fuel.

2.3.2. Gasoline chemical composition

One important property of gasoline is its chemical composition, which determines all subsequent chemical properties (octane numbers, H/C ratio, LHV, etc.) and physical properties (distillation curve, density, etc.). The PIONA range of typical gasoline fuels is shown in Fig. 6, along with representative molecular structures for each PIONA class. Gasoline is distilled from crude oil, and the initial cut comprises C_4 to C_{10} n-paraffins, isoparaffins, naphthenes (cycloparaffins), and aromatics. Various refinery processes are used to upgrade crude distillation products into fuels that meet gasoline specifications; these processes include alkylation, catalytic condensation, isomerization, and catalytic reforming [55], all of which are aimed at creating high-octane quality molecules in the gasoline molecular weight range.

Normal paraffins have the lowest octane quality of all gasoline hydrocarbons, and are not typically found in large quantities in market fuels. Iso-paraffins are generally found in larger quantities due to their higher octane numbers. Paraffins range in carbon numbers from C_4 to C_8 . Low molecular weight paraffins, such as n-butanes and isobutanes, are blended into gasoline to meet front-end

distillation requirements for cold-start under winter conditions. Other common paraffins include n- and isopentane and various isomers of hexane, heptane, and octane with multiple methyl substitutions. Octane number increases with the increased degree of methyl substitutions [56,57], so higher molecular weight paraffins (C_7 – C_8) in gasoline typically have one to three methyl substitutions. The mixture of n- and isoparaffins is highly variable, and because of the large number of possible isomeric species, no specific paraffinic structure is present at more than a few percent. For example, the widely used primary reference fuel surrogates, n-heptane and iso-octane, are only present in small quantities (less than 1%) in real gasoline fuels.

The naphthenic content of gasoline is limited to below 20 vol%, since these compounds have low octane quality and are easily converted to aromatics via reforming. Typical naphthenes found in gasoline are in the C_5 to C_8 range, and include species such as cyclopentane, cyclohexane, methyl cyclopentane, methyl cyclohexane, and dimethyl cyclohexane isomers. Cyclopentane has the highest octane number among the cycloalkanes.

Olefins (alkenes) are also found in limited quantities due to their poor oxidative stability, which reduces the storage life of gasoline fuels. Furthermore, olefins are often useful precursors for other value added chemicals (e.g., polymers). Typical olefins range from C_5 to C_8 and include linear and branched pentene and hexene isomers. Due to the presence of double bonds in the molecular structure, they have high octane numbers; but they also display high octane sensitivity.

Aromatics are the highest molecular-weight hydrocarbons in gasoline fuels, falling in the C_6 to C_9 carbon number range. The end of the gasoline distillation profile is typically comprised of high molecular weight alkylbenzenes. Aromatics have high octane numbers, but they are typically limited to below 30–35 vol%, due to their propensity to increase soot (particulate matter) emissions. Furthermore, benzene is a known carcinogen, so its concentration in

Fig. 6. (Top) Typical PIONA range for U.S. market gasoline fuels. Reproduced from Pitz et al. [10] with permission from SAE International. (Bottom) Representative molecular structures in gasoline fuels. Reproduced from Sarathy et al. [58] with permission from Elsevier Publishing.

gasoline is limited to below one vol%. For these reasons, the aromatic hydrocarbons in gasoline fuel are limited to toluene, m-xylene, o-xylene, (p-xylene is a valuable commodity chemical, not blended into gasoline), ethylbenzene, and various trimethyl benzene isomers. Toluene is the most predominant aromatic found in gasoline, followed by the xylene isomers.

In addition to hydrocarbon components, gasoline fuels may also contain various oxygenated additives. Traditionally, oxygenates such as methyl t-butyl ether (MTBE), ethyl t-butyl ether (ETBE), t-amyl methyl ether (TAME), diisopropyl ether (DIPE), methanol, ethanol, and t-butanol have been added to gasoline to improve its anti-knock quality. The use of MTBE as an octane enhancer is prohibited in North America, but many Asian countries still use it. Ethanol is by far the most widely used oxygenate additive for gasoline fuels, and may be blended up to 85 vol% (E85) into gasoline fuels; the most commonly found blends contain ten vol% (E10) in North America and five vol% (E5) in Europe. Recently, interest in renewable fuels has motivated research on blending other oxygenates, such as propanol and butanol isomers [59,60], pentanol isomers [61–64], cyclic oxygenates (e.g., furans and alkyl furans) [65–67], aromatic oxygenates and esters derived from levulinic acid (e.g., ethyl levulinate, methyl levulinate, etc.) [68,69].

The exact chemical composition of gasoline fuels can be determined by ASTM D6730, which utilizes high resolution gas chromatography (GC). This DHA test method determines the individual hydrocarbon components in SI engine fuels, including mixtures containing oxygenates, with boiling ranges up to 225 °C (498 K). The D6730 method is accurate for mixtures containing up to 25 wt% olefins, which makes it acceptable for most practical gasoline fuels. However, mixtures containing higher olefin content, or olefins larger than C₇, require a separate multidimensional GC method (e.g., ASTM D1319) to obtain accurate olefin percentages.

A detailed analysis of individual components in gasoline fuels is usually unavailable, or not required by ASTM standards. Typically, gasoline suppliers only provide information on the aromatic, olefinic, oxygenate (ethanol or MTBE), carbon, hydrogen and oxygen contents, and H/C ratio, as shown in Table 2. Normally, this information, together with the octane rating, is sufficient to develop a surrogate fuel with a reasonable level of chemical fidelity. Carbon and hydrogen content are important for determining the H/C ratio, and these are measured using ASTM D5291 methodology. Oxygen content and the concentration of oxygenated additives are measured by ASTM D4815, which is suitable for determining MTBE, ETBE, TAME, DIPE, t-amyl alcohol, and C₁ to C₄ alcohols, and/or D5599 for other oxygenates. The aromatic content is measured by ASTM D5580, which utilizes gas chromatography to quantify benzene, toluene, ethylbenzene, xylene isomers, and C₉ and heavier aromatics. The total olefinic content is measured by ASTM D6550, which is based on supercritical-fluid chromatography.

2.3.3. Gasoline anti-knock properties and octane number

Perhaps the most important chemical property of gasoline fuel is its antiknock quality, which is determined by the ability of the fuel/air mixture to resist autoignition. Knock occurs because of autoignition of the unburned fuel/air mixture in the end-gas, ahead of the advancing flame front in a SI engine; the presence of knock limits engine efficiency [8,16]. The knocking tendency of a fuel/air mixture depends on the pressure and temperature evolution with time and on the anti-knock quality of the fuel. The anti-knock, or octane quality, is traditionally measured by the research and motor octane numbers, RON and MON. The MON test is run at 900 rpm with an intake temperature of 149 °C; the RON test is run at an engine speed of 600 rpm and an intake temperature of 52 °C in a single-cylinder CFR engine. These tests are run using procedures set in ASTM D2699 for RON and ASTM D2770 for MON. All practical fuels have RON higher

than MON, and the difference between RON and MON is known as octane sensitivity (S).

If a target surrogate is intended to mimic only autoignition phasing in engines running under premixed conditions (where different fuels are subjected to the same pressure and temperature evolution), it should match both RON and MON of the target gasoline. A toluene/PRF (TPRF) mixture can be found to match any target RON and MON [70], and chemical kinetic calculations on such a surrogate can predict knock onset in knocking engines [70,71]. However, TPRF surrogates for high octane sensitivity gasolines (e.g., above seven) have toluene fractions which exceed 30%. Such surrogates with high aromatic fractions do not accurately represent the hydrocarbon distribution in practical gasoline fuels.

2.3.4. Relationship of chemical properties to engine combustion processes

Several important chemical properties of gasoline were highlighted in the previous sections. Chemical properties inherently affect combustion processes in an engine because the molecular structure impacts reactivity. However, it is necessary to ascertain the importance of chemical properties on various engine processes and to determine what level of chemical fidelity is needed for a surrogate to emulate a real gasoline fuel. The following section summarizes recent literature relating various fuel chemical properties to engine combustion processes and performance measures. The effects of fuel chemical properties on deposit formation are not discussed in detail as this is primarily related to fuel sulfur content, olefin content, aromatic content, and presence of detergents [72,73]. Increasing fuel aromatic and olefin content has a statistically significant effect on promoting deposit formation [74].

The efficiency, and hence CO₂ emissions, of SI engines depends strongly on octane requirements, which determine the knock limited operating range. Higher octane fuels enable earlier spark timing, which can improve combustion efficiency and power output at higher compression ratios. Di Iorio et al. [75] showed that blending oxygenates, such as ethanol, MTBE, and ETBE, increase the octane number, thereby improving combustion performance. This results in decreased HC and carbon monoxide (CO) emissions, as well as lower particulate matter emissions in oxygenated fuels due to the displacing of aromatics [76–78]. Machado et al. [79] conducted a careful study of gasoline fuel composition on the SI engine calibration and performance, with a specific focus on the relationship between octane number and composition. The content of aromatics, n-paraffins, and isoparaffins was varied in a gasoline base fuel containing anhydrous ethanol, and the effect of each blending component on engine combustion was assessed. The authors found that n-paraffins are suitable blending components for engine conditions that are not sensitive to knock because they permit higher stoichiometric fuel/air ratios and higher H/C ratios, which increases combustion efficiency and decreases fuel consumption. However, when the engine is operated at conditions sensitive to knock, aromatics and isoparaffins can be blended to produce a higher octane rating fuel. isoParaffins are superior to aromatics due to their higher stoichiometric fuel/air ratio and higher H/C ratios, which improves combustion efficiency and reduces particulate matter emissions. The authors demonstrated the need for flexible engine control systems that can optimize engine performance based on the fuel used [79]. This fuel blending concept has led to recent interest in octane-on-demand (OOD) [80–82], which offers the potential to vary fuel composition, and hence its octane number, depending on the engine operating requirements.

The chemical composition of gasoline fuel has a direct impact on engine emissions. A comprehensive study by Hochhauser et al. [83] investigated the effects of aromatic, olefin, and MTBE content on vehicle emissions. It was shown that the addition of MTBE reduces HC and CO emissions. It is well accepted that oxygenated additives,

such as ethers and alcohols [60,84], improve combustion efficiency, thereby reducing particulate matter (i.e., soot), HC, CO emissions. In modern vehicles, increasing the aromatic content increases hydrocarbon and particulate emissions [78] while lowering oxides of nitrogen (NO_x). However, the addition of oxygenated aromatics (e.g., 2-phenylethanol, anisole, etc.) can improve the soot-NO_x tradeoff [85–87]. Increasing olefin content corresponds to lower NO_x emissions and higher hydrocarbon emissions [83,88].

Modern DISI engines are shown to be sensitive to fuel composition and antiknock quality. As mentioned previously, modern DISI engines have negative *K* values [89], so fuels with lower MON values (i.e., higher *S*) extend the knock-limited operating range. Davies et al. [90] studied the fuel effects on DISI combustion with a focus on octane appetite; they showed that higher sensitivity fuels (high RON and low MON) perform better in modern engines. Furthermore, high sensitivity fuels were shown to have higher burning velocity, thereby improving fuel efficiency and cyclic variability. They also noted that higher burning velocity fuels may be more prone to preignition, and hence superknock [90].

Machado et al. [91] showed that various TPRF (toluene/n-heptane/isooctane) surrogate mixtures, each blended with 25 vol% ethanol, behaved differently in a multi-cylinder DISI engine due to variations in their antiknock index (AKI) values and stoichiometric A/F ratios. A reference gasoline with an AKI of 89.2 was tested alongside ten different surrogates at a range of speed and load operating points. Their results showed that TPRF/ethanol mixtures with AKI values and stoichiometric A/F ratios close to the reference gasoline could match engine torque, fuel consumption, and specific fuel consumption across the entire operating range.

A recent study by Ahmed et al. [92] assessed the impact of gasoline chemical properties and composition of DISI engine combustion, performance, and emissions. The study was unique in that two well-characterized non-oxygenated gasolines with similar AKI, but varying *S*, were experimentally investigated at various load points and spark timings with early injection timings. The goal was to determine whether fuels with similar knocking characteristics in a standard cooperative fuel research (CFR) engine (i.e., similar AKI) behave differently in DISI engines. The authors showed that gasoline with higher aromatic content resulted in higher hydrocarbon and soot emissions [92]. Interestingly, they also noted that if the fuel octane number is held constant, a gasoline fuel with lower heat capacity (e.g., constant pressure, *C_p*) will result in higher end-gas temperatures, making it more prone to knock. Furthermore, the fuel burn duration was found to be dependent on fuel composition (e.g., H/C ratio), as well as thermodynamic properties of the fuel, which affect in-cylinder temperature and pressure. Thus, in DISI engines heat capacity is an important chemical property to consider during surrogate fuel formulation, as this determines the conditions at which combustion occurs.

The previous discussion focused on the impact of gasoline chemical properties on SI engine combustion and emissions. However, gasoline-like fuels may also be utilized in low temperature combustion (LTC) engine strategies such as HCCI, PCCI, etc. The combustion process in LTC engines is notably different, and therefore fuel chemical properties have different effects than in SI engines. Most notably, to obtain the desired onset of heat release and combustion phasing, an appropriate ignition quality is required in HCCI engines. An ignition quality metric for HCCI engines has received attention in the literature [8,40,93,94], and is naturally linked to the chemical properties of the fuel. In PCCI and PPC engines, where fuel is injected late in the cycle to achieve stratification, both fuel chemical properties (e.g., ignition quality) and physical properties (e.g., spray formation, vaporization, etc.) are important.

Shibata et al. [93] proved that the evolution of low temperature heat release (LTHR) plays a critical role in operation of HCCI engines. Paraffinic fuels were shown to have appreciable LTHR, while

aromatics did not display LTHR behavior. Olefins and naphthenes (cycloalkanes) display minor LTHR but behave more like LTHR inhibitors than LTHR promoters, when compared to paraffins. The authors linked a fuel's measured HCCI engine high temperature heat release (HTHR) characteristics to its conventional RON and MON metrics, obtained in an SI engine. They showed that RON correlates with the HTHR characteristics under engine conditions when the fuel combustion displays minor LTHR characteristics. However, MON was shown to correlate with HTHR characteristics under conditions without LTHR [93].

The effect of fuel composition on HCCI engine combustion was investigated by Truedsson et al. [95,96] by investigating various PRF mixtures and mixtures of n-heptane, isooctane, toluene, and ethanol. Their aim was to develop an HCCI autoignition index to rank fuels, similar to the RON and MON metric for SI engines. The autoignition temperature and magnitude of LTHR were identified as relevant metrics of ranking ignition quality of fuels in HCCI engines. The authors demonstrated that increasing n-heptane concentration increases LTHR and decreases AIT, while toluene increases AIT and acts as an LTHR inhibitor. Ethanol was also shown to increase the AIT and suppress LTHR. These findings indicate that chemical composition (e.g., paraffin, aromatic, alcohol) has similar qualitative effects in HCCI engine autoignition and SI engine knock. However, quantitatively, the HCCI ranking of fuel autoignition is not directly correlated with SI engine RON and MON ratings. This indicates that the effect of chemical composition depends strongly on engine operating conditions (e.g., temperature, pressure, and equivalence ratio).

To further understand fuel composition effects on autoignition quality, Lacey et al. [94] studied the effects of refinery stream gasoline blends in an HCCI engine. They tested 17 gasoline fuels with ethanol content ranging from 0% to 100%, and mixtures with various amounts of aromatics, olefins, and saturates (paraffins/isoparaffins). A broad range of RON, MON, and *S* were captured in the blends. They showed that HCCI combustion phasing is strongly dependent on the RON and MON of the fuel, as well as its composition (i.e., fraction of aromatics, olefins, saturates, and ethanol). They defined a revised form of the octane index (i.e., Ol_{JKZ} , where JKZ denotes the authors' initials [94]) to describe fuel ignition characteristics under various engine conditions. The $Ol_{JKZ} = RON - K' * S + \kappa * (\text{aromatics})^2 * (\text{olefins} + \text{saturates}) + \epsilon * (\text{aromatics} * \text{ethanol})$, where *K'*, *κ*, and *ε*, are constants that depend on engine operating conditions [94]. The authors showed that Ol_{JKZ} , which depends on fuel composition, can accurately describe ignition characteristics of fuel in an HCCI engine.

The effects of fuel composition on HCCI engine emissions were also tested by Truedsson et al. [97] with a specific focus on NO_x, CO, and HC emissions. In general, emissions are low in HCCI applications; nevertheless, higher RON PRF mixtures were shown to yield greater NO_x emissions because of the higher in-cylinder temperatures achieved. Adding ethanol or toluene to a high octane mixture reduced NO_x emissions. Increasing the PRF octane number decreased HC emissions, due to higher in-cylinder temperature and less fuel trapped in the crevices. The addition of toluene was found to increase HC emissions, while ethanol reduced HC emissions by promoting fuel oxidation. CO emissions were not found to be directly linked to fuel composition, rather, in-cylinder temperature inhomogeneity (leading to cold spots) was found to be the primary reason why CO was not being oxidized to CO₂.

The importance of fuel chemical properties in LTC engines depends on injection timing. In HCCI combustion, fuel is injected very early, with plenty of time to vaporize and mix before burning; therefore, the combustion process is primarily determined by fuel chemical properties. In PCCI or PPC operating modes, the fuel is injected late in the cycle, so there is less time for fuel vaporization and mixing. As a result, the combustion process is affected by both chemical and physical properties. Aronsson et al. [98] investigated the effect of fuel properties on LTHR in HCCI and PPC engines. They

showed that increasing iso-octane concentration increased LTHR in the PPC mode, while decreasing LTHR in the HCCI mode. Ethanol and toluene additions increased the fraction of LTHR when operating under the PPC mode, but it decreased LTHR under HCCI combustion operating conditions. Their results showed that fuel chemical properties strongly impact HCCI engine operation, but are less important at later injection times, corresponding to PPC.

