Preprint of: Martin, C.D., Shepherd, J.E. "Low temperature autoignition of Jet A and surrogate jet fuel." Journal of Loss Prevention in the Process Industries, 71, 104454, 2021. Final version at: https://doi.org/10.1016/j.jlp.2021.104454

Low temperature autoignition of Jet A and surrogate jet fuel

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ARTICLE INFO

Keywords:
Autoignition
Thermal Ignition
Jet A
Surrogate Fuels
ASTM-E659

ABSTRACT

An experimental study of the low-temperature and low-pressure autoignition of Jet A and surrogate fuels was conducted using the ASTM-E659 standardized test method. Two surrogate fuels (Aachen and JI mixtures), their individual components and two batches (POSF-4658 and POSF-10325) of standardized Jet A were tested using the ASTM-E659 method for a range of fuel concentrations and temperatures. The ignition behaviors were categorized into four distinct ignition modes. The individual hydrocarbon components had a wide range of ignition behaviors and minimum autoignition temperatures (AIT) values depending on the molecular structure. The two Jet A batches showed similar ignition behavior with measured AITs of 229 ± 3°C and 225 ± 3°C respectively. Both surrogates exhibited similar ignition behavior to Jet A with comparable AITs of 219 ± 3.1°C (Aachen) and 228 ± 3°C (JI) with the JI mixture proving to be a more suitable surrogate to Jet A in the low-temperature thermal ignition regime.

1. Introduction

1.1. Autoignition Background

The study of thermal ignition has been of interest to the combustion community for over a century with initial motivation arising from areas like process safety where the use, storage and shipment of combustible liquids was rapidly becoming commonplace in many areas of the world economy. This led to the development of standardized methods for determining minimum autoignition (AIT) or self ignition temperature (SIT) criteria for spontaneous thermal ignition of a given substance in air at atmospheric pressure.

A comprehensive summary of the early efforts to create an AIT test was given by Setchkin (1954). His studies led him to develop what would become the forerunner to the modern day ASTM-E659 standardization for determination of the AIT (ASTM, 2005). In this test, a small quantity of liquid fuel (0.05 to 0.5 mL) is injected into a preheated flask containing hot air with ignition determination made by visual observations and temperature measurements. Setchkin's study found that the minimum AIT is typically decreased as combustion chamber size is increased. Depending on the substance, this can have a large effect ($50-100$°C) on the measured AIT. From this and other details uncovered in these early studies it became clear that the AIT is not a fundamental property of a substance alone but is rather highly dependent on the method and apparatus used in its determination. More recent work at PTB has further illustrated this fact through studies on the influence of increased pressure, nitrogen dilution levels, and combustion vessel volume on AIT (Hirsch and Brandes, 2005; Brandes and Hirsch, 2017a,b).This makes it crucial to fully understand the methodology used in obtaining an AIT value if it is to be of any use in practical analysis and engineering design applications where conditions may differ significantly from the standard tests.

A similar test was also proposed by Zabetakis et al. (1954) in the same year as Setchkin (1954), with the major differences being the use of a 200 mL Erlenmeyer flask in place of the larger spherical flask and the use of the flask temperature instead of the gas temperature to report the test condition. This apparatus seems to also have been the forerunner of a separate AIT standardization, ASTM-D2155, which was discontinued in 1978 in favor of the E659 standard (ASTM, 1976), as well as the current international standard (ISO/IEC, 2017).

Although the ASTM-E659 is the now the widely accepted standard in North America for AIT determination, literature sources rarely specify this as the method used in obtaining their reported AIT's. Many safety data sheets (SDS) and chemical databases cite the origin of reported AIT numbers, but in almost all cases these sources are simply other chemical databases or property handbooks which do not claim to have performed any testing themselves or have cited a different test method for AIT determination, e.g., Sax (1957); Zabetakis (1965); CRC (1983); NFPA (1991);

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USCG (1999); Zakel et al. (2019). As a consequence, it is challenging to determine the origin of reported AIT numbers or the details of the testing method. This lack of consistency in the literature complicates the comparison of AIT values of different fuels or the same fuels tested by different research groups.

The nature of the data also hampers the development of models for the prediction of the AIT based on molecular properties alone. Affens et al. (1961) used the same apparatus as Setchkin (1954) in an effort to correlate ignition behavior to chemical structure for various classes of alkane and aromatic substances. They noted some correlations between a decrease in chain length, methyl groups, unsaturation, and chain branching with an increase in the minimum AIT for aliphatic hydrocarbons as well as a correlation between existing side chains and side chain length and increased AIT for alicyclic compounds and aromatics (Affens et al., 1961). More recently, a study by Tsai et al. (2012) attempted to fit a model to the AIT of 820 compounds reported in the DIPPR database based on a set of molecular descriptors. This approach was moderately successful (36°C mean absolute error) in reproducing experimental AIT values. Given the manual nature of the injection process and the wide range of fuel vapor pressures and viscosities examined in these studies, it is not surprising that there are significant discrepancies between test data and predictions based solely on molecular structure.