The previous section on physical properties discussed the effect of volatility on LSPI in DISI engines. Chemical properties can also impact LSPI because they impact the fuel octane rating and burning rate. Amann et al. [99] investigated fuel composition effects on LSPI in high performance SI engines. Four fuels with varying aromatic and oxygenate (ethanol) content, but similar RON, MON, and AKI, were tested. They discovered that fuel composition strongly affects the frequency and magnitude of LSPI. Increasing the level of aromatics was found to increase LSPI frequency, while increasing oxygenate content and decreasing aromatic content decreased LSPI frequency. Unexpectedly, they also showed that despite having similar RON and MON as the other test fuels, low aromatic gasoline showed an increased propensity for conventional end-gas knock/autoignition in the DISI engine. This was attributed to the low aromatic gasoline displaying LTHR prior to the main heat release event.

2.4. Surrogate formulation strategies/methodologies

To this point, discussion has focused on important physical and chemical properties of gasoline fuels and their impact on engine combustion processes. A surrogate fuel mixture, comprising a limited number of components, can be formulated to match various physical and chemical target properties of the real gasoline fuel. This section described various approaches for formulating gasoline surrogate fuels. The methodology of formulation for surrogates of diesel and aviation fuels is also relevant to the present study, as the general approach is similar. The reader is referred to notable works on formulation of diesel and aviation fuel surrogates [12,33,67,100–107].

The target properties to be matched, and their link to the engine combustion processes to be replicated by the surrogate, are the first issues to be addressed. For example, if only spray droplet formation and vaporization are to be captured, a surrogate that matches a limited set of physical properties of the real fuel may be sufficient, neglecting any chemical properties as targets. The most important property to be replicated for gasoline fuels is autoignition behavior; this is true for both SI and CI engines operating on gasoline-like fuels. To predict autoignition phasing (if the P/T trajectory with time is the same as followed by the gasoline), the RON and MON of the surrogate should be the same as that of the gasoline. A toluene, heptane, iso-octane mixture can always be found to match a given RON and MON. Other properties to match with those of the gasoline, such as carbon/hydrogen ratios, have also been suggested [10], although the importance or actual necessity of doing so has not been demonstrated in engine tests. Physical properties such as volatility, viscosity and heat of vaporization must be replicated if the surrogate is to model spray and mixture formation, e.g., in gasoline compression ignition (GCI) engines. Knowledge of laminar burning velocity could be useful in judging the possibility of pre-ignition; it could also be useful for predicting flame development rates in SI engines. Fuel effects on flame development, though likely to be small, might be of interest as engine designers seek ever greater efficiency. However, this will require additional information about turbulence in the engine and its effect on the laminar flame.

Obviously, the surrogate will become more complex, since it has more properties to match. In fact, it is probably not possible to match both physical and chemical properties fully and maintain the complexity of the surrogate at a manageable level. Ultimately, it is a matter of judgement. Equally important is that the accuracy of any computational prediction will also depend on the computational

model used. Even if the surrogate matches the gasoline properties well; if the computational model—for example, chemical kinetics or mixing—is not adequate, then the predictions of the model will not be accurate. Also, the complexity of the surrogate (for chemical kinetics for instance) will also affect the complexity of the chemical kinetic model and detract from its usefulness. In GCI combustion for example, the focus might be to design a complementary mix for complex spray and turbulent flow models; a simple kinetic model with chemistry for a small number of surrogate components is needed to integrate with the flow models.

Pitz et al. [10] stated that gasoline surrogates should be formulated to match the target real fuel properties and HCCI engine performance characteristics; the important fuel property targets are LHV and H/C ratio. LHV should be matched within $\pm 5\%$ of the reference gasoline so that fuel flow to the engine is similar, in order to maintain a similar fuel energy input. Real gasoline fuels have H/C ratios between 1.6 and 2.0, therefore surrogate fuel mixtures should be in the same range. Targeting the H/C ratio is important because air/fuel ratio depends on this value. If the H/C ratio is well matched by a surrogate fuel, then air flow to the engine will be similar between the real gasoline fuel and its surrogate. The important engine properties to match are combustion phasing of 10% mass fraction burned (CA10) and 50% mass fraction burned (CA50). The CA10 is normally related to the onset and magnitude of LTHR; a surrogate that matches the CA10 of a target gasoline fuel essentially matches its low temperature chemical reactivity. CA50 is the most important combustion parameter in an HCCI engine because it ultimately determines engine performance and emissions. A surrogate mixture that matches the RON and MON of a target gasoline will have the same CA50 in an HCCI engine [108,109].

A general methodology for gasoline surrogate fuel formulation for HCCI engines was presented by Puduppakkam et al. [110]. First, a palette of surrogate fuel components was selected, which contained molecules representative of the various chemical class in real gasoline fuels. The surrogate components were then blended in proportions needed to match various target properties of the real fuel, keeping combustion targets in mind. If combustion simulations were to be performed, then chemical kinetic models needed to be assembled for the surrogate fuel components. The authors outlined target properties that should be matched, including the molecular structure, distillation curve, octane numbers, LHV, and H/C ratio. Matching the molecular composition helped to match various physical properties of the fuel. Matching several points along the distillation curve (e.g., T10, T50, T90) ensured that the surrogate matched the spray characteristics of the real gasoline. As noted previously, matching octane numbers is necessary to capture the combustion phasing and knocking characteristics. LHV determines the cumulative heat release upon combustion, while the H/C ratio determines emission characteristics, so these properties should be matched in a surrogate fuel. Puduppakkam et al. [110] outlined a computational methodology (Fig. 7), to formulate a surrogate that matched defined target properties. The methodology minimizes an objective function to optimize a surrogate formulation that matched distillation curve, LHV, H/C ratio, RON, and MON value. The methodology is flexible in that various target properties may be included or removed (e.g., O/C ratio may be added for oxygenated fuels).

Su et al. [111] outlined a similar approach for the development of surrogate fuels for transportation fuels, including gasoline. The target properties of interest included physical properties, such as density, LHV, volatility, and viscosity, and chemical properties, such as H/C ratio and ignition quality (i.e., RON). They used an optimization algorithm to determine the surrogate mixtures that best matched the target properties. Each target property was also given a weighing factor to quantify its importance, as well as error tolerances for convergence checking. The methodology was used to formulate a

Fig. 7. Flow chart for surrogate fuel formulation from Puduppakkam et al. [110]. Reproduced with permission from SAE International.

surrogate that accurately reproduced the combustion behavior of a target fuel under LTC engine conditions.

A unique approach to gasoline surrogate formulation was presented by Mehl et al. at Lawrence Livermore National Laboratory [112]. Like the previous approaches, a palette of surrogate species was first defined, together with target properties to be matched. The target properties included gasoline paraffin content, aromatic content, olefin content, H/C ratio, RON, and MON. The authors presented a novel methodology to determine the RON and MON for a proposed surrogate mixture. The methodology performed chemical kinetic simulations under homogeneous batch reactor conditions to predict the ignition delay time of a surrogate mixture. A mapping of ignition delay times for various mixtures with known RON and MON was then utilized to determine the RON and MON of the proposed surrogate mixture [112]. This methodology for predicting RON and MON is accurate, but it requires high fidelity chemical kinetic models. Badra et al. [113] demonstrated that ignition delay time simulations which considered the actual volume-time history of the fuel/air mixture in the CFR engine could better predict measured RON and MON values of toluene/n-heptane/isooctane surrogate mixtures.

A common theme in surrogate formulation methodologies is the attempt to match multiple target properties with a combination of species in a palette. This requires predicting, without actually measuring, the properties of various candidate surrogate mixtures to find one that best matches the properties of the target fuel. Pera and Knop [114,115] showed that H/C ratio, O/C ratio, LHV, molecular weight, RON, and MON could be calculated using simple linear molar blending rules. Morgan et al. [116] showed that non-linear blending rules more accurately predict RON and MON, and similar results have also been shown for ethanol blending with gasoline surrogates [117,118]. Physical properties, such as volatility characteristics (i.e., distillation curve), are more difficult to estimate because they are not additive. Slavinskaya et al. [119] and Huber et al. [33] have shown that the distillation characteristics of mixtures requires calculating vapor-liquid equilibrium. This can be achieved by selecting an appropriate equation of state and mixing rules for estimating the properties of mixtures. Similar thermo-transport models [120–124] have been shown to be useful for predicting gasoline droplet heating and evaporation characteristics and formulating surrogates. Ahmed et al. [125] and Abianeh et al. [126] later demonstrated that various estimation methods for target properties could be introduced into an optimization algorithm that formulates a surrogate capable of matching multiple target properties with a minimum of error.

In summary, this section offers a general outline for formulation of a surrogate mixture to match a gasoline fuel of interest. It is

imperative to first determine which physical and chemical properties should be chosen as target properties, as well as their relationship to the combustion technology and the operating conditions of interest. Once the target gasoline properties are selected, a surrogate fuel can be formulated from a mixture of palette components. The optimal mixture of components is best determined using a computational algorithm that assigns a weight to each target property and then solves an objective function to minimize the error against all the target properties. Subsequent sections will discuss experimental and computational studies performed on gasoline surrogate mixtures and relate them to investigations performed on real gasoline fuels.

3. Fundamental combustion experiments on gasoline and surrogate fuels

Gasoline fuels are primarily used in spark ignition engines and in advanced low-temperature combustion counterparts. Fuel combustion in internal combustion engines is complex and may comprise fuel injection, spray, vaporization, fuel–air mixing, heat and mass transfer, ignition and combustion. Targeted engine experiments may be carried out on real gasoline and proposed surrogate mixtures to assess how well the surrogate captures real fuel behavior, such as heat release rate, combustion phasing and emissions. Such experiments are typically performed at selected engine operating conditions, and therefore, may not cover the entire spectrum of practical scenarios to which the fuel will be subjected. Also, depending on the engine operating mode, the observed trends may be affected by physical as well as chemical properties of the real fuel and surrogate mixture. Lastly, engine experimental data cannot be directly used to develop and validate detailed chemical and physical models for the surrogate mixtures.

Fundamental combustion experiments carried out in well-designed chemical reactors and/or canonical flames may provide valuable data that can be used to (i) understand trends and comparisons among various fuels and fuel surrogates, (ii) build detailed chemical models to propose optimal surrogates, and (iii) describe fuel behavior over wide ranges of engine operating conditions. Such fundamental experiments may be able to decouple the physical and chemical aspects of fuel behavior and are ideal for understanding the effects of the chemical structure on fuel autoignition and emissions, for example. When the focus is solely on fuel chemistry, the experiments are designed so that chemical kinetic processes govern the fuel oxidation, while physical/mixing processes play a negligible role.

There are two key goals in performing and presenting fundamental combustion experiments on gasolines and surrogates: (a) to demonstrate, in well-controlled experimental conditions, that the surrogate matches the combustion behavior of the target gasoline, and (b) to provide data that can be used to develop and validate detailed chemical kinetic models of gasoline surrogates. If a surrogate successfully emulates, for example, the autoignition behavior of real fuel in a shock tube (ST) and a rapid compression machine (RCM), will such a surrogate also reproduce the knock timing or heat release rate of real fuel in an engine? The answer rests on two important points: the experimental conditions tested in ST / RCM must overlap with the engine operating conditions, and the ignition process in the engine must be dominated by fuel chemistry. In the first consideration, the temperatures (500–2000 K), pressures (1–60 bar) and equivalence ratios (0.2–4) covered in modern ST / RCM facilities do overlap appreciably with engine operating conditions. Secondly, the ignition process in HCCI engines, for example, is indeed dominated by fuel chemistry [127]. Likewise, the knock timing in SI engines is predominantly controlled by the autoignition behavior of the end gas, as illustrated in a recent review paper by Zhi et al. [128].

Researchers have developed and used a variety of fundamental experiments to understand the combustion chemistry of various fuels. Each reactor/experiment provides data on specific aspects of

the chemical kinetic behavior of the fuel, and each experimental apparatus has its *sweet spots* and its limitations. Therefore, data obtained from the so-called *ideal reactors* should not be universally categorized as ideal, and care must be exercised in using these data for building chemical kinetic models and for understanding fuel chemistry.

Before the literature data on gasoline and gasoline surrogates is presented, it is important to briefly describe the advantages and challenges associated with various kinds of fundamental devices in which these data are obtained. Specifically, the additional complexities faced when working with distillate fuels and fuel mixtures will be discussed and compared to single-component fuels.

3.1. Challenges of gasoline measurements

3.1.1. Ignition measurements in shock tubes

Fuel autoignition quality is critical in determining the operating regime of SI engines. This is typically measured in terms of the research and motor octane numbers (RON, MON), with the help of ASTM standard tests carried out in CFR engines. These octane numbers cannot be directly used to build or validate chemical kinetic models; however, it has previously been shown [112] that homogeneous ignition delay times may be correlated with the octane ratings. As an illustration of this relationship, Fig. 8 [113] plots ignition delay times as a function of RON and MON of a number of three-component TPRF (n-heptane / isooctane / toluene) fuels. It can be clearly seen that there is a strong correlation between RON/MON and homogeneous ignition delay times at the specific conditions chosen carefully by Mehl et al. [112].

The homogeneous ignition delay time (also known as the induction time) is defined as the time it takes for a homogeneous fuel/air mixture at a specific temperature and pressure to explode, resulting in rapid increase of temperature/pressure and heat release. Although ignition delay time is a global indicator of fuel oxidation behavior, it

is strongly influenced by the underlying elementary reactions, and thus it provides a very stringent target for kinetic model development and validation.

The shock tube stands as the ideal homogeneous batch reactor for measuring ignition delay times as a function of temperature, pressure and mixture fraction. A shock wave heats and pressurizes the fuel/air mixture almost instantly and the environment behind the reflected shock wave is adequately modeled as a zero-dimensional (homogeneous) reactor. Shock tubes have historically been used to measure high temperature ignition delay times, which tend to be of the order of a few microseconds to a couple of milliseconds. Over these times, the shock tubes behave almost ideally where the pressure behind the reflected shock waves remains nearly constant.

Some of the challenges encountered during the measurement of ignition delay times of gasoline fuels are examined here briefly.

a) Long ignition delay times: Most commercial gasolines have relatively high RON (91–97), and boosted engines are expected to utilize fuels with even higher octane ratings. The addition of ethanol and use of knock inhibitors (e.g., MTBE) results in high octane gasolines with relatively long ignition delay times, particularly at low temperatures and in the NTC region. It is very important to characterize the fuel reactivity at low temperatures and NTC to accurately describe the LTHR and ITHR, which are critical in the design of modern low-temperature combustion (LTC) engines.

Typically, shock tubes were used to measure only high temperature ignition delays, as accessible test times were limited to < 2 ms. Recently however, longer driver sections and driver gas tailoring have enabled much longer test times [2]. Although the driver gas tailoring theory is well-established [129], in practice, achieving long test times requires considerable effort and experimentation. Additionally, the gradual increase of pressure (dP/dt) behind reflected shock waves becomes significant when measuring long ignition delay times, particularly for small diameter shock tubes. It is very important to carefully characterize the dP/dt for each shock tube and provide the value for the specific experiments being reported. It should also be noted that dP/dt might not be the same for tailored and non-tailored experiments. Fig. 9 shows that long test times may be achieved by adding N_2 or CO_2 to He in the driver section of the shock tube. Sometimes a buffer gas [4] must be added between the driver and driven gases to avoid pressure bumps at the contact surface. Varying compositions of driver gases and buffer gas are needed for specific test times and temperatures. It can be very difficult to avoid over- or under-tailoring, as demonstrated in Fig. 9b, by the contact surface expansion.

Finally, it has recently been observed that shock tube ignition delay data might be affected by pre-ignition and flame propagation over long test times [130]. Fig. 10 shows various ignition types observed for low temperature oxidation of n-hexane and n-heptane. The intermediate temperature cases (Fig. 10b) show a marked, gradual rise of pressure, reminiscent of flame propagation, before the main ignition event. Such pre-ignition energy release can artificially shorten the otherwise homogeneous ignition delay times; therefore, care must be exercised in using long ignition delay shock tube data which might be shortened by non-ideal effects such as the dP/dt and the pre-ignition.

b) Fuel vaporization: Since gasoline fuel is comprised of hundreds of compounds with varying boiling points, it is important to have an efficient strategy for fuel vaporization. The liquid fuel should be injected into a heated chamber, such as a mixing vessel, where the temperature of the vessel is high enough to ensure vaporization of all gasoline components. Depending on the high carbon content of the gasoline and aromatic fraction, a vessel temperature in the range of 80–150 C might suffice. Fuel

Fig. 8. Calculated ignition delay times for stoichiometric TPRF/air mixtures versus RON and MON at (a) 835 K and 20 bar, (b) 825 K and 20 bar. Figure adapted from Badra et al. [113] with permission from Elsevier Publishing.

Fig. 9. Demonstration of long test times in the low pressure shock tube facility at KAUST (diameter: 14 cm, driver length: 9.1 m, driven length: 9.1 m). Figure adopted from Tamour Javed PhD Thesis [131].

vaporization may be verified by sampling fuel from the mixing vessel and comparing the GC (gas chromatograph) spectrum with that of the liquid fuel. At these high mixing temperatures, there is a small but finite likelihood that some fuel components could undergo decomposition. This can also be checked by sampling the fuel mixture from the mixing vessel at varying residence times. Lastly, the heavy fuel components could condense if there are any cold spots within the mixing vessel or mixing manifold, or the (usually long) line connecting the vessel with the shock tube driven section. Some molecules can also adsorb to metallic surfaces. Passivating the vessel and shock tube walls with the fuel can help reduce adsorption losses. Fuel loss by condensation or adsorption may be quantified either with a laser absorption diagnostic (e.g., using a 3.39 μm HeNe laser in the shock tube), or by sampling the fuel mixture from the shock tube and running GC or FTIR (Fourier Transform Infrared Spectrometer) tests.

- c) *Thermodynamic properties:* The calculation of reflected shock temperature and pressure necessitates the measurement of incident shock velocity and knowledge of the thermodynamic properties of the fuel mixture. This requires knowing the detailed composition (DHA: detailed hydrocarbon analysis) of the gasoline. Thereafter, a thermodynamic surrogate that mimics the thermal properties of the gasoline can be set up.
- d) *Compositional changes:* It is well known that gasoline fuels may undergo compositional changes if stored for long periods and/or improperly stored. For example, if the container is not sealed well, some of the lighter components may evaporate. Over a long storage period, oxygen reactions in the head space of the storage container may also degrade the gasoline. Whenever possible, it is best to store the fuel in refrigerated

conditions. Compositional analysis of the fuel should be performed at the time of procurement/production and at the time of experimental usage to determine if there have been changes to the composition.

3.1.2. Ignition measurements in rapid compression machines

Rapid compression machines (RCMs) are generally used to measure long ignition delay times which are not accessible by shock tubes. This is particularly important for high octane gasolines where ignition delay times may exceed 5 ms for initial temperatures lower than ~ 900 K for initial pressures ranging 10–20 bar. Therefore, to effectively study the fuel NTC behavior, the RCM ignition delay data play a critical role. Also, the differences among various fuels are amplified in the NTC and low-temperature regions.

The challenges encountered in RCM measurements of gasoline ignition delay times are very similar to those mentioned for shock tubes. Some additional considerations are as follows:

- a) As a general rule, it is not advisable to use RCMs for measuring ignition delay times less than ~ 5 ms. This is because, for such relatively short ignition delay times, considerable chemical reactions occur during the piston compression phase. Although the compression stroke can be modeled during reactive simulations, as illustrated in Fig. 11, assigning a specific initial temperature to such ignition delay experiments becomes ambiguous.
- b) Fuel adsorption could be a bigger concern in RCM experiments as the combustion chamber has relatively high surface-to-volume ratio. Therefore, sampling of the fuel mixture from the RCM combustion chamber may be used to confirm the fuel/air mixture composition.

Fig. 10. Various types of pressure profiles (energy release patterns) observed during shock tube ignition delay time measurements. (a–c) are for 2% n-heptane/44% O₂/Ar and (d) is for 5% n-hexane/47.5% O₂/Ar. Figure adopted from Javed et al. [132] with permission from Taylor & Francis.

c) Reactive simulations of RCM ignition delay experiments for gasoline fuels are performed using a chemical kinetic surrogate. Thermal properties of the kinetic surrogate may be different than thermal properties of the real fuel, or an adequate thermal surrogate of the fuel. This would result in a different end-of-

compression (EOC) temperature than is experimentally observed. The optimal solution would be a surrogate that matches both the thermodynamic and kinetic behavior of the real fuel.

- d) For RCM experiments, EOC temperatures can be varied by changing the initial temperature and/or the composition of the bath gas by mixing N₂ with Ar or CO₂. Variation in bath gas composition may affect third body reaction rates, which should be modeled carefully while simulating RCM experiments.
- e) Due to the long test times accessible with RCMs, it is possible to differentiate various fuels in the NTC and low-temperature regions. However, it should be considered that ignition can potentially start in the cold boundary layer, particularly when measuring ignition delay times in the NTC region. This behavior may be detected by analyzing the pressure traces carefully for evidence of pre-ignition and flame propagation prior to the bulk homogeneous ignition.
- f) Heat transfer losses in rapid compression machines are modeled by employing a varying volume time-history derived from non-reactive pressure trace measurement. This approach works reasonably well for single stage ignition. For two-stage ignition phenomenon, heat release during the first stage may alter the overall heat loss characteristics considerably over those modeled using non-reactive experiments. For example, this could result in over-prediction of ignition delay times compared to

Fig. 11. Effect of compression stroke on the first stage and overall ignition delay time. Open symbols represent reactive calculations performed considering the RCM compression stroke. Solid line simulation is obtained by initializing the reactive calculations at the end of compression stroke. Figure adopted from Sung and Curran [133] with permission from Elsevier Publishing.

Fig. 12. Temperature measurement in a rapid compression machine using chirped-laser absorption spectroscopy. Simulated temperature is obtained by running a zero-dimensional reactive simulation. $P_c = 9.21$ bar, $T_c = 742$ K, 2.56% n-pentane/20.46% O_2 /75.98% N_2 /1%CO. Figure adopted from Nasir and Farooq [134] with permission from Elsevier Publishing.

the measured data. Nasir and Farooq [134] presented a novel temperature measurement in a rapid compression machine (Fig. 12). The temperature measured by laser absorption for first stage heat release was lower than predicted by the zero-dimensional simulation. The higher predicted temperature during the first stage also expedited the second stage ignition in the simulation. Among various solutions proposed to model two-stage ignition, simulating the two-stage ignition process with a multi-zone model provided a good compromise compared to full CFD simulation [135]. However, such multi-zone models are not universal and must be adjusted to the specific RCM; also, multi-zone models increase computational cost significantly compared to the zero-dimensional kinetic simulations.

- g) Finally, it should be mentioned that RCMs used in the literature vary in their design and geometry; heat loss characteristics and crevice confinement are very different from one machine to another. This makes comparison of ignition delay data across various machines difficult. Meaningful comparisons can only be made with the help of simulations that consider respective heat losses in individual machines.

3.1.3. Flame speed measurements

Flame speed is critical to modeling flame propagation in SI engines and is an important validation goal for the high-temperature chemical kinetic mechanism. Although the flame propagation in real engines is turbulent, laminar flame speed measurements in ideal reactors provide the data needed to constrain the reaction models. It is important to understand flame speed variation as a function of equivalence ratio, initial temperature and initial pressure. Various kinds of reactors/apparatus are used for flame speed measurements.

The challenges encountered during flame speed measurements of gasoline fuels are somewhat dependent on the experimental methodology used for flame speed determination. The reader is referred to a recent review by Egolfopoulos et al. [136] in which the challenges and uncertainties associated with various laminar flame experiments are exhaustively discussed. Some pertinent points are mentioned below:

- a) In general, adequate fuel vaporization is important for liquid fuels, and particularly for multi-component liquid fuels such as gasoline. For example, it is important to use heated tube between the evaporator and the burner; Sileghem et al. [137] reported that fuel condensation in non-heated tubes can lead to over-estimation of burning velocities, particularly for rich mixtures. On the other hand, over-heating of the fuel stream, or hot

spots, can lead to premature fuel decomposition, especially for large molecules.

- b) Liquid fuels are usually introduced via syringe pumps, or liquid flow regulators, which must be properly calibrated and should have dependable accuracy to avoid serious uncertainties in the equivalence ratio. This is usually not an issue for gaseous fuels as the mass flow controllers tend to be of greater accuracy.
- c) For stagnation flames, such as the counterflow configuration, discrepancies exist in the extrapolation of measured flame speed to zero strain rate (K) using either linear or non-linear extrapolation methods (these uncertainties tend to be bigger for larger molecules relevant to gasoline surrogates [136]). These issues arise from differential diffusion effects for mixtures of large molecular weight fuels, particularly under rich conditions.
- d) For spherically expanding flames, partial pressure methodology is used to fill the chamber for each experimental run. It is very important that pressure transducers of appropriate range are used and that these transducers are well-calibrated. For multi-component liquid fuels, as discussed earlier, the heating and vaporization requirements can be quite stringent and care must be taken to avoid hot/cold spots. It may also be advisable to sample the reactant mixture and confirm the composition by GC/MS techniques. Finally, issues similar to the extrapolation complexities in stagnation flames also affect data interpretation from spherically expanding flames.
- e) The heat-flux method provides an advantage in that the flame speed is obtained via interpolation rather than extrapolation. However, this method is also affected by several uncertainties such as boundary conditions at the burner surface, flame instability, flame-wall interactions leading to loss of radicals, temperature and flow velocity measurements.

3.1.4. Speciation with jet-stirred reactors and low-pressure flames

A jet-stirred reactor (JSR) and/or low-pressure flame, coupled with GC-MS, FTIR or TOF-MS may be used to measure intermediate species and products of fuel oxidation. Such speciation data are useful for validating the detailed chemistry of the surrogate models being developed for the gasoline. Recently, there have been wide-ranging studies utilizing synchrotron-based vacuum ultraviolet (UV) photon ionization; this methodology has resulted in a wealth of valuable speciation data which have greatly increased understanding of intermediate fuel chemistry. Some key experimental speciation challenges are discussed briefly:

- a) Similar to other fundamental combustion experiments on gasoline fuels, adequate vaporization and avoidance of fuel condensation is very important, particularly for gasolines with a relatively high boiling point.
- b) For low-pressure flames, measurement of flame temperature as a function of height above the burner is critical for the usefulness of the data. Thermocouples [138], laser-induced fluorescence (LIF) [139] and laser absorption methods [140] have been utilized to measure the flame temperature profile. However, all of these methods have inherent uncertainties and limitations, and the uncertainties on the measured temperature lead to challenges in adequately modeling the speciation data.
- c) A sampling probe may lead to significant distortions and non-idealities in the otherwise unperturbed flame. These non-idealities and uncertainties were addressed previously [136,141,142], and must be taken into consideration when using speciation data for model development and validation.
- d) Additional challenges arise during the analyses of the raw experimental data. The intermediates/products are formed from various gasoline components and are quite complex. Also, the peaks of the fuel components and their fragments interfere with

analysis of the intermediates/products. The uncertainty of product quantification becomes greater compared with single-component fuel speciation experiments.

3.2. Fundamental combustion experiment literature

3.2.1. Autoignition studies in shock tubes and rapid compression machines

Despite the importance and practical implications of gasoline fuels, ignition delay time measurements of distillate gasolines are scarce in the literature. Primarily, three types of gasoline fuels have been studied in homogeneous reactors of shock tube and rapid compression machines. RD387 gasoline was used in several previous studies [15,143,144], and represents the non-oxygenated, regular grade gasoline used in the U.S. with an average octane number, $(RON + MON)/2$, of 87 and an H/C ratio of 1.85. Two recent studies [145,146] have used oxygenated RON 95 gasolines. The third type of gasoline fuels being investigated are the FACE (fuels for advanced combustion engines) gasolines.

One of the first ignition delay time studies on distillate gasoline (RD387) was carried out by Gauthier et al. [143]. Ignition delay times were measured behind reflected shock waves over a broad range of conditions; 15–60 bar, 900–1300 K, 0.5–2.1 ϕ . The effect of exhaust gas recirculation (EGR) on ignition delay times was also examined by adding 20–30% of synthetic EGR mixture composed of CO_2 , H_2O , O_2 and N_2 . The entire NTC behavior was not observed due to the lack of experimental data at lower temperatures, which would have required longer shock tube test times. An interesting feature of the work was the comparison of the gasoline ignition delay times with experimentally measured ignition delays of two ternary surrogates of n-heptane/isooctane/toluene. The surrogates and the gasoline matched well over the experimental conditions of their study, as shown in Fig. 13. However, the differences between surrogates and real fuels are expected to be pronounced at lower temperatures, which were not covered in the work of Gauthier et al. [143]. A curious feature of the work was the use of two surrogates which matched in their volumetric and molar fractions, respectively. We hypothesize that the authors' goal was to match the gasoline composition in molar ratios of 63/20/17% (surrogate B) for isooctane/toluene/n-heptane, but made the surrogate in volumetric 63/20/17% fractions (surrogate A) in error.

The lack of low-temperature data in the work of Gauthier et al. [143] motivated Kukkadapu et al. [144,147,148] to study RD387 autoignition in a rapid compression machine over 650–900 K and

Fig. 13. Ignition delay times of RD387 gasoline and two TPRF surrogates (A and B). $P = 45$ –60 bar. Solid line represents quadratic fit to gasoline data. Figure adopted from [143] with permission from Elsevier Publishing.

pressures of 20 and 40 bar. The RD387 used in this study had a slightly different H/C ratio of 1.87, but similar values of RON (91) and sensitivity (8.3) as the RD387 used by Gauthier et al. [143]. As seen in Fig. 14, the RCM measurements clearly showed the NTC behavior for gasoline ignition, which was not apparent in the shock tube study of Gauthier et al. [143]. Another important contribution of the RCM study was the measurement of first-stage ignition delays in addition to the overall (or total) ignition delay. The first-stage ignition delays are highly valuable for understanding and predicting the fuel reactivity in the NTC and low-temperature regions. Through their RCM measurements, Kukkadapu et al. [144,147,148] found that the ternary surrogate of n-heptane/isooctane/toluene proposed in the work of Gauthier et al. [143] failed to capture the RD387 ignition at low temperatures. A newly proposed four-component surrogate [149] comprised of n-heptane / isooctane / toluene / 2-pentene agreed better with the measured ignition delay times of the gasoline. Although Kukkadapu et al. [144,147,148] demonstrated the importance of multi-component surrogates for capturing low temperature autoignition behavior of gasoline fuels, it was not possible to generalize these results as their work focused only on one specific gasoline. Also, despite the better performance of the four-component surrogate, some disagreements with the gasoline ignition were still observed at lean fuel conditions in the rapid compression machine.

Fig. 14. Total and first-stage ignition delay times of RD387 gasoline measured in a rapid compression machine at $P_c = 20$ bar. Figure adopted from [144] with permission from Elsevier Publishing.

Chung et al. [145] focused on the two-stage ignition behavior while studying the autoignition of a RON 95 gasoline in a rapid compression machine. Pressure time-history profiles and ignition delay times of the gasoline were compared with pure components (isooctane, n-heptane, 1-heptene, 2-heptene, 3-heptene) as well as surrogate mixtures comprised of three components (n-heptane, isooctane, toluene) and seven components (n-heptane, isooctane, cyclohexane, toluene, cyclohexene, 1,3-cyclohexadiene, ethanol). It was argued that addition of cyclic alkenes to the surrogate mixture is important in emulating first stage and total ignition delay behavior of the gasoline.

Agbro et al. [146] recently studied the influence of 20% n-butanol addition to the autoignition of a reference RON 95 gasoline in a rapid compression machine at 20 bar and 678–858 K. The addition of n-butanol resulted in longer ignition delay times at the low temperatures of the study, as expected. However, at temperatures higher than 800 K, the gasoline/n-butanol blend exhibited slightly shorter ignition delay times than pure gasoline. Suitably formulated TPRF and TPRF/n-butanol surrogates were also tested experimentally and these, respectively, reproduced the autoignition behavior of gasoline and gasoline/n-butanol blend reasonably well.

Several autoignition studies of FACE gasolines have been carried out at KAUST, with collaborative contributions from various laboratories around the world. As discussed earlier, FACE gasolines comprise fuels with varying RON, MON, sensitivity and chemical composition; therefore, the use of these widely different gasolines can provide the data and knowledge needed to formulate a generalized surrogate formulation strategy.

The first autoignition study on FACE gasolines was carried out by Sarathy et al. [150] on FACE A and C, having similar octane numbers (RON and MON ~84) but varying compositions. It was shown that both gasolines exhibited comparable ignition delay times over the wide range of experimental conditions (715–1500 K, 10–40 bar, $\phi = 0.5$ and 1), and a PRF surrogate adequately captured the ignition requirements of these gasolines. Five- and six-component surrogates for FACE A and C, respectively, were formulated in this work, based on the DHA (detailed hydrocarbon analysis) of the two gasolines. These multi-component surrogates provided slightly better agreement than the PRF surrogate at the very low temperatures of the study.

Sarathy et al. [58] recently studied the autoignition and surrogate formulation for two high octane FACE gasolines, F and G. These two gasolines had very similar antiknock indices, $(RON + MON)/2$, of 91.6 and 91.3. Apart from compositional differences, the two fuels had different octane sensitivities (FACE F: RON = 94.4, S = 5.6; FACE G: RON = 96.8, S = 11). Ignition delay time measurements in shock tube and rapid compression machine showed that both gasolines were equally reactive at high temperatures ($T > 900$ K). At low temperatures, FACE F having lower RON was slightly more reactive than FACE G. On the other hand, FACE F having lower octane sensitivity displayed greater NTC behavior than FACE G. Experiments performed in the rapid compression machine also revealed the decrease of low-temperature heat release (LTHR) and increase of intermediate-temperature heat release (ITHR) with increasing octane sensitivity. These experimentally observed trends are shown in Fig. 15. It can also be clearly seen that FACE A and C, having RON of 84, have shorter ignition delay times in the NTC region and at low temperatures. Experimental ignition delay times were compared against two-component PRF, ternary TPRF, and multi-component surrogates. Autoignition of low-sensitivity (S = 5.6) FACE F was captured equally well by all three surrogate types; however, only the multi-component surrogate performed well in reproducing the ignition behavior of high-sensitivity (S = 11) FACE G gasoline.

Javed et al. [151] recently carried out a shock tube and rapid compression machine ignition delay study on two low octane gasolines, FACE I and J, over 650–1200 K, 20–40 bar and $\phi = 0.5$ and 1. These

two gasolines have similar AKI of ~70 and similar octane sensitivities of < 3. However, their compositions are quite different: FACE I being primarily paraffinic while FACE J contains about 30% (by mole) aromatics. The two fuels exhibited very similar ignition delay times over the wide range of experimental conditions. Experiments and simulations performed with PRF and multi-component surrogates showed that a PRF surrogate can adequately capture the reactivity of both gasolines, with the PRF surrogate being slightly more reactive at the low temperature conditions of the rapid compression machine.

Relevant to these low octane FACE gasolines are two recent studies carried out on Saudi Aramco light naphtha (RON = 64.5, MON = 63.5) and Haltermann straight run naphtha (RON = 60, MON = 58.3). Javed et al. [152] and AlAbbad et al. [153a] measured ignition delay times of these naphtha fuels in a shock tube and rapid compression machine over a wide range of experimental conditions. They also carried out experimental measurements of PRF and multi-component surrogates for the two fuels. It was shown that PRF surrogates adequately captured the naphtha reactivity at high temperatures and in the NTC region. However, the PRF surrogates were more reactive at low temperature conditions, the differences being greater for higher fuel concentration cases ($\phi = 1$ and 2). Multi-component surrogates, formulated by matching the fuel octane numbers, H/C ratio, carbon type and distillation curve, reproduced the fuel ignition behavior over the entire range of temperatures, as shown in Fig. 16.

Finally, Lee et al. [154] recently carried out a detailed study on the autoignition of two oxygenated certified gasolines, supplied by Haltermann (RON = 91, MON = 83.4, ethanol = 8 vol%) and Coryton (RON = 97.5, MON = 86.6, ethanol = 4 vol%). Experiments were performed over 650–1250 K, pressures of 10–40 bar and equivalence ratios of 0.45, 0.9 and 1.8. Fig. 17 shows that both gasolines exhibited similar ignition delay times at high temperatures ($T > 900$ K). At intermediate temperatures, the Haltermann gasoline, having lower RON and lower sensitivity, exhibited higher reactivity and greater NTC behavior than the Coryton gasolines. At the very low temperatures ($T < 700$ K), both fuels again exhibited similar ignition delay times. The differences between the two gasolines were more pronounced at lower pressures and higher equivalence ratios. Three different types of surrogates were formulated for each gasoline. These included three-component TPRF surrogates, four-component TPRF/ethanol surrogates and eight-component surrogates. Surrogate performance was analyzed using detailed chemical kinetic simulations and partial experimental ignition delay measurements of the surrogates. At low temperatures, the TPRF surrogates were much less reactive than their corresponding gasolines. On the other hand, both four-component and eight-component surrogates adequately captured the ignition delay times of oxygenated gasolines over the wide range of experimental conditions.