A significant issue in interpreting and modeling the ASTM-E659 test is the lack of characterization or control of the mixing processes between the fuel and hot air. The formation of droplets, vaporization and diffusion of the fuel into the air, convective motion and the potential impingement of the fuel on the hot flask surface make this a very challenging situation to measure and model. The fuel-air mixture is likely to be highly nonuniform as is the temperature distribution due to the cooling effects of fuel vaporization. Despite the widespread use of ASTM-E659 and related test methods, the inherent variability and complexity has inhibited scientific investigations and modeling efforts. A brief summary and discussion of some of these issues related modeling and theoretical treatment of AIT is presented in Hattwig and Steen (2004).

Although widely used in safety assessment and setting design criteria, it is apparent that the ASTM-E659 test is not always an appropriate method for evaluating industrial thermal ignition hazards. In the particular case of aircraft, most of the hot surfaces encountered are metals (steel, nickel and titanium alloys, and aluminum) rather than glass as in ASTM-E659 testing. These are important considerations since the surface material can have a significant effect on the ignition thresholds for some fuels ($>$ 100°C variation) (Smyth, 1990). However the influence of surface material is only minor in cases where the surface is not catalytically effective and surface reactions do not dominate (Roth et al., 2017). Even more important than surface material are the differences between the confined flow within the vessel used in ASTM-E659 testing and unconfined or partially confined external flows that occur in many industrial situations. The heated surface geometry and residence time in the thermal layer (Jones and Shepherd, 2020) can be significantly different in actual hazards than in ASTM-E659 testing. This is important because fuel decomposition and the formation of the ignition kernel has been observed to take place preferentially close to the heated surface (Coronel et al., 2019). For some geometries, the orientation of the heated surface has also been shown to play an important role in the ignition process. Velagala et al. (2020) studied this issue for the case of heated hemispheres in a range of orientations which resulted in distinct differences in the development of thermal plumes in the bulk flow which ultimately led to different ignition kernel locations and delay times.

Heating transients and ignition events can also occur over much longer times than the 10 minutes examined in ASTM-E659 testing. Longer duration experiments can lead to significant fuel decomposition as well as unusual ignition transients without any obvious rapid energy release (Boettcher et al., 2012). These types of tests near the autoignition threshold are therefore complicated by the existence of these longer duration, weaker ignition modes or "cool flames" which blur the traditional definition of ignition. In the ASTM-E659 guidelines some general ignition criteria is given as the appearance of a luminous flame accompanied by a temperature rise of at least a few hundred degrees (ASTM, 2005). Some further discussion is also given on cool flames and preflame reactions for cases which don't meet the ignition criteria. However, in the present study there was found to be more nuance in these near threshold reactions for many of the fuels studied, especially multi-component fuels like Jet A. A spectrum of ignition events ranging from non-luminous slow reaction to rapid and luminous flames is observed as a function of fuel composition and amount. We have classified the events into four categories by the magnitude of the temperature rise and visible luminosity in order to summarize our results but this classification is subjective. The wide range of observed behavior demonstrates the complexity of autoignition and the challenges of determining a threshold temperature that is appropriate for all situations.

Studies of autoignition behavior of commodity fuels have been conducted using heated shock tubes and rapid compression machines (RCMs) to measure ignition delay times. In comparison to ASTM-E659 testing, these studies have well-controlled conditions and instrumentation that enables validation of chemical reaction models of ignition. However, the test gas temperatures are significantly higher than those relevant to low temperature thermal hazards and the minimum AIT conditions examined in ASTM-E659 testing. These ignition studies (Vasu et al., 2008; Wang and Oehlschlaeger, 2012; Liang et al., 2012; Zhukov et al., 2014; De Toni et al., 2017) have also mainly been conducted at elevated pressures ($8 - 51$ atm) which are uncharacteristic of thermal ignition hazards in aircraft and industrial hazards associated with accidental releases. These studies examined kerosene fuels (including Jet A) however with the typical wide variation in composition found in commodity supplies (Edwards, 2017). The variability in commodity fuels and the associated uncertainty in the experimental results has motivated the development of surrogate fuels as well as standardized batches of Jet A to facilitate comparison between experimental studies.

1.2. Surrogate Fuels

Commodity fuels like gasoline, diesel or Jet A typically consist of hundreds of different hydrocarbon species in imprecise and varying quantities, even between different batches of the same fuel. This complexity makes it difficult both to accurately reproduce experimental results across distinct fuel batches and to model the reaction mechanisms leading to ignition. As an alternative, suitably representative mixtures of hydrocarbons, called surrogate fuels, can be developed to mimic a few important commodity fuel characteristics such as laminar flame speed, ignition delay time, cetane number and distillation curve while consisting of only a handful of species in well controlled concentrations (Mueller et al., 2012; Chen et al., 2016; Kim and Violi, 2018). This makes surrogates much more amenable to experimental reproducibility as well as numerical modeling because the species and reaction pathways to consider are both far fewer in number and typically much better understood than they are for many components of the commodity fuel. Several surrogate fuels have been developed in the literature to mimic Jet A ignition behavior at high pressures and a range of temperatures similar to the studies previously mentioned ($T = 645 - 1750$ K at $8.5 - 20$ atm). These surrogate fuel studies have used the existing shock tube and RCM data from the previously mentioned studies as sources of validation of their proposed surrogate blends (Dean et al., 2007; Dooley et al., 2010; Chen et al., 2016). Few if any of these detailed surrogate studies have been performed in the very low-temperature (< 600 K) and low pressure regime of autoignition likely due to the scarcity of data available in this regime for model validation. Some simple fuels like n-hexane have been studied extensively at these conditions (Mével et al., 2019) but these studies have not yet been performed on larger hydrocarbon molecules that are more characteristic of Jet A. For this reason, it is unclear if the previously developed surrogates are relevant to autoignition of Jet A at low pressure and temperature conditions.

Two Jet A surrogates from the literature have been identified in this study for their relevance to matching ignition behavior as well as for their simplicity in composition. These surrogates are: (1) the Aachen surrogate (Honnet et al., 2009): n-decane/1,2,4-trimethylbenzene, (80/20 wt%), and (2) the JI surrogate (Chen et al., 2016): n-dodecane/iso-cetane/trans-decalin/toluene, (29.15/46.51/19.40/4.94 wt%). These surrogates were formulated in an effort to match high-temperature and high-pressure autoignition behavior of Jet A so it is crucial to determine if their usefulness can be extended to Jet A studies focused on the low temperature and low pressure regime of thermal ignition. This is indeed one of the main goals of the present study. To validate these surrogates' ignition behavior in the regime of interest, two well-controlled and extensively studied (Edwards, 2017) blends of Jet A were also examined: POSF-4658 and POSF-10325. These fuel blends also provide a quantifiable baseline for comparison with the surrogate samples on a chemical level which is shown in Table 1.

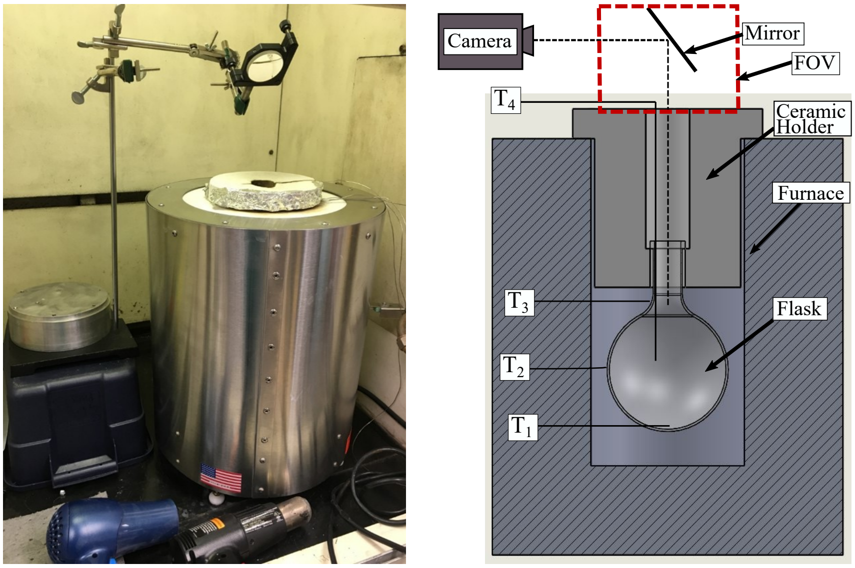
In studying multi-component liquid fuels like these surrogates and Jet A, there are several difficulties one must be aware of. The major challenge in performing experiments in particular is the discrepancy between the gas phase and liquid phase compositions owing to differences in vapor pressure of the individual species. This is especially important in this work as all ignition takes place in the vapor phase. Therefore in order to appropriately match the Jet A ignition behavior with a surrogate, it is the vapor phase composition that must be matched. This approach is taken in the literature with the computational formulation of the JI surrogate which was designed to match the distillation curve of Jet A in order to match both droplet evaporation and ignition behavior (Chen et al., 2016). Other surrogate studies like that of the Aachen surrogate instead simply attempted to reduce to as few representative components as possible and to roughly capture the properties of the alkanes and aromatics with one compound of each without a comprehensive analysis of the physical chemistry at play in the mixture (Honnet et al., 2009).