Fig. 18 plots ignition delay times of eight gasoline fuels at initial pressure of 20 bar and a range of initial temperatures. Several interesting trends may be observed. At high temperatures, all gasolines have almost identical ignition delay times. The NTC region clearly manifests the dependence of ignition delay times on RON and sensitivity (RON – MON). The two low-octane FACE fuels, I and J, have the lowest ignition delay times in the NTC region. The two mid-octane FACE fuels, A and C, have longer ignition delay times. Finally, the high-octane gasolines (FACE F and G, Coryton and Haltermann) have the longest ignition delay times in the NTC region. These fuels also exhibit slower reactivity at the very low temperatures. Coryton and FACE G have the highest sensitivity (~ 11) among the high octane fuels and thus exhibit relatively less NTC behavior. On the other hand, FACE F has the lowest sensitivity (5.6) among this group of high-octane fuels and thus exhibits the steepest NTC character.

Apart from the handful of studies devoted to real gasoline fuels, there have been a relatively large number of experimental autoignition studies carried out on gasoline surrogates. These include studies

Fig. 15. - Ignition delay times of FACE F and G measured in a rapid compression machine. Figure adopted from [58] with permission from Elsevier Publishing.

on PRFs [34,155–157], TPRFs [158–160], n-heptane/toluene [40,161,162], isooctane/toluene [41,161], ethanol blends [163–165], and other multi-component blends [45,161,164,166–168]. These references and the relevant experimental details are listed in Table 3. These studies on gasoline surrogates have been very helpful in validating the chemical kinetic mechanisms of multi-component surrogate mixtures.

3.2.2. Laminar flame speed studies

Similar to ignition delay times, flame speed measurements of distillate gasolines are limited in the literature. One of the first measurements of gasoline flame speed were performed by Zhao et al. [169] on a research gasoline (CR-87) having an octane number of 87. Experiments were performed using the stagnation jet-wall flame configuration and particle image velocimetry (PIV), where laminar burning velocity was obtained by linear extrapolation of stretched flame speed to zero stretch speed. Measurements were carried out over a range of equivalence ratios (0.6–1.4), atmospheric pressure and initial temperatures of 353 K and 500 K. Comparison of the measured data with previous PRF 90 laminar speeds showed that PRF could serve as a suitable surrogate for laminar flame speeds of CR-87 gasoline.

Jerzembeck et al. [170] measured laminar burning velocities of a commercial gasoline and a PRF 87 surrogate using the constant volume bomb and Schlieren method. The authors did not provide specifications for the gasoline; however, from comparisons with the PRF 87 surrogate, it may be assumed to have a RON of 87. Flame speeds were measured at initial temperature of 373 K, equivalence ratios ranging 0.7–1.2 and initial pressures ranging 10–25 bar. Overall, the results showed that PRF 87 can capture the burning velocities of the gasoline over the range of experimental conditions, with some deviations at rich conditions. A reduced high temperature PRF mechanism was also shown to perform satisfactorily for predicting laminar flame speeds.

Tian et al. [171] measured laminar burning velocities of European EN 228 gasoline (RON > 95) and compared the gasoline data with ethanol and 2,5-dimethyl furan (DMF) as alternative candidate fuels. These measurements were performed in a constant volume vessel using high speed Schlieren visualization. Experimental conditions spanned equivalence ratios of 0.6–2.0 and initial temperatures of 323–373 K. As seen in Fig. 19, burning velocities of DMF matched with those of gasoline within 10%; while ethanol burning velocities were larger by ~30–40%. Similar work performed by Dirrenberger et al. [172], using the heat flux method, showed that the burning velocities of a commercial

Fig. 16. Measured (symbols) and simulated (lines) ignition delay times of light naphtha. Solid lines represent simulations performed using a five-component surrogate. Dashed lines represent simulations performed with a two-component PRF 64.5 surrogate. Figure adopted from [152] with permission from Elsevier Publishing.

Fig. 17. Ignition delay times of Coryton gasoline (black) and Haltermann gasoline (red). Filled points are shock tube and open points from RCM. Figure adopted from Lee et al. [154] with permission from Elsevier Publishing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

oxygenated gasoline TAE7000 (RON $\sim$ 95.6) matched very well with a three-component TPRF (toluene/n-heptane/isooctane) surrogate over a wide range of equivalence ratios and initial temperature of 358 K. They also showed that up to 15% of ethanol

Fig. 18. Ignition delay times of various gasoline fuels measured in shock tube and rapid compression machine. (Fuel name followed by RON).

addition to the gasoline had negligible influence on the burning velocities.

Sileghem et al. [137] utilized the heat flux method to report laminar burning velocities of a commercial non-oxygenated Exxon gasoline over equivalence ratios of 0.7–1.3 and initial temperatures of 298–358 K. They formulated a three-component TPRF surrogate using the energy fraction mixing rule and showed that the surrogate matched the burning velocities of the gasoline very well over a wide range of initial temperatures and equivalence ratios, as illustrated in Fig. 20. Using the mixing rule, they also argued that a two-component PRF surrogate would only work well at lean conditions, and that toluene addition to the surrogate is necessary to emulate burning velocities of commercial gasolines containing many aromatic fractions.

Burning velocities of a wide range of ternary TPRF mixtures and three FACE gasolines J (RON = 70), C (RON = 85) and F (RON = 95) were investigated by Manna et al. [173] at elevated pressures up to 6 bar, initial temperatures of 358 K and equivalence ratios of 0.8–1.6. Similar to Sileghem et al. [137], they showed that PRF surrogate can capture burning velocities of real gasoline only at lean conditions. For each gasoline, Manna et al. [173] formulated three-component TPRF surrogates to capture burning velocities over the wide range of their experimental conditions. In a later work, Manna et al. [174] studied the influence of ethanol addition (60 and 85 vol%) to FACE C gasoline and its TPRF surrogate. They concluded that burning velocity enhancement from ethanol addition was similar in both the gasoline and TPRF surrogate.

Fig. 21 compares laminar burning velocities of gasoline fuels reported in various studies. These gasolines had varying RON and compositions. However, it may be argued that laminar burning velocities are more sensitive to gasoline composition and are negligibly affected by the RON. For example, the higher velocities measured by Dirrenberger et al. [172] may be attributed to the presence of oxygenates in the gasoline used in that study, but the non-availability of detailed composition (DHA) makes it difficult to compare burning velocities of different gasolines.

There have been several studies of laminar burning velocities on gasoline surrogate mixtures, such as PRFs [175–178], TPRFs [174,178], ethanol blends [177–179], and butanol blends [180,181]. These are listed in Table 3 and serve as benchmark studies for validating high-temperature kinetic mechanisms of multi-component mixtures.

3.2.3. Speciation studies of gasoline oxidation

Ignition delay times and laminar burning velocities are important global targets for the development and validation of chemical kinetic models of gasoline surrogates. However, time/space-resolved measurements of combustion species (radicals, intermediates, products) can provide stringent targets for model validation. Such measurements have historically been performed for pure components and simple mixtures. Very few studies have measured species' profiles for distillate gasolines.

Chen et al. carried out a detailed speciation study on FACE A and C [182] and F [183] gasolines in a jet-stirred reactor (JSR) from high to low temperatures, pressure of 10 bar and equivalence ratios ranging 0.5–2. Combustion species were sampled with a probe and analyzed using gas chromatography (GC) and Fourier transform infrared spectroscopy (FTIR). Measured species' profiles were compared with simulations using a simple PRF surrogate and two multi-component surrogates. As seen in Fig. 22, the simulated profiles from the three surrogates for FACE A and C are similar and do a reasonably good job of capturing the overall gasoline reactivity and two-stage oxidation behavior. Some disagreement was observed in the prediction of ethylene and propene, which may be attributed to the detailed chemistry of these alkenes.

Table 3

Fundamental experimental studies of gasoline and gasoline surrogates.

Reference	Fuels	Experimental device	T, P, mixture fraction
Ignition Delay Time Studies			
Gauthier et al. [143]	Gasoline RD 387, TPRF surrogates	Shock tube	850–1280 K, 15–25 and 45–60 bar
Kukkadapu et al. [144]	Gasoline RD 387	Rapid compression machine	647–955 K, 20 and 40 bar
Kukkadapu et al. [147]	Gasoline RD 387, TPRF surrogate, 4-component surrogate	Rapid compression machine	650–900 K, 20 and 40 bar
Kukkadapu et al. [148]	TPRF surrogate, 4-component surrogate	Rapid compression machine	665–950 K, 20 and 40 bar
Chung et al. [145]	Gasoline 95, 3-component surrogate, 7-component surrogate	Rapid compression machine	670–1000 K, 25 bar
Agbro et al. [146]	Gasoline 95, Gasoline/butanol blend, TPRF surrogate, TPRF/butanol surrogate	Rapid compression machine	678–858 K, 20 bar
Sarathy et al. [150]	FACE A gasoline, FACE C gasoline, PRF surrogate	Shock tube, rapid compression machine	715–1500 K, 10, 20 and 40 bar
Sarathy et al. [58]	FACE F gasoline, FACE G gasoline	Shock tube, rapid compression machine	650–1270 K, 20 and 40 bar
Javed et al. [151]	FACE I gasoline, FACE J gasoline	Shock tube, rapid compression machine	650–1200 K, 20 and 40 bar
Javed et al. [152]	Light naphtha, PRF surrogate, 5-component surrogate	Shock tube, rapid compression machine	640–1250 K, 20 and 40 bar
AlAbbad et al. [153a]	Straight run naphtha, PRF surrogate, TPRF surrogate, 5-component surrogate	Shock tube, rapid compression machine	650–1250 K, 20 and 60 bar
Lee et al. [154]	Haltermann gasoline, Coryton gasoline, TPRF surrogate, 4-component surrogate, 8-component surrogate	Shock tube, rapid compression machine	650–1250 K, 10–40 bar
Vanhove et al. [161]	n-heptane/toluene, isooctane/toluene, isooctane/1-hexene, 1-hexene/toluene, isooctane/1-hexene/toluene	Rapid compression machine	600–900 K, 4–16 bar
Fieweger et al. [155]	PRF 60, PRF 80, PRF 90	Shock tube	700–1250 K, 40 bar
Callahan et al. [156]	PRF 90, PRF 95, PRF 100	Rapid compression machine, Flow reactor	600–900 K, 20 bar
Tanaka et al. [157]	PRF 50, PRF 75, PRF 90	Rapid compression machine	750–850 K, 40 bar
AlAbbad et al. [153b]	PRF 70, PRF 80, PRF 91, PRF 95	Shock tube	750–1250 K, 20 and 40 bar
Javed et al. [158]	TPRF 70, TPRF 80, TPRF 91, TPRF 97.5	Shock tube, rapid compression machine	750–1250 K, 20 and 40 bar
Li et al. [160]	TPRF 87, TPRF 95 blends	Shock tube	1100–1600 K, 10–20 bar
Cancino et al. [163]	ethanol/isooctane, ethanol/isooctane/toluene/n-heptane/diisobutylene	Shock tube	720–1220 K, 10–30 bar
Fikri et al. [164]	n-heptane/isooctane/ ethanol, n-heptane /toluene /isooctane /diisobutylene	Shock tube	690–1200 K, 10–50 bar
Herzler et al. [162]	n-heptane/toluene	Shock tube	620–1180 K, 10–50 bar,
Cancino et al. [165]	ethanol/isooctane/n-heptane/toluene	Shock tube	690–1200 K, 10–50 bar
Hartmann et al. [208]	n-heptane/ toluene, isooctane/ toluene	Shock tube	700–1200 K, 40 bar
Zhang et al. [293]	n-heptane/ butanol	Shock tube	1200–1500 K, 2 and 10 bar
Yahyaoui et al. [166]	isooctane/toluene/1-hexene/ETBE	Shock tube,	1390–1880 K, 2–10 bar
Yahyaoui et al. [167]	1-hexene/toluene	Shock tube,	1360–1860 K, 2–10 bar
Sakai et al. [159]	n-heptane/isooctane/toluene	Shock tube	1200–1600 K, 2.5 bar
AlRamadan et al. [168]	2-butanol/tert-butanol, TPRF/2-butanol/tert-butanol	Shock tube	800–1200 K, 20 and 40 bar
Flame Speed Studies			
Zhao et al. [169]	CR-87 gasoline	Stagnation jet-wall flame	353 K and 500 K, 1 bar, $\phi = 0.6–1.4$
Jerzembeck et al. [170]	Commercial gasoline, PRF surrogate	Constant volume vessel	373 K, 10 and 25 bar, $\phi = 0.8–1.2$
Tian et al. [171]	EN228 gasoline, dimethyl furan, ethanol	Constant volume vessel	323 K and 373 K, 1 bar, $\phi = 0.6–2$
Dirrenberger et al. [172]	TAE7000 gasoline, TAE7000 + 15% ethanol, TPRF surrogate, 4-component surrogate	Perforated plate burner	358 K, 1 bar, $\phi = 0.6–1.6$
Sileghem et al. [137]	Exxon 708,629 gasoline, TPRF surrogate	Flat flame burner	298–358 K, 1 bar, $\phi = 0.7–1.3$
Mannaa et al. [173]	FACE C gasoline, FACE F gasoline, FACE J gasoline, PRF surrogates, TPRF surrogates	Constant volume vessel	358 K, 1–6 bar, $\phi = 0.8–1.6$
Mannaa et al. [174]	FACE C gasoline, FACE C gasoline + ethanol, TPRF surrogates, four-component surrogates	Constant volume vessel	358 K, 1–6 bar, $\phi = 0.8–1.6$
Huang et al. [175]	PRF 0, PRF 85, PRF 90, PRF 95, PRF 100	Counter flow burner	298 K, 1 bar, $\phi = 0.7–1.4$
Liao et al. [178]	PRF 85, PRF 90, PRF 95, TPRF blends, ethanol/isooctane/n-heptane blends	Flat flame burner	298–400 K, 1 bar, $\phi = 0.8–1.3$
Bradley et al. [176]	PRF 90	Constant volume vessel	358 and 450 K, 1–10 bar, $\phi = 0.8$ and 1
van Lipzig et al. [177]	n-heptane/isooctane, n-heptane/ethanol, isooctane/ethanol, n-heptane/isooctane/ethanol	Perforated plate burner	298 and 338 K, 1 bar, $\phi = 0.6–1.3$
Gülder et al. [179]	isooctane/ethanol	Constant volume vessel	350–600 K, 1 bar, $\phi = 0.75–1.4$
Broustail et al. [180]	Butanol/isooctane, ethanol/isooctane	Constant volume vessel	350 K, 1 bar, $\phi = 0.8–1.4$
Broustail et al. [181]	Butanol/isooctane, ethanol/isooctane	Constant volume vessel	423 K, 1–10 bar, $\phi = 0.7–1.4$
Speciation Studies			
Chen et al. [182]	FACE A gasoline, FACE C gasoline	Jet-stirred reactor	530–1250 K, 10 bar, $\phi = 0.5–2$ (183 is Bingjie et al.)
Chen et al. [183]	FACE F gasoline	Jet-stirred reactor	530–1250 K, 10 bar, $\phi = 0.5–2$
Selim et al. [184,185]	FACE A gasoline, FACE C gasoline, PF 84	Low-pressure laminar burner	20 Torr, $\phi = 1$
Javed et al. [186]	FACE A gasoline, FACE C gasoline, PRF 84	Shock tube	1350–1550 K, 2 bar, $\phi = 1$
Yahyaoui et al. [166]	isooctane/toluene/1-hexene/ETBE	Jet-stirred reactor	750–1200 K, 10 bar, $\phi = 1$
Yahyaoui et al. [167]	1-hexene/toluene	Jet-stirred reactor	750–1170 K, 10 bar, $\phi = 0.5–1.5$
Dagaut et al. [190]	1-butanol/isooctane/toluene/1-hexene	Jet-stirred reactor	770–1220 K, 10 bar, $\phi = 0.3–2$
Dagaut et al. [191]	Ethanol/isooctane/toluene/ 1-hexene	Jet-stirred reactor	770–1220 K, 10 bar, $\phi = 0.3–2$
Dagaut et al. [193]	n-heptane/MTBE, n-heptane/ETBE	Jet-stirred reactor	570–1150 K, 10 bar, $\phi = 1$
Dagaut et al. [187]	PRF10, PRF 50, PRF 70, PRF 90	Jet-stirred reactor	550–1150 K, 10 bar, $\phi = 1$
Dagaut et al. [192]	ethanol/n-heptane	Jet-stirred reactor	530–1070 K, 10 bar, $\phi = 0.5$ and 1
Dubreuil et al. [188]	n-heptane/isooctane, n-heptane/toluene	Jet-stirred reactor	550–1000 K, 10 bar, $\phi = 0.2–0.7$
Wilke et al. [194]	n-heptane/alkenes, n-heptane/isooctane, n-heptane/MTBE	Flow reactor	570–920 K, 1 bar, $\phi = 1$

(continued)

Table 3 (Continued)

Reference	Fuels	Experimental device	T, P, mixture fraction
Lenhert et al. [195]	1-pentene/toluene/n-heptane/isooctane	Flow reactor	600–800 K, 8 bar, $\phi = 0.5-1$
Hori et al. [189]	n-heptane/toluene	Micro-flow reactor	300–1300 K, 1–5 bar
Togbe et al. [193]	Methanol/isooctane/toluene/1-hexene/	Jet-stirred reactor	770–1140 K, 10 bar, $\phi = 0.35-2$
Diffusion Flame Studies			
Marciq [198]	Gasoline, gasoline/ethanol blends	Coflow diffusion flame	1 bar
Khosousi et al. [199]	Gasoline, gasoline/ethanol blends	Coflow diffusion flame	1 bar
Lemaire et al. [200]	Gasoline, gasoline/ethanol blends, gasoline surrogate/ethanol blends	Turbulent spray flames	1 bar
Bieleveld et al. [201]	Gasoline 87, gasoline 91, PRF 87, PRF 91, n-heptane/isooctane/toluene/methylcyclohexane surrogate,	Counterflow diffusion flame	1 bar
Choi et al. [202]	n-heptane/isooctane, n-heptane/toluene, isooctane/toluene	Counterflow diffusion flame	1 bar
Kashif et al. [203]	n-heptane/toluene, isooctane/toluene	Coflow diffusion flame	1 bar

Fig. 19. Unstretched laminar flame speed at initial temperature of 323 K and initial pressure of 1 bar. Fig. adopted from [171] with permission from The American Chemical Society.