Table 1
Comparison between composition of Jet A blends and surrogate fuels

		% by Weight			
		POSF-4658	**POSF-10325**	**Aachen Surrogate**	**JI Surrogate**
Alkanes	n-alkanes	19	19.98	80	29.17
	iso-alkanes	31.34	29.69	-	46.53
	cyclo-alkanes	28.42	31.79	-	-
	Total	78.76	81.46	80	75.7
Aromatics	alkylbenzenes	13.69	12.9	20	4.94
	alkylnapthalenes	1.76	2.34	-	-
	aycloaromatics	5.79	3.29	-	19.41
	Total	21.24	18.53	20	24.35
Average Molecular Formula		$C_{11.69}H_{22.62}$	$C_{11.4}H_{22.1}$	$C_{9.77}H_{19.7}$	$C_{12.49}H_{25.22}$
H/C ratio		1.935	1.939	2.016	2.019

2. Experiments

The procedure and testing apparatus employed in this study was the same as that described in the ASTM-E659 standardized test specification for the determination of the AIT and so the test method is only briefly discussed. The test apparatus is pictured in Fig. 1 along with a schematic representation of the combustion vessel contained within the furnace. A small liquid sample of the fuel to be tested was injected via syringe into a uniformly heated 500 mL flask containing room air and left open to the atmosphere. The lights were turned out and the sample was observed via a mirror mounted above the flask opening using a Phantom VR3746 high speed camera which was manually triggered upon ignition of the sample. The gas temperature within the flask was also recorded and monitored during each test in order to determine the extent of self heating occurring in the sample and to provide a secondary indication of ignition via the presence of a sharp temperature spike. This was also used to obtain a measure of ignition delay time, τ_{ign} which was defined as the time between fuel injection and ignition. Typically these events were very easily distinguished in



(a) (b)

Figure 1: (a) ASTM-E659 test apparatus. (b) Schematic showing a cross section of the internal heated region with thermocouple locations highlighted and camera field of view (FOV)

Table 2
JI surrogate (Batch 1) results from GC-FID analysis

	% by Weight			**Vapor Pressure[a] (kPa)**
Fuel	**Target**	**Measured**	**% Error**	-
n-dodecane	29.15	29.80	2.24	0.012
iso-cetane	46.51	46.43	0.15	0.004
decalin	19.40	20.66	6.49	0.116
toluene	4.94	3.10	37.2	2.903

[a] $T = 20°\mathrm{C}$; Sund (2019)

the temperature profile with the injection corresponding to a steep temperature drop by a few degrees and the ignition evidenced by a sharp temperature rise. However, as will be discussed in section 3.1, some temperature profiles did not exhibit such a sharp spike in temperature which led to the classification of multiple distinct ignition modes.

Each test was limited to no more than 10 minutes, at which point if ignition had not yet been observed then a non-ignition case was recorded. If instead a flame appeared or the temperature profile indicated some steep temperature increase then an ignition or cool flame event was recorded. However, in many cases it would become clear that the sample was not going to ignite long before the 10 minute limit as self heating typically only lasted for around five minutes after injection for the substances studied here. After the gas temperature leveled off, it was usually evidence that a limit had been reached and the temperature would begin to decay. In these cases, the sample was observed for an additional two minutes after the level off and if the decay continued then the test was considered as a non-ignition case and preparation for the next test would begin. Preparation for the next test included the use of a hot air gun or blow dryer applied to the top of the apparatus for up to 30 seconds in order to purge the flask of any remaining ignition products or unburnt fuel. Following purging, temperature adjustments were made via a temperature controller and the furnace was allowed to return to equilibrium at the new set temperature.

2.1. Equipment

The furnace used was a Mellen CV12 crucible furnace with a 13.3 cm diameter by 20 cm deep cylindrical heated volume capable of achieving temperatures up to 1250°C. A PID controller (Love Controls series 16B) system was used to set the furnace at the desired temperature and was accurate to 1°C. A schematic cross section of the apparatus is shown in Fig. 1b which illustrates the location of the 500 mL round bottom borosilicate flask within the heated volume along with the four thermocouples used to monitor the temperature evolution during a test. The flask was suspended and secured in the furnace by means of an insulating ceramic holder fabricated using a fused silica casting compound.

The location of the four type K thermocouples are also shown in the schematic in Fig. 1b with the gas temperature being read from T_4 which was suspended approximately in the center of the flask volume. Preliminary tests to characterize the apparatus showed that the location of the gas phase thermocouple within the volume had little effect on the reading (±0.5°C) providing indication of temperature uniformity within the flask at elevated temperatures. The thermocouples were constructed from 36 gauge (0.127 mm diameter) wire and sheathed in stainless steel for protection. The temperatures at the bottom, side, and neck of the flask's outer wall were monitored via T_1,T_2,and T_3 respectively. The temperature of the flask wall was much less uniform than the gas, with typical variations of up to 5°C when set near 250°C or 10 – 15°C above 400°C.

Temperature profiles were recorded from the time of injection through any self heating or ignition event using an OMEGA HH520 four channel data logger calibrated to the nearest 0.1°C up to 600°C and 1°C for higher temperatures. All channels were sampled at 1 Hz as per the ASTM-E659 specification. Reported experimental errors were estimated based on both the standard error limits for type K thermocouple probes and the reported error of the HH520 datalogger itself.

2.2. Surrogate Fuel Preparation

An early attempt at mixing the surrogates was made using a Tree Model HRS3100 scale calibrated to the nearest 0.001 g to weigh out the individual compounds, but this method proved unreliable as shown by GC-FID (Gas Chromatography with Flame Ionization Detector) measurements (Sund, 2019). The first batch of surrogate used a mixture of trans- and cis-decalin (the AITs of these isomers are similar) and the mixture is much easier to obtain in larger

Table 3
Classifications of various ignition modes observed in ASTM-E659

Ignition Mode	Name	Luminosity	Temperature Rise (ΔT)	Timescale for reaction
I	Ignition	Large	Large	< 2.5 mins
II	Cool Flame	Small	Small	$0.25 - 4$ mins
III	Non-Luminous Cool Flame	None[a]	Large	$1 - 5$ mins
IV	Rapid Reaction	None	Small	$0.5 - 2$ mins
-	Non-Ignition	None	<15°C	$> 4 - 5$ mins

[a] Faint glow only visible to naked eye and small puff of smoke

quantities than either isomer individually. The second batch of the surrogate which was used for the AIT testing used only the trans-decalin isomer. The mass fractions obtained in the GC-FID analysis as well as target values are shown in Table 2.

The results showed that for the JI surrogate, two of the four components had relatively large percent errors in their measured mass fractions (toluene and decalin). These two components also both happened to have the smallest target mass fractions and toluene in particular had the highest vapor pressure by far at room temperature. As a result, it was determined that there were two possible factors at play in producing such larger errors, (1) inaccurate mixing and (2) poor sealing/storage of the fuel batch. To address these issues, two changes were made in mixing the second batch of JI, namely (1) the use of pipettes to measure out the components volumetrically, and (2) the use of higher quality storage vessels (PTFE lined caps) and a chemical refrigerator to maintain the batch at a low temperature in order to lower the vapor pressure of the entire mixture and mitigate the preferential loss of lighter compounds over time. The second batch was mixed on a volumetric basis using graduated pipettes into a large 146 mL total batch in order to minimize volume measurement errors especially in the more dilute components. This batch was then stored in an ABS flammable storage refrigerator maintained at 3°C and smaller quantities were extracted for use in the autoignition experiments.

3. Results and discussion

3.1. Classifications

Throughout the range of ignition tests conducted here, there were 4 distinct ignition modes observed along with non-ignition cases. These ignition behaviors were classified as (I) Ignition, (II) Cool Flame, (III) Non-Luminous Cool Flame and (IV) Rapid Reaction. These were distinguished using a combination of visual evidence as well as the reading of the gas phase thermocouple (T_4). Qualitatively the differences between these modes are summarized in Table 3. This classification is limited mainly to qualitative descriptors since the temperature rises and timescales for the same ignition mode can vary substantially between two different fuels or even different compositions of the same fuel. For instance mode III ignition events for n-decane were seen to produce a temperature rise of 50 – 200°C on timescales of between one and a half and three and a half minutes for various fuel volumes while for Jet A these events were only capable of 25 – 70°C temperature increases on similar timescales. Luminosity was determined via the use of high speed video capture of the approximate field of view shown as the red rectangle in the schematic of Fig. 1b.

A representative time series of images and temperature traces for each of the first three ignition modes is shown in Fig. 2. The thermocouple traces display the difference between the initial gas temperature and the peak temperature measured by T_4 and are used to define the peak temperature rise. In some cases the visual evidence alone was not sufficient to distinguish between ignition modes I and II so the thermocouple trace was used for classification. Mode II ignition was always characterized by a longer ignition delay time as well as a lower peak temperature as compared to mode I events for the same fuel. Mode III also had a far longer timescale than the other modes which further distinguished it from the other modes. Mode IV was unique in that the reaction delay occurred on a similar timescale as that of a normal mode I ignition but resulted in a very small temperature spike, in some cases comparable to non-ignition cases.