Selim et al. studied speciation of the same gasolines, FACE A and C [184], as well as PRF 84 [185], in a low-pressure (20 Torr) flame coupled to vacuum-ultraviolet synchrotron photoionization time-of-flight molecular beam mass spectrometry. The authors utilized a novel approach, comparing quantities of interest to discern the differences between the intermediate species profiles of both gasolines

Fig. 20. Laminar burning velocities of non-oxygenated Exxon gasoline and TRF (toluene/isooctane/n-heptane) at initial temperatures of 298, 318, 328, 338 and 358 K. Predictions of the energy fraction mixing rule are also shown. Figure adopted from Sileghem et al. [137] with permission from Elsevier Publishing.

and the chemical kinetic simulations of surrogate mixtures. In agreement with previous autoignition studies on FACE A and C [150], they concluded that PRF surrogates are suitable for capturing the detailed flame chemistry of alkane-rich gasolines.

Javed et al. [186] applied four simultaneous laser-based diagnostics in a shock tube study to measure species' profiles during the high temperature oxidation of FACE A, C and PRF 84 surrogate. As shown in Fig. 23, they observed that the two gasolines and their PRF surrogate produced very similar radical pool (OH), intermediate species (CO) and products (CO_2 , H_2O), thereby explaining their nearly identical ignition delay times at high temperatures.

There have been several speciation studies on gasoline surrogate mixtures, such as PRFs [186–188], n-heptane/toluene [188,189], alcohol blends [190–193], and other multi-component mixtures [72,166,167,194,195]. These are listed in Table 3 and serve as good targets for validating the detailed kinetic mechanisms of multi-component mixtures.

3.2.4. Gasoline surrogate studies in diffusion flames

Section 2 of this paper highlighted the role of fuel physical and chemical kinetic properties on PM (i.e., soot) formation in engines. For example, it was shown that the fuel volatility characteristics, aromatic content, oxygenate content, and antiknock quality all influence PM formation in engines. It is important for surrogate fuel simulations to emulate the soot formation characteristics of real fuels, in order to design gasoline engines with lower PM emissions. Soot in SI engines is typically formed due to insufficient fuel/air mixing or

Fig. 21. Comparison of gasoline burning velocities reported in various studies.

Fig. 22. Mole fractions (MF) of various species measured in a jet stirred reactor during the oxidation of FACE A and FACE C gasolines. Simulations by a PRF surrogate and two multi-component surrogates are also shown. Figure adopted from [182] with permission from Elsevier Publishing.

from fuel spray impinging on the wall and not completely vaporizing [196,197]. Both scenarios create rich pockets or diffusion flamelets where soot can be formed and not completely oxidized.

Diffusion flames are often used to study the tendency of a specific fuel to form soot particles. Since the addition of oxygenated species (such as ethanol) to hydrocarbons is expected to reduce soot formation, a few studies have been dedicated to carry out diffusion flame

experiments of gasoline and ethanol blends. Marciq [198] performed coflow flame experiments on E0 (pure gasoline), E20 (20% ethanol / 80% gasoline), E50 (50% ethanol / 50% gasoline) and E85 (85% ethanol / 15% gasoline). Soot size distribution was measured as a function of height above the burner using scanning mobility particle sizer (SMPS). It was found that the addition of up to 50% ethanol to gasoline had little effect on flame properties. The E20 and E50 flames

Fig. 23. Laser-based measurements of species' profiles during the oxidation of FACE A, FACE C gasolines and PRF 84 surrogate in a shock tube. Initial temperature is ~ 1450 K and initial pressure is 2 bar. Figure adopted from [186] with permission from Elsevier Publishing.

Fig. 24. Measured soot volume fraction distributions in the E0, E20, E50, and E85 flames. Peak soot volume fraction in each flame is indicated. Figure adopted from [199] with permission from Elsevier Publishing.

behaved almost the same as the E0 flame. However, the E85 flame resulted in 4–7 times reduction in nuclei mode mass and a reduction factor of about two in the size of soot agglomerates compared to the E0 flame.

Recently, Khosousi et al. [199] studied the same fuels as Marciq [198] in a similar configuration of coflow laminar diffusion flames. However, in contrast to Marciq [198], Khosousi et al. [199] heavily diluted the fuel stream with nitrogen to prevent the flames from smoking. They also measured radially-resolved soot volume fraction distributions by employing a two-dimensional line-of-sight attenuation (2D-LOSA) technique and an Abel inversion algorithm [199]. The measured volume fractions in Fig. 24 show decreasing amounts of soot with increasing ethanol fraction. However, the suppression of soot only becomes significant for 50% or more ethanol. A numerical model and gasoline surrogate proposed in the study predicted the experimentally observed trends.

Lemaire et al. [200] used a turbulent spray flame to study the influence of ethanol addition to gasoline on soot formation tendency. Spatially resolved measurements of soot volume fraction and polycyclic aromatic hydrocarbons (PAHS) were made by simultaneous applications of LII and LIF. They observed that 10–30% addition of ethanol to gasoline significantly reduced the concentration of soot precursors (PAH) and about 25–81% reduction in the total quantity of soot. Experiments performed with gasoline surrogates and surrogate/ethanol blends adequately reproduced the gasoline and gasoline/ethanol soot production trends. The results also indicated that the gasoline/ethanol soot oxidized faster than the pure gasoline soot.

Bieleveld et al. [201] employed a counterflow diffusion flame technique to study the extinction and autoignition of two gasolines (RON 87 and 91), PRF surrogates and multi-component surrogates comprising n-heptane / isooctane / toluene / methylcyclohexane. Experiments and calculations performed with a semi-detailed kinetic mechanism showed that the extinction/ignition characteristics of PRF 87 and PRF 91 were different from those of the corresponding gasolines. However, two multi-component surrogates were able to reproduce the combustion characteristics of the gasoline fuels. The results affirm that a simple PRF surrogate is not adequate to model the combustion and emission behavior of a fully blended gasoline.

Choi et al. [202] and Kashif et al. [203] utilized counterflow and coflow diffusion flames, respectively, to investigate sooting tendency of gasoline surrogates comprised of binary mixtures of n-heptane, isooctane and toluene.

A few other studies of gasoline and surrogates include the works of Liu et al. [204] on a RON 87 gasoline and blends of n-heptane/isooctane/toluene using sub-millimeter droplets, Farouk et al. [205] on PRF droplet burning, Baumgardner et al. [206] on PRF and n-heptane/n-butanol blends in a constant volume combustion device, and Naser et al. [207] on PRF and TRF (n-heptane/toluene) in an ignition quality tester.

3.2.5. Future experimental work

The literature presented demonstrates that there has been considerable work done on gasoline surrogate components and surrogate mixtures. However, research on gasoline fuels in fundamental combustion devices has been inadequate. Such work is necessary to build a sound basis for surrogate formulation strategies and kinetic mechanisms of gasoline surrogates. These experiments should encompass global reactivity data (ignition delay times, flame speeds, extinction, autoignition) as well as details of reactivity trends (species time-histories). The fuels chosen for experimentation should span a wide range of properties (RON, MON, H/C ratio, distillation range, oxygenation, composition) that would be expected in current and future energy conversion devices.

4. Chemical kinetic modeling of gasoline surrogate fuel combustion

The chemical kinetics of gasoline was previously discussed in the context of experimental work performed on surrogate mixtures and full boiling range refinery gasoline fuels. Numerical simulations can also aid understanding the effects of gasoline fuel composition on combustion properties and engine performance. These simulations rely on chemical kinetic models comprising a series of elementary reaction steps that describe the molecular-level transformations of reactants (i.e., fuel/air) to intermediate and product species, as well as thermal energy. Chemical kinetic models are capable of simulating reactions in the flame zone that result in heat release, the ignition characteristics of fuel/air mixtures, and the formation of major and minor pollutant species.

Gasoline fuels contain hundreds of different molecules, and developing such kinetic models for each individual component is unmanageable. Kinetic models are only available for surrogate fuel mixtures comprising a limited number of components. This section presents available chemical kinetic models for various pure hydrocarbon and oxygenated species that can be used in gasoline surrogate fuel mixtures. Kinetic models for surrogate mixtures are then presented, with insights into engine-relevant phenomenon that these models provide, such as flame propagation, engine knock, and pollutant formation mechanisms.

4.1. Chemical kinetic models for pure components

As described previously, gasoline fuel components can be divided into five main hydrocarbon classes (paraffins, isoparaffins, olefins, naphthenes, and aromatics) and oxygenates. The kinetic models for each individual component comprises a set reaction classes and rate coefficient estimations, which can be assigned manually or via automatic generation tools (e.g., NETGEN [209], EXGAS [210,211], Reaction Mechanism Generator [212–216], and Genesys [217]). The models are developed in a hierarchical manner because combustion proceeds via a series of elementary steps that fragments the parent fuel into smaller intermediate species, which subsequently react to form stable products. This concept is well represented by the Dooley et al.'s [218] schematic representation of real fuel combustion kinetic phenomena, as shown in Fig. 25. Complex fuels contain many chemical structures, but when burned, the intermediates produced contain much fewer distinct chemical functionalities. Reactions involving these chemical intermediates characterize the small

Fig. 25. Schematic by Dooley et al. [218] representing the high temperature combustion kinetics of complex fuel mixtures. It stresses the importance of smaller intermediate species in the combustion of larger hydrocarbons. Figure reproduced from [218] with permission from Elsevier Publishing.

species radical pool, which governs important combustion processes (e.g., ignition delay, flame propagation, emissions formation). The schematic highlights the importance of having a common high fidelity small molecule reaction mechanism (or “core mechanism”), on top of which the reaction mechanism for larger hydrocarbons can be developed. These core mechanisms typically include detailed and well validated reaction mechanisms for oxidation and pyrolysis of hydrogen and C_1 – C_4 hydrocarbon species. Popular core mechanisms for developing gasoline fuel surrogates models include NUI Galway's AramcoMech [219–222], Princeton Mechanism [223–226], San Diego Mechanism [227–229], Politecnico di Milano's CRECK mechanism [201,230], and Stanford's Foundational Fuel Chemistry Model (FFCM-1) [231]. The reactions for larger hydrocarbons are added to the core reaction mechanism. The following sub-sections summarize available kinetic models for larger hydrocarbons, which could be combined to create gasoline surrogate kinetic models.

Table 4 is an overview of the available kinetic models published since 2000. Table 4 presents information for various n-alkanes, isoalkanes, cycloalkanes, alkenes, aromatics, and oxygenated fuels that are typically found in gasoline. Molecular formula and boiling points are also presented for quick identification of surrogate components with desired physical properties. Table 4 focuses on comprehensive chemical kinetic models, which have been validated across a broad range of temperatures and pressures. Several comments on the validity range of the developed chemical kinetic models are given in Table 4. As clarified in the following section, the merging of hydrocarbon mechanisms requires a common core mechanism, so wherever possible, the core mechanism utilized in the model is highlighted.

4.1.1. Paraffins/n-Alkanes

n-Alkanes (or paraffins) are the most widely studied class of hydrocarbons in gasoline fuels. Previous significant reviews by

Simmie [232] and Battin-Leclerc [233] have highlighted many important aspects of n-alkane kinetic modeling. The fact that they have been widely studied, both experimentally and numerically, has resulted in high fidelity chemical kinetic models which are readily adopted into gasoline surrogate kinetic modeling studies. The high temperature oxidation kinetics of n-alkanes is well understood, as it is initiated by H-atom abstraction from the fuel, and typically followed by scission of the C–C bond β to the radical site (i.e., β -scission), as shown in the red box in, left panel. The resulting products are a smaller alkyl radical and an alkene, of which the former undergoes further β -scission, and the latter is consumed by H-atom abstraction. At very high temperatures (i.e., above 1250–1400 K) or in the absence of oxygen, reactivity is initiated by unimolecular decomposition of the fuel to form two alkyl radicals (i.e., pyrolytic C–C scission). Other important reactions include alkyl radical isomerizations, alkenyl radical decompositions, and retroene reactions. Detailed descriptions of the various high temperature reactions classes in n-alkane oxidation are presented in the literature [232,234,235].

In general, the high temperature oxidation mechanism controls engine-relevant phenomenon such as premixed laminar flame speed, premixed flame extinction, and high temperature ignition delay (i.e., above ~ 1000 K). An interesting observation is that the high temperature oxidation behavior of n-alkanes typically found in transportation fuels are remarkably similar. This is best exemplified by the work of Ji et al. [236], in which the authors experimentally studied the premixed laminar flame speeds and extinction strain rates for C_5 – C_{12} n-alkanes in air. The authors found that all n-alkanes larger than C_5 exhibit the same laminar flame speed and extinction strain rates, as shown in Fig. 26. The reason for the similarity is well captured by chemical kinetic models, and can be attributed to the fact that all large n-alkanes decompose at high temperatures to a similar pool of radical species (mainly H, CH_3 , C_2H_5 , and C_3H_7). The

Table 4

Comprehensive chemical kinetic models for various gasoline surrogate components published since 2000.

Molecule	Molecular Formula	MW (g/mol)	Boiling Point (K)	Reference, Year	# of Species and # of Reactions	Comments
n-butane	C4H10	58.12	272	Healy et al., 2010 [246]	238 species and 1328 reactions	Validated against ignition delay times from 690–1430 K, up to 45 bar, and various equivalence ratio
				Cord et al., 2012 [285]	NA	Validated against species profiles at 550–800 K, 1 bar and $\phi = 1$
iso-butane	C4H10	58.12	261	Healy et al., 2010 [286]	230 species and 1328 reactions	Validated against ignition delay times from 590–1567 K up to 30 bar and various equivalence ratios
n-pentane	C5H12	72.15	309	Bugler et al., 2016 [247,248]	NA	Validated against ignition delay times (ST and RCM) at 643–1718 K, up to 20 bar and various equivalence ratios
				Bugler et al., 2017 [287]	NA	Slight modifications on multi-oxygenated species. Validated against species profiles (JSR) at 500–1100 K up to 10 bar and various equivalence ratios
				Cai and Pitsch, 2014 [288]	107 species and 1135 reactions	Optimized model. Validated against ignition delay times at 600–1491 K and 1.9 bar (stoichiometric mixture)
2-methylbutane	C5H12	72.15	301	Bugler et al., 2016 [247,248]	NA	Validated against ignition delay times from 643–1718 K, up to 20 bar and various equivalence
2,2-dimethylpropane	C5H12	72.15	283	Bugler et al., 2016 [247,248]	NA	Validated against ignition delay times from 643–1718 K, up to 20 bar and various equivalence
n-hexane	C6H14	86.18	341	Zhang et al., 2015 [249]	NA	Validated against ignition delay times from 627–1365 K (ST) up to 32 bar and various equivalence ratios
n-heptane	C7H16	100.21	372	Zhang et al., 2016 [250]	1268 species and 5336 reactions	Validated against ignition delay times at 726–1412 K up to 38 bar of stoichiometric mixtures
				Hu et al., 2017 [289]	702 species and 3123 reactions	Validated against ignition delay times at 1100–1600 K up to 10 bar and various equivalence ratios
				Karwat et al., 2013 [290]	NA	Validated against ignition delay times and species profiles at 660–710 K and 9 bar
				Hakka et al., 2015 [291]	244 species and 2310 reactions	Validated against species profiles (JSR) at 550–1100 K and 1.06 bar and $\phi = 3$
				Seidel et al., 2015 [292]	349 species and 3686 reactions	Validated against auto-ignition timing, flame speeds and species compositions at 500–2000 K up to 40 bar and $\phi = 1.69$.
				Zhang et al., 2013 [293]	734 species and 3142 reactions	Validated against ignition delay time at 1200–1500 K up to 10 bar and at $\phi = 0.5$ and 1.
				Herbinet et al., 2012 [294]	NA	Validated against species compositions at 500–1100 K and 1.06 bar and $\phi = 1$
				Dagaut and Togbe, 2010 [295]	564 species and 2589 reactions	Validated against species mole fractions at 530–1070 K and 10 bar and $\phi = 0.5$ and 1.
				Cai et al., 2016 [251]	624 species and 2727 reactions	Validated against ignition delay times across a range of temperatures and pressures up to 42 bar.
2-methylhexane	C7H16	100.21	363	Mohamed et al., 2016 [296]	1187 species and 4567 reactions	Validated against ignition delay times at 740–1258 K at 20 and 40 bar and various equivalence ratios .
				Wang et al., 2017 [245]	NA	Validated against ignition delay times and species profiles at low temperatures up to 40 bar and various equivalence ratios.
heptane isomers	C7H16	100.21		Westbrook et al, 2001 [262]	NA	Validated against ignition delay times at 600–1400 K up to 50 bar at $\phi = 1$.
n-octane	C8H18	114.23	398	Sarathy et al., 2011 [234]	NA	Validated against species profiles (JSR, at 550–1150 K up to 10 bar) and ignition delay times at 574–1500 K up to 40 bar and various equivalence ratios .
				Westbrook et al., 2009 [235]	NA	Validated against thermolysis (measuring fuel conversion) at 623–893 K and 1 bar.
				Cai et al., 2016 [251]	624 species and 2727 reactions	Validated against ignition delay times across a range of temperatures and pressures up to 42 bar.
2,2,4-trimethylpentane (iso-octane)	C8H18	114.23	372	Atef et al., 2017 [297]	2768 species and 9920 reactions	Validated against ignition delay times at 630–1800 K up to 50 bar and different equivalence ratios.