For the mode I events, the images show that the initial explosion progresses rapidly and the flame quickly expands out the top opening of the flask before burning out. For the case shown in Fig. 2, the first image shows an ignition

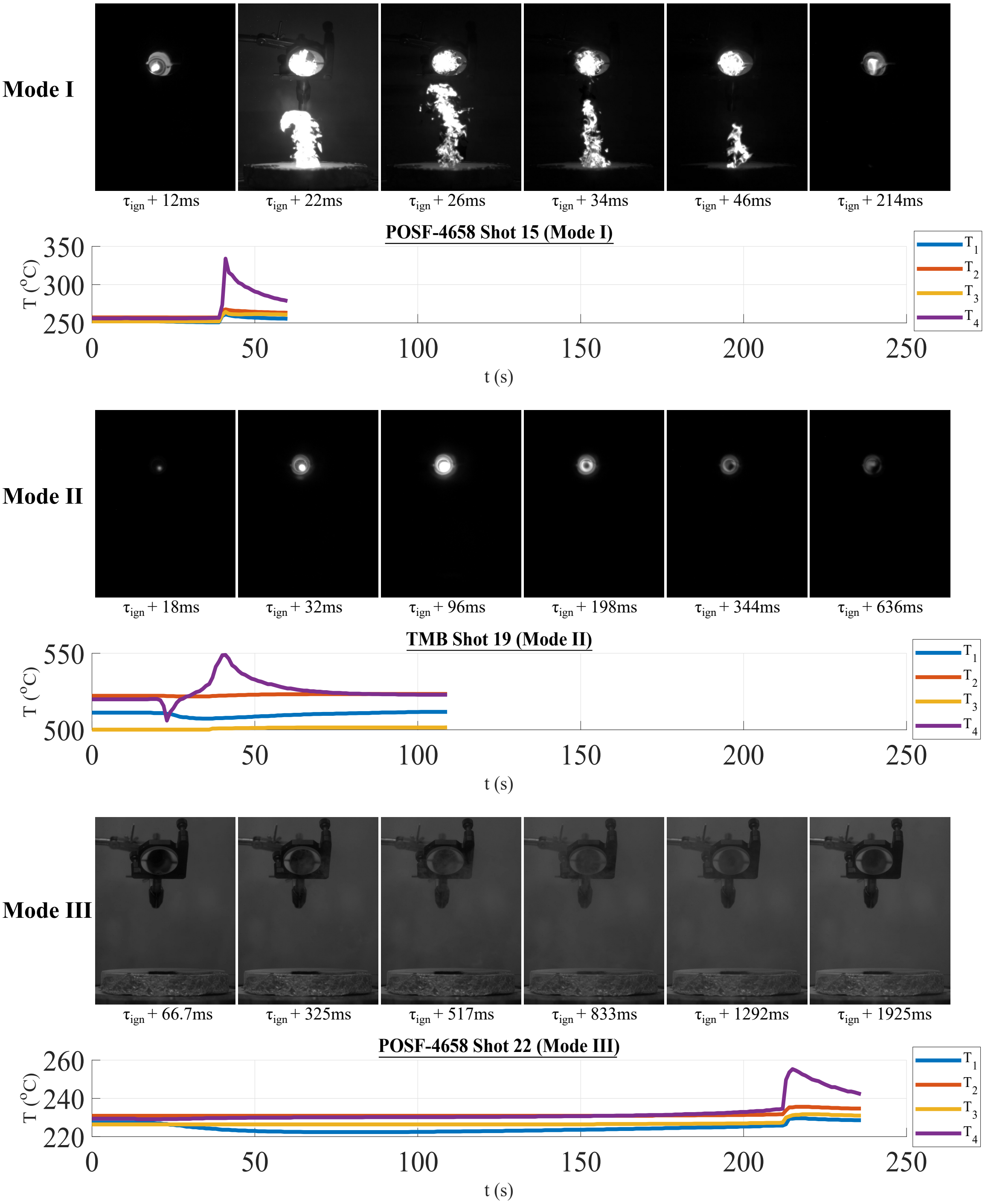


Figure 2: Representative ignition events for 3 distinct ignition modes: (I) Ignition, (II) Cool flame, (III) and Non luminous cool flame (Note these correspond to POSF-4658 Shot 15, TMB Shot 19, and POSF-4658 Shot 22)

kernel forming within the flask as observed in the mirror followed by a series of images showing the flames expansion into the region above the testing apparatus in a period of around 14ms. The final three images show the longer period over which the flame in the outer region becomes extinguished while the gas within the flask continues to burn. All four thermocouple traces show a quick rise, for T_4 this is of order 100°C. The rapid decay following the peak is due to the expulsion of the products from the open top as well as heat transfer to the vessel.