(continued)

Table 4 (Continued)

Molecule	Molecular Formula	MW (g/mol)	Boiling Point (K)	Reference, Year	# of Species and # of Reactions	Comments
octane isomers (2-methyl heptane, 3-methylheptane, 2,5-dimethylhexane)	C8H18	114.23	392	Li et al., 2016 [298]	NA	Validated against laminar flame speeds at 363–393 K and at 0.1 MPa and various equivalence ratios
				Chaos et al., 2007 [225]	107 species and 723 reactions	Iso-octane/n-heptane. Validated against ignition delay times (ST), premixed laminar-burning velocities, variable pressure flow reactor and species profiles (JSR) at 950–1450 K up to 15 bar and various equivalence ratios.
				Curran et al., 2002 [299]	NA	Validated against ignition delay times((ST), species concentrations (JSR and FR) at 550–1700 K up to 45 bar and various equivalence ratios.
				Malewicki et al., 2013 [300]	NA	Validated against ignition delay times and species profiles at 835–1757 K up to 65 bar and various equivalence ratios.
n-nonane	C9H20	128.21	424	Sarathy et al., 2015 [234,254–256]	NA	Validated against species profiles (JSR, at 550–1150 K up to 10 bar) and ignition delay times at 574–1500 K up to 40 bar and various equivalence ratios.
benzene	C6H6	78.11	353	Westbrook et al., 2009 [235]	NA	Validated against thermolysis (measuring fuel conversion) at 623–893 K and 1 bar.
				Cai et al., 2016 [251]	624 species and 2727 reactions	Validated against ignition delay times across a range of temperatures and pressures up to 42 bar.
toluene	C7H8	92.14	384	Yang et al., 2015 [301]	263 species and 1374 reactions	Validated against species concentration profiles at 300 K, 30 Torr and various equivalence ratios.
				Saggese et al., 2013 [302]	NA	Validated against ignition delay times and species profiles at 1100–1366 K up to 9.51 bar and various equivalence ratios.
m-xylene	C8H10	106.16	412	Pitz et al., 2001 [303]	NA	Validated against ignition delay times at 1300–1900 K up to 9.4 bar and various equivalence ratios.
				Metcalfe et al., 2011 [304]	329 species and 1888	Validated over a wide range of experimental conditions in flow reactor, shock tube, jet-stirred reactor, and flames.
				Zhang et al., 2017 [266]	NA	Validated against shock tube and rapid compression machine ignition delay at temperatures 624–1459 K, pressures 20–40 bar, equivalence ratio 0.5–2.0, and with mixtures of dimethylether.
				Yuan et al., 2015 [305]	NA	Validated against species profiles, flame speeds and ignition delay times at 920–1100 K up to 45 bar and various equivalence ratios.
				Andrae, 2013 [306]	635 reactions and 137 species	Validated against species profiles and ignition delay times at 1210–1480 K up to 50 bar and various equivalence ratios.
o-xylene	C8H10	106.16	417	Tian et al., 2011 [307]	273 species and 1740 reactions	Validated against flame data.
				Detilleux and Vandooren, 2011 [308]	NA	Validated against mole fraction profiles of 18 species at pressures up to 36 Torr.
p-xylene	C8H10	106.16	411	Gail and Dagaut, 2007 [309]	189 species and 1359 reactions	Validated against species profiles in JSR at 900–1400 K, 1 bar and various equivalence ratios.
ethylbenzene	C8H10	106.16	409	Zhao et al., 2015 [310]	236 species and 1331 reactions	Validated against mole fraction profiles of flame species at 40 kPa and various equivalence ratios.
				Gail et al., 2005 [311]	160 species and 1175 reactions	Validated against ignition delay times at 900–1300 K up to 1.4 tm and various equivalence ratios.
				Yuan et al., 2016 [312]	229 species and 1563 reactions	Validated against ignition delay times, laminar flame speeds and species concentration profiles at 850–1500 K up to 10 bar and various equivalence ratios.
				Husson et al., 2013 [313]	285 species and 1411 reactions	Validated against mole fraction profiles in JSR at 750–1100 K, 800 Torr and various equivalence ratios.
				Li et al., 2011 [314]	176 species and 804 reactions	Validated against of mole fraction profiles of flame species at 4 kPa, 300 K and various equivalence ratios.

(continued)

Table 4 (Continued)

Molecule	Molecular Formula	MW (g/mol)	Boiling Point (K)	Reference, Year	# of Species and # of Reactions	Comments
1,2,3-trimethylbenzene	C9H12	120.19	449	Gudiella and Brezinsky, 2012 [315]	NA	Validated against species formation in shock tube oxidation at 20 and 50 bar, lean to rich equivalence ratios, and a temperature range of 1017–1645 K.
1,2,4-trimethylbenzene	C9H12	120.19	442	Weng et al., 2017 [316]	544 species and 3248 reactions	Validated against species profiles at 700–1100 K, 1 bar and $\phi = 2$.
cyclopentane	C5H10	70.13	322	Rashidi et al., 2017 [317]	NA	Validated against concentration profiles at 740–1250 K, 10 bar and various equivalence ratios.
cyclohexane	C6H12	84.16	354	Buda et al., 2006 [318]	513 species and 2446 reactions	Validated against mole fraction profiles (750–1050 K) and ignition delay times (650–900 K) up to 10 bar and various equivalence ratios.
				Serinyel et al., 2013 [319]	NA	Validated against mole fraction profiles at 500–1100 K and 1.07 bar and various equivalence ratios.
				Silke et al., 2007 [276]	NA	Validated against ignition delay times and species profiles at 650–1150 K up to 12.5 bar and various equivalence ratios.
methylcyclohexane	C7H14	98.19	374	Pitz et al., 2007 [320]	NA	Validated against ignition delay times(RCM) and species profiles (flow reactor) at 680–900 K up to 20 bar.
				Orme et al., 2006 [321]	NA	Validated against ignition delay times at 1200–2100 K up to 4 bar and various equivalence ratios.
				Weber et al., 2014 [322]	1540 species and 6498 reactions	Validated against ignition delay times at 600–900 K up to 50 bar and various equivalence ratios.
				Wang et al., 2014 [323]	249 species and 1570 reactions	Validated against ignition delay times at pressure range of 30–7600 Torr.
ethylcyclohexane	C8H16	112.22	405	Wang et al., 2015 [324]	540 species and 2825 reactions	Validated against species concentrations(JSR), ignition delay times (ST) and laminar flame speeds at 900–1348 K up to 760 Torr and various equivalence ratios.
dimethylcyclohexane	C8H16	112.22	401	Eldeeb et al., 2016 [325]	NA	Validated against ignition delay times at 1049–1544 K up to 12 bar and various equivalence ratios.
1-pentene	C5H10	70.13	303	Cheng et al., 2016 [326]	316 species and 1805 reactions	Validated against laminar flame speeds, ignition delay times above 100 K and up to 10 bar, and various equivalence ratios.
1-hexene	C6H12	84.16	337	Fan et al., 2016 [327]	122 species and 919 reactions	Validated against ignition delay times and laminar flame speeds at 800–1350 K up to 10 bar at various equivalence ratios.
				Yahyaoui et al., 2006 [328,329]	177 species and 1171 reactions	Validated against ignition delay times at 1270–1700 K at 0.2 MPa and various equivalence ratios, and species profiles (JSR) at 1270–1700 K up to 1 MPa and various equivalence ratios.
				Touchard et al., 2005 [330]	NA	Validated against cool flame and autoignition delay times at 615–850 K up to 10.9 bar and $\phi = 1$.
hexene isomers	C6H12	84.16		Mehl et al., 2008 [331]	100 species and 900 reactions (sub-mechanism)	Validated against ignition delay times at 750–1050 K up to 1.1 MPa and various equivalence ratios.
di-isobutylene (DIB)	C8H16	56.11	2662	Metcalfe et al, 2007 [283]	NA	Validated against ignition delay times at 1200–1550 K up to 4 bar and various equivalence ratios.

concentrations of the various radical species and their formation rates are remarkably similar despite the size of the parent n-alkane fuel [237]. These findings support the thesis of Dooley et al. [218], which states that only distinct chemical functionalities govern the reactivity of fuels; and in the case of large n-alkanes, the size of the carbon chain is not a distinct chemical functionality with respect to high temperature reactivity. An important implication of this finding is that in replicating the high temperature combustion characteristics of a target gasoline fuel, any n-alkane (n-pentane or larger) could be a suitable surrogate to represent all the n-alkanes in the gasoline.

The activation energy for alkyl radical decomposition reactions is around 30 kcal/mol [238], so at lower temperatures (i.e., below 900–950 K) these reactions are unimportant. Therefore, the n-alkane oxidation mechanism is dominated by a series of low temperature auto-oxidation reactions. This scheme has been previously described in detail in articles by Zador et al. [239] and Battin-Leclerc [233]. It includes the early schemes postulated by Cartlidge and Tipper [240], refined by Knox [241] and Cox and Cole [242], and extended by Wang et al. [243–245].

Fig. 26. Comparison of experimentally determined premixed laminar flame speeds and extinction strain rates of mixtures of air with n-pentane, n-hexane, n-heptane, and n-octane. Unburnt gas temperature was 353 K. Figure is taken from Ji et al. [236] and reproduced with permission from Elsevier Publishing.

The classic low temperature oxidation mechanism is widely used to explain the process leading to ignition of n-alkanes at low temperatures, as well as the monotonic decrease in ignition delay time with temperatures below ~ 800 K. At intermediate temperatures of ~ 800 – 900 K, several reactions overcome their activation energy to become competitive with the reactions leading to chain branching. First, the ROO radical can undergo a concerted elimination reaction, leading to the formation of an alkene and HO_2 radical, widely accepted as a chain terminating route because HO_2 radical is not as reactive as OH radical. Second, the QOOH radical can undergo cyclization to form a cyclic ether and an OH radical, which is a chain-propagating pathway. These two competing pathways are responsible for the negative temperature coefficient behavior observed in n-alkane ignition at temperatures of ~ 800 – 950 K, in which ignition delay time increases with increased temperature.

Table 4 presents comprehensive chemical kinetic models for various n-alkanes found in gasoline fuels. It is clear that well validated kinetic models exist for all the important n-alkanes, i.e., n-butane, n-pentane, n-hexane, n-heptane, and n-octane. Arguably the most up-to-date and widely validated n-alkane mechanisms include those developed at NUI Galway by Henry Curran's group for n-butane [246], n-pentane [247,248], n-hexane [249], and n-heptane [250]. These models are capable of predicting ignition phenomenon at a range of temperatures, speciation profiles in flames and flow reactors, and high temperature flame phenomenon (e.g., laminar flame speed, extinction, etc.). All these models are built on the same base chemistry (i.e., AramcoMech), therefore making them easy to merge for gasoline surrogate fuel kinetic modeling. They have also been useful for developing comprehensive models for C_8 and larger n-alkanes, as recently demonstrated by Cai et al. [251] by optimizing and extrapolating rate rules. It is important to note that none of these models contain the aforementioned 3rd O_2 addition reaction mechanism.

A comparison of the simulated homogeneous gas-phase ignition delay times of various n-alkanes is presented in Fig. 27 for initial conditions of 25 bar and stoichiometric fuel/air mixtures. It is clear that high temperature (above ~ 950 K) ignition delay times of n-alkanes are similar. Similar ignition delay times are also observed at low temperatures (below ~ 725 K) for C_5 – C_7 n-alkanes. However, in the intermediate temperature regime (750–950 K), there is a clear difference in the reactivity of various n-alkanes. The ignition delay time decreases with increasing carbon chain length, which is directly relevant to observed octane number decrease with increasing chain

length. This indicates that there is a strong relationship between homogeneous gas-phase ignition delay times and octane numbers. The differences in ignition delay times for various n-alkanes is attributed to the number of consecutive secondary CH_2 (i.e., methylene) in the carbon chain. Secondary C–H bonds enable low temperature chain branching pathways because their low bond dissociation energy facilitates hydrogen abstraction and intramolecular H-atom migration reactions. In the context of low temperature reactivity, Won et al. [252] and Lapuerta et al. [253] have shown that the ratio of methylene to methyl (CH_2/CH_3) groups is a distinct chemical functionality that controls ignition. Larger n-alkanes have higher CH_2/CH_3 ratios and therefore shorter ignition delay times in the intermediate temperature regime.

These findings are important for gasoline surrogate fuel formulation and kinetic modeling because they imply that predictions of n-alkane ignition characteristics—and thereby antiknock quality—are sensitive to n-alkane carbon number. Therefore, surrogate fuel studies focusing on ignition and/or combustion phasing at intermediate

Fig. 27. Simulated homogeneous gas-phase ignition delay times for various n-alkanes at 25 bar, stoichiometric fuel/air mixtures.

temperatures need to select n-alkane surrogate components that are representative of those present in the real fuel. This can be achieved by selecting n-alkanes at the low and high end of the carbon number spectrum, so that when they are blended together in appropriate proportions, they match the reactivity of the n-alkane mixture in the real fuel.

4.1.2. isoParaffins/isoAlkanes

isoAlkanes, or isoparaffins, are alkanes hydrocarbons with one or more alkyl substitution. This class of molecules constitutes an important fraction of gasoline fuels, in which methyl and ethyl substitutions are arranged on a carbon backbone. Despite their predominance in gasoline fuels, there is a dearth of fundamental combustion kinetic studies of such species, especially true for ignition at low and intermediate temperatures. The most widely studied isoalkane is 2,2,4-trimethylpentane (isooctane), because it is a primary reference fuel surrogate. Most gasoline fuels comprise various isomers of heptane (nine possible isomers) and octane (18 possible isomers); isomers of other alkanes also exist. As shown in Fig. 28, C7 isoalkanes have higher octane numbers than their n-alkane counterpart (i.e., n-heptane). Octane number increases with the number of alkyl substitutions, and the latter is also dependent on the position of the alkyl substitutions. Kinetic modeling of various octane and decane isomers by Sarathy et al. [234,254–258] has provided chemical kinetic explanations for the variations in ignition delay time, and hence octane number, observed with varying number and location of alkyl substitutions. These kinetic aspects are discussed in more detail below.

The high and low temperature oxidation of isoalkanes is conceptually similar to that of n-alkanes. The same types of reactions occur; however, the primary effect of introducing alkyl substitutions is to alter the rates of various reactions, thereby changing branching ratios to the pool of reactive intermediate species. Alkyl substitutions introduce tertiary and quaternary carbon sites to the alkane structure, of which the former have lower C–H bond dissociation energies than primary C–H and secondary C–H bonds. This reduces the energy barrier for H-atom abstraction and H-atom migration reactions from tertiary C–H when compared to primary and secondary C–H bonds. Several studies exist on the higher temperature combustion kinetics of various isoalkanes. Exemplary studies depicting the role of methyl substitution on high temperature reactivity are those by Ji et al. [259] on laminar flame propagation of octane isomers and Liu et al. [260] on counterflow flame non-premixed flame ignition of octane and decane isomers. In the former work [259], the authors presented measured and simulated laminar flame speeds for various octane isomers, as shown in . Their results showed that branched isomers exhibit lower laminar flame speeds,

which is attributed to the increased production of H-atom scavenging resonantly stabilized intermediate radical species, such as allyl and isobutenyl radicals. The initial high temperature oxidation of the fuel molecules is similar between n-alkane and isoalkanes, but increasing the number of methyl branches alters the pool of C₁–C₄ intermediate species, which in turn alters the overall flame structure and reactivity.

As mentioned previously, altering the rates of internal H-atom migration also has important implications on low temperature radical chain branching, propagation, and termination reactions, which in turn affect ignition delay times. Introducing alkyl substitutions also increases the total number of primary C–H bonds, which are comparably less reactive than secondary and tertiary C–H bonds. For this reason, the critical parameter governing the low and intermediate temperature reactivity of isoalkanes is typically the relative amounts of CH, CH₂, and CH₃ functional groups [252,253]. This has been demonstrated and explained in chemical kinetic modeling studies of C₈ n- and isoalkanes [256].

Table 4 presents comprehensive chemical kinetic models for various isoalkanes found in gasoline fuels. Indeed, there is a lack of available kinetic models for isoalkanes larger than C₅. This makes it challenging to develop surrogate fuels, as the majority of isoalkanes found in real gasolines are in the C₆–C₈ range. As mentioned previously, 2,2,4-trimethylpentane has received the most attention from the kinetic modeling community. The heptane isomers have been modeled by Westbrook et al. [261,262], but the data available for model validation was limited at the time. A series of studies by Sarathy et al. [234,254–257,263] modeled three different octane isomers, but this was limited to mono- and di-methylated alkanes. Although only a limited number of isoalkane kinetic models are available for gasoline surrogate fuel kinetic studies, recent works by Won et al. [252,264] and Lapuerta et al. [253] have shown that the ignition characteristics of branched hydrocarbons can be accurately captured by a mixture of n-alkanes and highly branched isoalkanes that are to blended match the functional group distribution (i.e., CH, CH₂, CH₃) in the targeted isoalkane (or real fuel). This greatly facilitates the kinetic modeling effort, as it permits complex gasoline mixtures with many isoalkanes variants to be modeled as simpler mixtures of an n-alkane and a highly branched alkane.

4.1.3. Aromatics

Because they are known to have high octane numbers and high sensitivity, aromatics are widely used to improve octane in gasoline fuels. The maximum blending fraction of aromatics is typically below 30 vol% is US and European gasolines. Typical aromatics in the gasoline boiling point range include benzene, toluene, xylene isomers, ethylbenzene, and trimethylbenzene isomers. Benzene concentrations in gasoline fuels are extremely low due to its high toxicity and carcinogenicity.

The combustion kinetics of aromatics is different than that of n- and isoparaffins particularly, and in low and intermediate temperatures. Initiating the oxidation of aromatics is difficult because hydrogen atoms bonded to the aromatic ring have high bond dissociation energies. H-atom abstraction from alkyl aromatics, such as toluene, are easier to initiate because the formed benzyl radical is stabilized by the presence of the aromatic ring. The oxidation pathways of aromatics at high temperatures have been detailed by Brezinsky [265], but fewer studies are available at lower temperatures of relevance to ignition in gasoline engines. Recently, Zhang et al. [266] studied the low temperature oxidation chemistry of toluene by blending it with dimethyl ether, a highly reactive fuel which generates OH radicals that can initiate toluene oxidation.