For mode II events, it was typically observed that the ignition event is less energetic and the flame remains confined to the interior of the flask which is indicative of a low pressure rise and is consistent with the measured low temperature rise. For the Mode II case in Fig. 2, a faint ignition kernel is seen in the mirror followed by a more gradual increase in luminosity over the next few images. In the fourth mode II image a dark central region of soot formation is observed which grows to extinguish the flame in the final two images. Mode II was primarily observed in compounds with high ignition temperatures ($>$ 400°C) including the aromatics and iso-cetane. The T_4 thermocouple trace shows a pronounced drop due to the cooling effect of vaporization of the liquid fuel with possible contribution from endothermic reactions, followed by a slow rise to a peak with maximum rise of less than 25∘C. The liquid fuel apparently puddles on the bottom of the vessel and vaporization results a decrease in T_1 temperature followed by a slow return to the ambient value.

Mode III ignition events were more prevalent in heavier hydrocarbon species and were indicated by a brief and very dim glow visible to the naked eye only in complete darkness. Alternatively, a puff of smoke escaping from the flask could also be observed in these cases and was much easier to record with the current setup. A series of images for mode III is shown in Fig. 2. In the first image the background and mirror holding apparatus is entirely unobstructed but after a few hundred milliseconds a puff of smoke becomes visible beginning with the second image which persists over the next set of images for well over 1000 ms before dissipating fully in the final image. A temperature drop associated with fuel vaporization is observed on T_1 with a very slow return to ambient temperature. After a delay of about 210s, a temperature rise associated with exothermic reaction is observed on all four thermocouples with a maximum rise of about 25°C observed on T_4.

Mode IV was similarly non-luminous but was distinguished by a much smaller temperature rise and shorter timescale for the peak temperature to be reached as compared to mode III. These events were observed primarily for multi-component mixtures including the Jet A blends and surrogate fuels.

The results of the ASTM-E659 ignition testing are presented here for each of the Jet A batches and surrogates studied. These data are summarized for each fuel by separate plots containing each ignition test as a data point in the temperature-composition space. Also plotted are the reported AIT values from the literature sources discussed in section 1.1. However, these numbers are always reported as a global minimum with no associated composition given so these values are plotted as constant lines across the compositional domain. The peak temperature rise during each test (ΔT) was also recorded and is shown here for two fuels. Tests were also performed with the molecular components of each surrogate as well as n-hexane but complete results are not presented here.

A global equivalence ratio (ϕ) was defined in order to more easily compare results from fuels of different structure and molecular weight by putting the seemingly arbitrary fuel volumes into context. This ϕ is defined based on the vapor space for each fuel sample as if the fuel mass were fully vaporized and mixed homogeneously with air and is calculated by the equation

$$\phi = \frac{m_{fuel}/(\rho_{air} V_{flask})}{(F/A)_{stoich}} \tag{1}$$

where m_{fuel} is the fuel mass, V_{flask} is the flask volume, ρ_{air} is the air density, and $(F/A)_{stoich}$ is the stoichiometric fuel to air mass ratio. Using this parameter, it is much easier to see what the effect of having a fuel rich ($\phi > 1$) or fuel lean ($\phi < 1$) mixture is on the ignition behavior and to interpret the different ignition modes.

3.2. Alkanes

Three normal alkanes (n-hexane, n-decane, and n-dodecane) were studied along with one branched alkane (iso-cetane, also known as 2,2,4,4,6,8,8-heptamethylnonane). These compounds were chosen for study because they are the molecular components for both of the surrogate fuels studied (Aachen and JI). n-hexane was also chosen for study due to extensive previous work from our group on n-hexane ignition in various test conditions, see Boettcher et al. (2012, 2013); Mével et al. (2014); Coronel et al. (2018); Mével et al. (2019).

The first fuel studied was n-hexane for this reason and some early attempts were made to perform statistical analysis on the ignition results in a similar manner to previous spark ignition studies (Bane et al., 2013). For this reason much of the data was obtained for the same composition and the overall parameter space was not well explored. However as can be seen in Fig. 3 and some of the other samples studied, there is very little variability in the outcome of ignition events near the auto ignition temperature. The temperature range bounding ignition and non-ignition is typically contained within 5 − 10°C making statistical analysis challenging since this temperature interval is comparable to the measurement error of the temperature data acquisition system. An example of statistical analysis performed on the n-hexane data is presented in Fig. 3b. The experimental data points were used to compute the logistic curve and 95% confidence limits as described by Bane et al. (2013), where $P_{ign} = 1$ indicates ignition and $P_{ign} = 0$ indicates non-ignition. The literature (NFPA, 1991) value of AIT intersects the logistic curve at 40% probability, within a few degrees of the temperature corresponding to 50% probability of ignition. Though reasonably successful in application to the n-hexane data, statistical analysis of the data was found to problematic for other fuels where the measurement uncertainty became larger (e.g. for aromatics) or little to no crossover was observed in the outcomes of repeated trials at similar test conditions.