Toluene oxidation is primarily initiated by hydrogen abstraction from the methyl group of toluene, thereby forming the benzyl radical. Minor pathways include H-atom abstraction from the ring or O radical addition to the ring. Both these radicals lead to the formation

Fig. 28. The nine isomers of heptane and their measured RON/MON values.

of cresol or cyclopentadienone. In the presence of large amounts of OH and HO₂ radicals, the benzyl radical leads to the formation of an alkoxy intermediate that decomposes to form either benzaldehyde and H radical or formaldehyde and benzene. These reactions of resonantly stabilized benzyl radicals with other radicals is a key contributor to the lack of low temperature reactivity of aromatics. There are no low energy isomerization reactions that can lead to radical chain branching intermediates.

The oxidation of other alkylaromatics, such as xylene isomers and trimethylbenzene isomers, follows pathways similar to toluene. H-atom abstraction from the methyl group alpha to the ring leads to the formation of a benzylic radical. Subsequent reactions of the benzylic radicals are similar to those in toluene. In the case of multiple substituted alkylaromatics where the methyl groups are adjacent (e.g., ortho-xylene and 1,2,3-trimethylbenzene), there is the possibility of O₂ addition to benzyl radical and subsequent internal H-atom migration from the adjacent methyl group. This pathway requires the formation of a seven-membered transition state that is highly strained. Nevertheless, it is still a possible route to low temperature chain propagation, or chain branching intermediates.

Detailed chemical kinetic models for aromatic fuels are presented in Table 4. The major focus to date has been on benzene and toluene models, which are readily adopted into gasoline surrogate kinetic models. Only a few models exist for the various isomers of xylene and trimethylbenzene. Indeed, there is a need to develop more robust kinetic models for larger alkylaromatics in the gasoline boiling point range. A suitable approach for gasoline surrogate kinetic modeling would be to focus efforts on toluene and 1,2,4-trimethylbenzene, because a mixture of these two aromatics can represent the general functional groups and relative positions of side chains found in various alkylaromatics hydrocarbons.

4.1.4. Naphthenes/Cycloalkanes

The naphthenic/cycloalkane content of gasoline is typically below 20 vol%, but may be higher in fuels derived from oil sands and shale. Their octane quality is typically increased by dehydrogenation during refining to produce aromatics. Nevertheless, a significant quantity exists in gasoline fuels, and their presence effects engine ignition quality and PAH/soot formation.

Cycloalkanes have the same molecular formula as mono-alkenes with the same carbon number, but their combustion chemistry is remarkably different. Early studies by Walker et al. [267,268] showed that oxidation chemistry of cycloalkanes is similar to that of n-alkanes, although the branching ratios to various low temperature reactive intermediates are considerably different. At high temperature pyrolytic conditions, cycloalkanes can undergo sequential dehydrogenation to form aromatic species, which explains their

high sooting tendency. Under high temperature oxidation conditions, cycloalkyl radicals are formed and ring-opening leads to eventual formation of dienes.

The low temperature oxidation of cycloalkanes proceeds in a similar manner as discussed earlier for n- and isoalkanes. Cycloalkyl radicals react with molecular O₂ to form alkylperoxy radicals. These can undergo concerted elimination reactions to form cycloalkenes and HO₂ radicals, or isomerize to QOOH radicals via internal H-atom migration reactions. QOOH radicals can react again with molecular O₂ and lead to eventual chain branching intermediates (e.g., ketohydroperoxides). The cycloalkane ring structure takes various conformation and introduces steric hindrances. Internal H-atom migration of alkylperoxy radicals is hindered due to the bicyclic and highly strained nature of the transition state. Therefore, concerted elimination reactions leading to radical chain termination are favored over internal H-atom migration reactions leading to radical chain branching.

As shown previously for n- and isoalkanes, homogeneous batch reactor ignition delay time simulations can be correlated with fuel octane numbers. Fig. 29 presents experimental and simulated ignition delay times for C₅ and C₆ n-alkanes and cycloalkanes. There is a clear difference in reactivity between n-alkanes and their cycloalkane counterparts below 900 K. Yang et al. [269,270] explained that conformational inhibition of the 1,5 H-atom migration (six-member ring transition state) chain branching pathway in cyclohexylperoxy radicals is responsible for their lower reactivity compared to n-hexane. Al Rashidi et al. [271,272] provided a similar explanation for the lower reactivity of cyclopentane compared to n-pentane; they attribute cyclopentane's lower reactivity to higher energy barriers in forming the strained bicyclic transition state, which increase the flux to concerted elimination reactions forming unreactive cyclopentene and HO₂ radicals. Methyl substitutions on cycloalkanes (e.g., methylcyclopentane and methylcyclohexane) lower the activation energy of 1,5 H-atom migration (six-member ring transition state) of cycloalkylperoxy radicals (RO₂ = QOOH) [269,270]. Therefore, methylcyclopentane and methylcyclohexane are more reactive than their non-substituted counterparts.

Comprehensive chemical kinetic models for cycloalkanes are presented in Table 4. To date, most of the kinetic modeling focus has been on cyclohexane and methylcyclohexane. The recent methylcyclohexane kinetic model by Weber et al. [273] has been validated across a broad range of pressures, temperatures, and mixture fraction conditions; it is recommended for use in gasoline surrogate kinetic models. Kinetic models for cyclohexane are not as well developed as those for methylcyclohexane, primarily due to the challenges in acquiring experimental data. A recent study by Vranckx et al. [274] measured ignition delay times at 15 bar and

Fig. 29. Comparison of experimental (left) and simulated (right) ignition delay times at 20 bar and stoichiometric fuel/air mixtures for n-pentane [248], cyclopentane [271,272], n-hexane [249], and cyclohexane [276]. Figure adapted from Al Rashidi et al. [272] with permission from Elsevier Publishing.

showed NTC behavior in the ~ 700 – 900 K temperature regime, which indicates complex low temperature oxidation chemistry. The authors found that current cyclohexane chemical kinetic models could not accurately capture experimental ignition delay data, and suggested future work be focused on improving the kinetics of low temperature oxidation pathways. Only one [271,272,275] comprehensive chemical kinetic model with detailed high and low temperature chemistry exists with cyclopentane. The model was developed based on theoretical calculations of the cyclopentyl radical decomposition and oxidation potential energy surfaces and pressure-dependent kinetics. Additional work is needed to develop a similar model for methylcyclopentane. Comprehensive and accurate chemical kinetic models for cyclopentane, methylcyclopentane, cyclohexane, and methylcyclohexane would be sufficient for formulating gasoline surrogate fuels with various cycloalkane hydrocarbons.

4.1.5. Olefins/alkenes

Olefins/alkenes represent a small fraction of gasoline fuel, but they have a notable effect on oxidative stability and autoignition characteristics. Olefins in gasoline are typically limited to C_5 – C_8 linear and branched hydrocarbons; however, they are also common intermediates in the oxidation of paraffins, which highlights their importance in gasoline combustion chemistry. These molecules are distinguished by the presence of double bonds in the hydrocarbon structure, which introduces allylic and vinylic hydrogens and resonantly stabilized intermediate radicals. The double bond adds to the complexity of their oxidation, especially at low temperatures where radical additions to the double bond are possible. The presence of olefins in gasoline can change its knocking tendency and soot emissions. Their octane numbers are higher than those of corresponding paraffins, and the double bond position has a notable effect on anti-knock quality.

The high temperature oxidation (above 1000 K) of olefins is initiated by the abstraction of allylic hydrogen atoms (β to the double bond), which have lower bond dissociation energies than vinylic and normal alkyl hydrogen atoms. The resulting allylic radicals exhibit electron delocalization and are extremely stable due to their resonance structure. These stable allylic radicals can undergo recombination reactions with other allylic radicals to produce larger chain hydrocarbons, which can lead to the formation of PAH species. This explains why alkenes display higher sooting tendencies than alkanes. As the carbon chain increases in 1-alkenes, the relative importance of the double bond on chemical kinetic reactivity decreases. For example, the reactivity of 1-octene is not significantly different than n-octane because hydrogen abstraction can proceed from one of the secondary carbon sites in the alkyl chain. As the double bond position moves towards the center of a molecule (e.g., 1-alkene to 2-alkene to 3-alkene), it tends to have a greater effect of the overall reactivity of the molecule. This is attributed to the fact that more secondary carbon sites are converted to allylic and vinylic sites as the double bond shifts.

The low temperature oxidation (below 1000 K) of alkenes influences its octane rating in engines [277]. Hydrogen abstraction from allylic sites becomes more common at lower temperatures due to the low activation energies. However, H-atom abstraction from normal secondary carbon sites is also possible, and the resulting allylic radicals react like those derived from n-alkanes. The subsequent addition of O_2 to the allylic radical is possible, but the resulting RO_2 radical is thermodynamically unstable [278]. As a result, subsequent isomerization and O_2 addition reactions leading to chain branching are hindered. This is the primary reason why alkenes display lower reactivity [279] and higher octane numbers under low temperature ignition conditions.

In addition to H-atom abstraction, OH, H, and HO_2 radical addition to the double bond is possible at very low temperatures (below 700 K). OH radical addition is the most important under typical

Fig. 30. Ignition delay times of hexene isomers (0.86–1.09 MPa, stoichiometric fuel/air mixtures). Symbols are experiments and lines are simulations. Figure reproduced from Mehl et al. [277] with permission from Elsevier Publishing.

engine conditions because OH is the predominant radical at lower temperatures. Waddington [280–282] was the first to show that OH addition to the double bond of alkenes leads to the formation of β -hydroxyalkyl radicals. These radicals add O_2 to form hydroxyalkylperoxy radicals, which subsequently isomerize and decompose to form aldehydes and OH radicals.

Fig. 30 from Mehl et al. [277] presents the role of double bond position on the autoignition of various hexene isomers in the low temperature oxidation regime. It is clear that alkenes display less NTC behavior than n-alkanes because the double bonds hinder low temperature oxidation pathways. NTC behavior becomes less pronounced as the double bond moves towards the interior of the molecule, because the double bond begins influencing a larger number of possible oxidation pathways. The ignition delay times of 3-hexene is significantly lower than 1-hexene because the former has two vinylic carbon sites, two allylic carbon sites, and two primary carbon sites, while the latter has one vinylic carbon site, one allylic carbon site, three secondary carbon sites, and one primary carbon site. Increasing the number of vinylic and allylic carbon sites, while reducing the number of secondary carbon sites, effectively decreases reactivity, and hence increases octane number.

Comprehensive chemical kinetic models for alkenes are presented in Table 4. Gasoline typically contains C_5 – C_8 alkenes, and very few comprehensive kinetic models exist in the literature. While many models are available for high temperature oxidation/pyrolysis conditions, due to the lack of comprehensive kinetic models for alkenes, we were unable to find many detailed models covering the typical temperature and pressure ranges encountered under real engine condition. Table 4 presents several alkene kinetic models that have been developed and validated at high temperatures. At present, it is recommended that 1-hexene be used as a surrogate in gasoline fuels because it has the most widely validated chemical kinetic model [277]. Models for other pentenes and hexenes are valid at high temperatures and should be used only under relevant combustion conditions. An interesting additive for improving the octane quality of gasoline is di-isobutylene (DIB), for which a kinetic model developed by Metcalfe et al. [283] can be used to study DIB blending effects on ignition quality [164,284].

4.2. Detailed chemical kinetic models for gasoline surrogate mixtures

Chemical kinetic models for gasoline surrogate mixtures are simply combinations of various pure component models. However, it is important for the individual fuel components to share a common core mechanism, so that they can be easily merged. Cross-reactions between fuel components are typically considered in the development of these models; however, an extensive analysis and

discussion by Battin-Leclerc [233] indicates that such cross-reaction terms are largely negligible in alkane mixtures, and mildly important in mixtures containing alkenes and/or aromatics. Indeed, fuel mixtures behave notably different than pure components, but the cross effects are realized in species and reactions within the intermediate radical pool (and rarely with the parent fuel molecules), which highlights the importance of a robust core mechanism.

The mixture of components included in a surrogate fuel kinetic model is defined based on the selected gasoline target properties, as described in Section 3. Traditionally, gasoline fuels were modeled as simple PRF mixtures with *n*-heptane and isooctane blended to match either the RON or the MON. However, it was quickly realized that an additional component—mainly an aromatic—is needed to match both the RON and MON, and thus TPRF mixtures became widely used. More recently, multicomponent mixtures that match additional gasoline properties (e.g., H/C ratio, average molecular weight, PIONA, distillation curve, etc.) were utilized to predict more complex combustion phenomenon. The following sub-sections describe the formulation of detailed gasoline surrogate chemical kinetic models. A subset of the models is employed to demonstrate the effects of surrogate fuel composition on important combustion properties, such as ignition delay times.

4.2.1. PRF and TPRF mixtures

The introduction of PRF detailed chemical kinetic models dates back to the late 20th century, when models for the low-temperature oxidation of *n*-heptane and isooctane were first developed [299,332–337]. These models were based on fundamental understanding of alkane oxidation chemistry proposed by Cox and Cole [242]. The primary focus of these PRF models was to understand autoignition characteristics and engine knock, as the octane rating methodologies are based on these surrogate mixtures. Morley et al.

[338] and Westbrook et al. [336] were amongst the first to develop PRF kinetic models and use them to understand the octane ratings of fuels. The latter team from LLNL typically validated their surrogate mixture kinetic models against a range of experimental data (ignition delay, flow and stirred reactors, and premixed laminar flame speeds), which made them widely applicable to predict combustion phenomenon other than knock-relevant autoignition. More recently, interest shifted from only modeling PRF surrogates towards developing models for TPRF mixtures. As mentioned previously, TPRF mixtures are needed if a surrogate is to match both the RON and the MON of the target gasoline fuel [70,114].

Table 5 lists several detailed chemical kinetic models for PRF and TPRF mixtures. These detailed models are useful for predicting a wide range of combustion phenomenon, including homogeneous gas-phase ignition delay, premixed laminar flame propagation, speciation profiles in reactors, and PAH and soot formation in flames. These models can also be reduced in complexity (as discussed in the next section) and used in CFD engine simulations.

An example of the predictive capabilities of detailed chemical kinetic models for PRFs is given here in the context of HCCI engine simulations. Operation of these engines may be controlled by the rate of heat release rate (ROHR) of the PRF/air mixture in-cylinder. Under HCCI conditions, ROHR is a function of the PRF mixture composition, equivalence ratio, intake air temperature, and intake air pressure. A recent experimental HCCI engine study by Vuilleumier et al. [339] investigated the effect of PRF mixture composition on ROHR at fixed intake pressure, equivalence ratio, and engine combustion phasing. In this study, numerical HCCI engine simulations were also performed using a detailed chemical kinetic model for PRF mixtures from LLNL [149]. Both experimental (left panel) and numerical (right panel) results are shown in Fig. 31. The experimental results show that PRF 100 (pure isooctane) and the mixture with

Table 5

Detailed chemical kinetic models for gasoline surrogate mixtures.

Fuel components		# of Species and # of Reactions	Comments
<i>n</i> -heptane/isooctane (PRF)	Curran et al., 2002 [299,333,346]	NA	LLNL. Validated against ignition delay times, speciation measurements in perfectly stirred and flow reactors, and HCCI engine combustion.
<i>n</i> -heptane/isooctane (PRF)	Westbrook et al., 2011 [347]	NA	LLNL. Validated against ignition delay times and speciation measurements in perfectly stirred flow reactors.
<i>n</i> -heptane/isooctane/toluene (TPRF)	Pires da Cruz et al, 2007 [348,349]	NA	CNRS-NANCY EXGAS. Detailed mechanism validated against ignition delay times, jet stirred reactor speciation profiles, and HCCI engine combustion.
<i>n</i> -heptane/isooctane/toluene (TPRF)	Park et al., 2017 [350]	2021 species and 8688 reactions	KAUST. Detailed mechanism validated against ignition delay times, laminar flame speeds, and PAH and soot measurements in counterflow diffusion flames.
<i>n</i> -heptane/isooctane/toluene/di-isobutylene/ethanol	Andrae, 2008 [351,352]	1121 species and 4961 reactions	Validated against ignition delay times and HCCI engine combustion.
<i>n</i> -heptane/isooctane/toluene/1-hexene/2-pentene	Mehl et al., 2011 [149]	1338 species and 5933 reaction	LLNL. Detailed mechanism validated against ignition delay times, laminar flame speeds, and perfectly stirred reactor speciation. 3–50 bar, 650–1200 K.
<i>n</i> -butane/ <i>n</i> -pentane/ <i>n</i> -hexane/ <i>n</i> -heptane/ <i>n</i> -octane/isopentane/isohexane/isooctane/1-pentene/2-pentene/1-hexene/2-hexene/3-hexene/methylcyclohexane/toluene/ <i>o</i> -xylene/ <i>m</i> -xylene/ <i>p</i> -xylene/ethanol.	Pudupakkam, Naik et al., 2011 [341–343]	1833 species and 8764 reaction	Reaction Design. Detailed mechanism validated against ignition delay times, laminar flame speeds, and perfectly stirred and flow reactor speciation. 1–50 bar, 650–1800 K.
<i>n</i> -heptane/isooctane/toluene/2-methylbutane/2-methylhexane/ <i>n</i> -butane/1-hexene/1,2,4-trimethylbenzene/cyclopentane	Sarathy et al. 2016 [58,150,182,184]	2315 species and 10,079 reaction	KAUST, LLNL, NUIG. Detailed mechanism validated against ignition delay times for FACE gasolines. 3–50 bar, 650–1200 K.
<i>n</i> -heptane/isooctane/toluene/di-isobutylene/methylcyclohexane/ethanol/ETBE	Hashimoto et al., 2013 [353]	1769 species and 5722 reactions	Detailed model validated against ignition delay times.

Fig. 31. Experimental (left) and numerically simulated (right) rate of heat release (ROHR) profiles as function of engine crank angle degree (CAD) for various PRF mixtures fuels at 1.4 bar intake pressure, $\phi = 0.4$, and combustion phasing (CA50) of 6 °aTDC. Figures reproduced from Vuilleumier et al. [339] with permission from SAE International.

5 vol% n-heptane (PRF 95) do not show prominent low temperature heat release (LTHR), which is characterized by the local rise in ROHR from -30 to -20 CAD after CA50. The existence of LTHR is due to low temperature oxidation reactions that lead to radical chain branching, and the detailed chemical kinetic modeling of PRF100 and PRF95 confirm that such reactions are not important. The lack of LTHR is attributed to the presence of a large fraction isooctane, which lacks low temperature reactivity.

Experimental results indicate that PRF85 with 15 vol% of n-heptane shows significant LTHR. Numerical simulations of PRF85 using the kinetic model from [149] cannot reproduce the experimentally observed LTHR behavior. Instead, PRF70 is the highest PRF mixture that displays LTHR in the numerical simulations. n-Heptane displays prominent low temperature reactivity due to the large fraction of CH_2 groups, and the magnitude of LTHR is directly proportional to its amount. A study by Hwang et al. [340] showed similar results, in which the volume fraction of n-heptane in the PRF simulations had to be changed to reproduce experimentally observed heat release characteristics. These results indicate that further work is needed in PRF kinetic models to improve the prediction of LTHR in HCCI engine simulations.

Detailed chemical kinetic models for TPRF mixtures can predict ignition delay times. Javed et al. [158] measured ignition delay times of various TPRF mixtures across a range of RON and S (RON 70, S 4; RON 80, S 5.7; RON 91, S 7.6; and RON 97.5, S 10.9) in both shock tubes and rapid compression machines. The authors conducted numerical simulations using the detailed chemical kinetic model from LLNL[149]. The exact mixture compositions are present in the original study; briefly, the n-heptane and isooctane concentrations decrease with increasing RON and S, while toluene content increases. The experimental and numerical results presented in Fig. 32 show a clear reduction in ignition delay time at intermediate temperatures of ~ 725 – 900 K as the TPRF number increases. Numerical simulations show that TPRF70 with the largest fraction of n-heptane has the shortest ignition delay time due to the low temperature reactivity of n-heptane, which produces OH radicals required for ignition. As the toluene fraction increases, the ignition delay time increases too. As mentioned previously, toluene lacks low temperature reactivity because it forms stable benzylic radicals, and further acts as a sink for OH radicals produced by n-heptane in the mixture. The net effect is an overall reduction in the reactivity of the TPRF mixture. Another interesting observation in experimental and numerical results is the difference in NTC behavior of the various mixtures. There is a clear change in slope of the ignition delay time versus temperature curve in the NTC region, as the

TPRF RON and S varies. Further discussion on this behavior is presented in the following section, within the context of multi-component gasoline surrogate mixtures.

4.2.2. Multicomponent mixtures

Gasoline surrogates with more than the typical three components (i.e., n-heptane, isooctane, and toluene) are termed multi-component mixtures. Such mixtures typically include the usual three components and additional components needed to replicate various target fuel properties. Important properties that require the addition of more components in the surrogate mixture include distillation curve, functional group or hydrocarbon class distribution, average molecular weight, and octane sensitivity. Real gasoline fuels have a broad distillation profile, which PRF and TPRF mixtures cannot replicate. Therefore, surrogates should include components that cover the entire boiling point range of typical gasoline fuels. Real gasolines also often contain naphthenes, olefins, and oxygenates, none of which are found in PRF and TPRF mixtures. If a surrogate is to match the hydrocarbon class distribution and functional groups of the real fuel, then molecules representing all hydrocarbon classes should be included in the surrogate.

Fig. 32. Measured (symbols) and simulated (lines) ignition delay times for various TPRF mixtures near 20 bar and stoichiometric fuel/air mixtures. Each mixture is identified by its RON (97.5, 91, 80, 70). Figure taken from Javed et al. [158] and reproduced with permission from Elsevier Publishing.

A summary of multicomponent gasoline surrogate detailed chemical kinetic models is presented in Table 5. The largest detailed chemical kinetic model for gasoline surrogates is currently available from Reaction Design and contains up to 20 components [341–343]. These include various hydrocarbons in the gasoline boiling point range as well as ethanol. The chemical kinetic model is utilized in Reaction Design's Surrogate Blend Optimizer [343], which formulates surrogates to match desired target properties of a real fuel. Puduppakam et al. [341] and Naik et al. [343] have shown that the species palette can be successfully utilized to create surrogate mixtures of various complexity, which replicate real gasoline fuel properties. The chemical kinetic model is large in size, so mechanism reduction is applied, and then CFD multi-zone engine simulations are conducted to predict important engine performance parameters.

The team at LLNL [112,149] has worked for many years on multicomponent kinetic surrogate models for gasoline fuels. These include mixtures of n-heptane, isooctane, and toluene with various alkenes (1-hexene and/or 2-pentene). The models are developed on the CO-C4 base chemistry from NUIG [219–222], which facilitates the addition of new components as kinetic models become available. Recently, LLNL, NUIG, and KAUST collaborated [58,150] to develop a gasoline surrogate kinetic model comprising 10 components with representatives from each of the major hydrocarbon classes. The kinetic model was used to simulate the ignition characteristics of FACE (fuels for advanced combustion engines) gasolines by the formulation of multicomponent surrogates that match various target properties (distillation curve, H/C ratio, octane number, PIONA, carbon types, and average molecular weight) [125]. The authors showed that ignition simulations with simpler PRF and TPRF surrogate for FACE gasolines can reproduce experimentally measured ignition delay times of the real gasoline at high temperatures. However, at low and intermediate temperatures, the authors found that simulations using multicomponent surrogates better replicate the ignition characteristics of the real fuels [58,150]. The 10-component model has also been used to simulate surrogate mixtures of high octane oxygenated gasolines containing ethanol [154] and low octane gasolines produced from light and heavy naphtha [152,153a].

To further understand the role of surrogate fuel composition on ignition characteristics, Singh et al. [344] measure the RON and MON of various multicomponent mixtures comprising n-heptane, isooctane, toluene, 1-hexene, and 1,2,4-trimethylbenzene. They showed that increasing the aromatic and olefin content in the mixture resulted in higher octane sensitivity. Furthermore, the authors utilized chemical kinetic simulations with the KAUST-LLNL-NUIG gasoline surrogate kinetic model [58,150] under homogeneous conditions to correlate ignition delay times with RON and MON. Fig. 33 presents a portion of the results from Singh et al. [344] for surrogate fuel mixtures listed in Table 6. All fuels covered have the same RON with varying levels of sensitivity and differing mixture composition. The goal of presenting this subset of fuels is to clarify the effects of mixture composition on octane sensitivity.

As shown in Fig. 33, all mixtures have similar ignition delay times at high temperatures (above 900 K), indicating that fuel composition does not significantly affect reactivity at these conditions. At low and intermediate temperatures there are notable differences in ignition delay times for the different mixtures; however, the effect of

Fig. 33. Simulated ignition delay times for various gasoline surrogate mixtures at 25 bar and stoichiometric fuel/air mixtures. Legend denotes the mixtures RON and sensitivity (S). Figure adapted from Singh et al. [344] with permission from The American Chemical Society.

fuel composition on ignition delay time varies depending on the specific temperature regime. An interesting observation is that near ~ 750 K, all the mixtures have the same ignition delay time, suggesting a strong correlation between RON and ignition delay time and this temperature (recall that all fuels are RON 91).

The qualitative variation of ignition delay time with temperature is indicative of the octane sensitivity of the mixture. The simplest surrogate presented is PRF 91 with a RON of 91 and zero sensitivity. The simulated ignition delay times of this fuel display significant NTC characteristics. Below ~ 750 K, PRF91 has the shortest ignition delay time, but above ~ 750 K it has the longest ignition delay time. This prominent NTC behavior is indicative of non-sensitive fuel [345]. Surrogate mixtures with increasing sensitivity show longer ignition delay times below ~ 750 K and shorter ignition delay times above ~ 750 K. Essentially, the NTC characteristic of the mixture is diminished as the octane sensitivity increases.

These phenomena can be directly linked to fuel composition. PRF91 is a purely paraffinic fuel that shows prominent low temperature radical chain branching chemistry below ~ 750 K, but as the temperature increases, competing chain propagating and chain terminating reactions inhibit reactivity, leading to the observed NTC behavior. Higher sensitivity mixtures contain larger fractions of aromatics and olefins, both of which contain carbon-carbon double bonds. These mixtures still include a significant amount of n-heptane, which undergoes radical chain branching reactions at low temperatures below ~ 750 K. However, the formed radicals reaction with the aromatics and/or olefins form resonantly stabilized intermediates, which do not lead to low temperature radical chain branching. As the temperature increases above ~ 750 K, n-heptane reacts to form HO_2 radicals (as opposed to OH radical), due to

Table 6

Composition, RON, and S of selected gasoline surrogate mixtures studied by Singh et al. [344].

Fuel mixture	isooctane (vol%)	n-heptane (vol%)	toluene (vol%)	1-hexene (vol%)	RON	MON	S
RON 91, S 0 (PRF 91)	91	9	0	0	91	91	0
RON 90.5, S 2.5	72.5	12.5	15	0	90.5	88	2.5
RON 91.7, S 6.5	58	7	15	20	91.7	85.2	6.5
RON 90.9, S 8.2	39	11	30	20	90.9	82.7	8.2

concerted elimination reactions; however, these HO₂ radicals can readily react with benzyl radicals to form OH and benzoyl radicals [161]. The production of OH radicals by these pathways results in a higher sensitivity fuel (i.e., higher aromatic content), having shorter ignition delay times in the intermediate temperature regime.

In summary, kinetic modeling simulations with multicomponent surrogate mixtures give deeper insight into the effects of molecular composition on important gasoline combustion properties, such as ignition delay. Novel gasoline engine technologies that rely on stratified or partially premixed charges may also be increasingly sensitive to physical properties of the gasoline fuel, such as density, viscosity, and distillation profile. Complex surrogate mixtures are typically needed to match the entire boiling point range of real gasoline fuels. Additional research will determine the required complexity of gasoline surrogates needed to replicate coupled chemical kinetic phenomenon (i.e., gas-phase reactivity) and physically driven phenomenon (i.e., mixture formation, spray characteristics, etc.).

5. Summary and outlook

Growing global demand for transportation is increasing the need for gasoline fuels. It is expected that gasoline fuels will be widely used in both SI and CI engines, with various fundamental research topics requiring attention. This review demonstrates the need for a fundamental understanding of gasoline combustion characteristics to overcome the challenges limiting the development of advanced gasoline engine technologies. These included, but were not limited to, mitigation of knock and superknock in SI engines, robust ignition and combustion control of gasoline in CI engines, and mitigation of harmful pollutant emissions. These practical engine phenomena were shown to be linked to several fundamental combustion properties, such as ignition delay time, laminar flame speed, heat release rates, and species formation. The development of surrogate mixtures, together with corresponding experimental and theoretical studies on gasoline fuels and their surrogates, were comprehensively discussed in this work.

Despite recent advances in our understanding of gasoline surrogate fuel formulation, experimental measurements and chemical kinetic modeling, this review identifies areas where significant research advances are required to overcome challenges facing the development of high efficiency and low emission gasoline engines. This review identifies an overarching fuel-engine design methodology that has evolved in recent decades. The general design process presented in Fig. 1 shows how fuels and engines can be optimized to maximize efficiency and decrease negative environmental impacts. Current challenges in the design process are highlighted in the following discussion, while future research directions are provided in Box 1.

The first step is to gain detailed knowledge of gasoline fuel production and engine technologies. The combustion characteristics of gasoline strongly depend on the type of crude oil, the refining process, and the blending of petroleum derived fuels with bio-derived components. The fuels must be well characterized, using not only standard ASTM or EN test methodologies, but also more advanced molecular characterization techniques. Technologies already exist to perform fuel production and characterization measurements needed for the proposed design process; but, improved simulation tools are needed to predict fuel properties based on production processes.

With a sound understanding of the physical-chemical characteristics of a gasoline fuel, the second step is to generate surrogate mixtures comprising a limited number of components. As shown in this review, this can be readily achieved using computational tools to match a range of gasoline fuel target properties. The primary challenge remains, wherein determining the important target

properties requires detailed knowledge of the engine combustion process. Therefore, a systematic study is needed to determine the relationship between various physical–chemical target properties and their impact on combustion processes in a specific engine hardware.

Once a surrogate is defined, it should be tested in fundamental combustion devices alongside the real gasoline fuel. As shown in this review, experiments in high pressure ignition devices, flow reactors, and laminar flames provide detailed insights into gasoline combustion chemistry. Despite the large amount of data available, there is a dearth of experimental measurements on complex mixtures comprising more than two or three surrogate molecules. Such information is needed for the development of kinetic models and understanding mixture effects. This leads to the fourth step in the design process: developing a surrogate chemical kinetic model. This review has shown that chemical kinetic models are available for many gasoline relevant molecules, but better models are still needed for cycloalkanes (naphthenes) and alkenes (olefins). Furthermore, the development of kinetic models for gasoline mixtures with many components is required.

The present review provides a detailed overview of steps one through four; and it has been shown that understanding complex gasoline fuel properties on combustion processes can help predict important phenomenon, such as heat release rates in advanced combustion engines and octane rating. However, significantly more research is needed to extend this approach to realistic engine environments. The sixth step in the design process requires translating the fundamental knowledge of gasoline combustion into complex engine hardware environments. Under such conditions, spray processes and mixing act together with gas-phase chemistry to control the combustion process. While many studies from engine literature have interpreted fuel/engine interactions, this review identifies a scarcity in the use of multi-component surrogates in engine research. The use of these complex surrogates in engine experiments and numerical simulations can help develop a more detailed understanding of gasoline fuel/engine interactions.

Finally, an important aspect of the design process is a fundamental understanding of fuel/engine combustion processes, emissions, and environmental impact. A large amount of experimental literature (e.g., [354,355]) already exists to study the link between fuels, combustion emissions (i.e., soot, NO_x, etc.) and environmental impact. However, an implementation of this knowledge into the design process requires large-scale computational simulations, which predict the effects of combustion emissions on regional and global air quality [356–358]. This realization of this framework can lead to new opportunities of designing optimal fuel/engine technologies with maximum efficiency and minimal environmental impact.

BOX 1 - Future directions for gasoline surrogate formulation research

- Insights into the relationship between gasoline composition and engine performance are achieved by studying surrogate mixtures in fundamental experiments. However, these experiments must be designed to investigate engine-relevant phenomenon. The fuel effects of on pre-ignition and super-knock can be better understood with fundamental experiments in ST and RCM. Recent work [132,359–361] has shown that ignition in these devices is not always homogeneous, and phenomenon such as early flame development and transition to detonation can be studied in ST and RCM.
- Spray combustion devices such as constant volume combustion chambers (CVCC) and ignition quality testers (IQT) have been extensively used to study diesel spray combustion

[207,362–365], but only a few studies exist on gasoline fuels [366,367]. Research should be directed towards acquiring liquid spray and combustion data for various gasoline fuels, surrogate mixtures, and injector geometries. This would also facilitate the development of high-fidelity spray combustion simulations.

- This review identified a lack of kinetic modeling validation data for practical gasoline fuels and multicomponent surrogate mixtures. Laminar flame speed measurements are needed at higher pressures (up to 30 bar) and unburnt gas temperatures (400–600 K). Total and first stage ignition delay time measurements at higher pressures (up to 100 bar) and lower temperatures (550–950 K) are required to validate kinetic models in the low temperature and NTC regimes. Speciation measurements in flames and flow reactors have been largely restricted to higher temperatures and lower pressures. Therefore, efforts are needed to better capture combustion intermediates at elevated pressures (> 1 bar) and low- to intermediate- temperatures (550–950 K). In particular, measurements are needed to understand mixture effects on oxidation intermediates in the low temperature regime and particulate matter formation at higher pressures.
- Engines experiments with multi-component surrogate mixtures are needed. These experiments should use the same surrogate mixtures as those used in fundamental devices (e.g., ST, RCM, flames), so a link can be established between fundamental and applied combustion systems. In addition, engine experiments with surrogate fuels will improve the accuracy of CFD engine simulations by removing uncertainties in the modeling of fully blended gasoline fuels.
- Chemical kinetic models for various gasoline surrogate components have advanced significantly in the last decade. However, consistency in thermochemical and kinetic rate parameters is currently limited to n-alkane models, and significant work is needed to improve kinetic models for other hydrocarbons. Improved models for C₆–C₈ isoalkanes, C₆–C₈ cycloalkanes, and C₇–C₉ aromatics are needed. Furthermore, kinetic models capable of simulations multicomponent mixtures (e.g., up to ten components) will be useful for determining if and when complex surrogate mixtures are needed.
- Engine combustion is governed by complex physical (e.g., droplet breakup, spray evaporation, air/fuel mixing) and chemical (e.g., gas-phase chemical reactions) processes, but it is often difficult to decouple fuel property effects, especially in new combustion concept engines [368,369]. Surrogate fuel mixtures offer an opportunity to study these processes separately. For example, mixtures with similar physical properties but widely varying chemical kinetic properties (e.g., various isomers of octane) could be investigated.
- Reduced mechanisms are regularly published to simulation gasoline surrogate mixture combustion in engines [370,371]. However, the release of reduced models often cannot keep up with the pace of advances in detailed chemical kinetic models. Therefore, new open-source model reduction tools should be developed to enable use of the latest detailed chemical kinetic models in CFD simulations.
- Research has been conducted on non-oxygenated gasoline fuels and their surrogates, but few fundamental studies exist on the effects of various additives to gasoline fuels. Common antiknock additives, such as ethanol and MTBE, have been studied in engines, but the underlying chemical kinetic mechanisms contributing to their improved antiknock

quality could be better investigated in fundamental devices. Indeed, it is widely known that blending octane numbers of additives (e.g., ethanol [118,372–374]) vary depending on base fuel octane number and composition. However, theoretical explanations and models capable of prediction blending octane can only be achieved by detailed studies with surrogate mixtures. These studies could improve the design of higher efficiency octane on demand technologies.

- Finally, a cradle-to-grave approach for gasoline fuel development research is needed. The environmental impact of new gasoline fuel production technologies as well as improvements in end-use engine technologies need to be analyzed and optimized together. Surrogate fuel mixtures are necessary for developing complex models to simulate fuel production, combustion, and environmental fate. Systems wide studies [375–378] on net CO₂ emissions and other environmental indicators offers the potential for optimal fuel/engine design.

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Supplementary materials

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