It was also found that certain factors like the injection location and the degree of decomposed fuel buildup on the

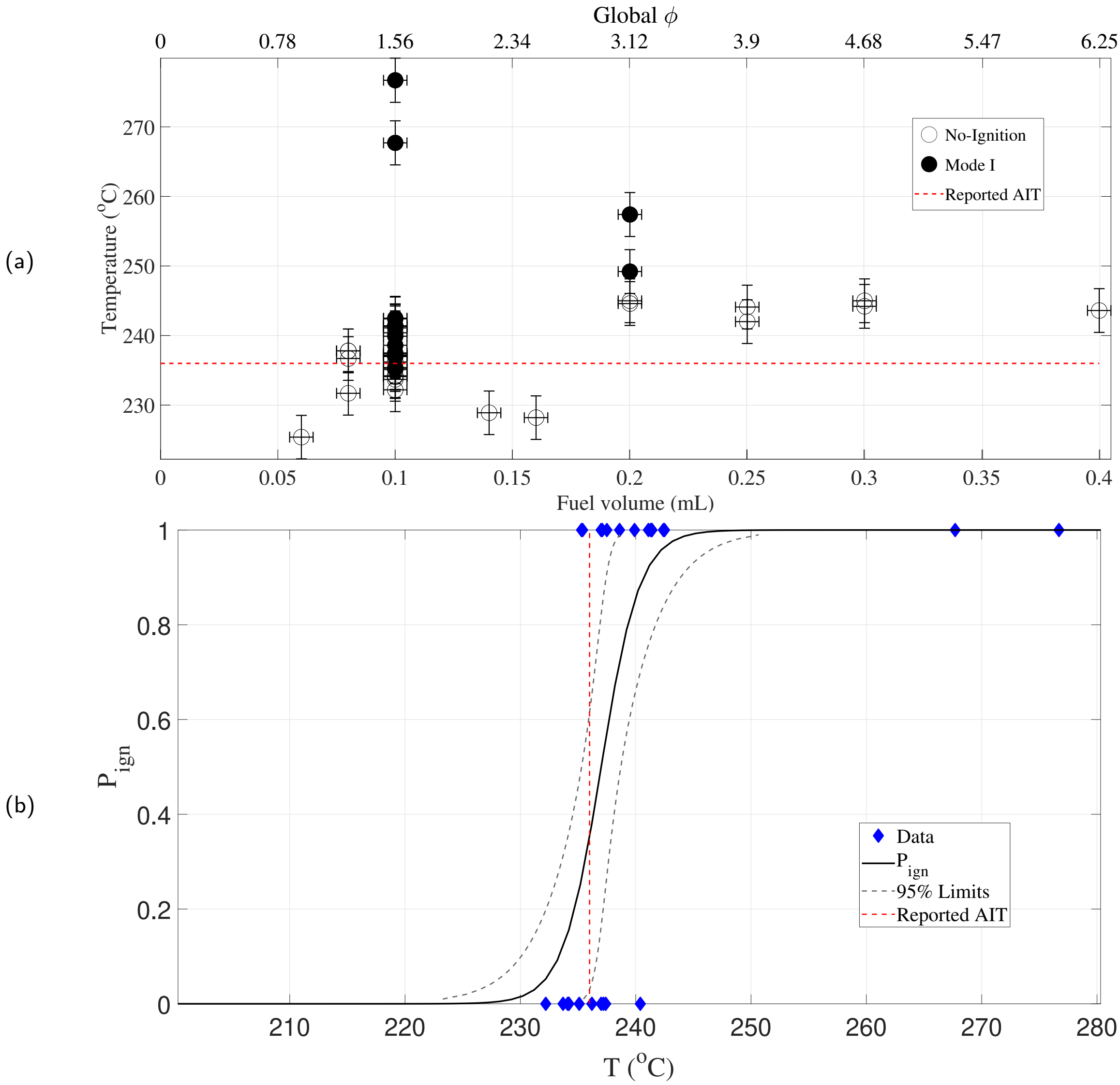


Figure 3: (a) n-hexane ignition testing results (b) n-hexane ignition statistical analysis using the logistic function (Fuel Volume = 0.1mL, Global $\phi = 1.56$)

flask surface due to repeated testing was able to impact ignition results. The impact on AIT was not fully quantified in the present study but seemed to be only a few degrees (< 5°C), which is of the same order as the measurement error and the range of ignition threshold data shown in Fig. 3b. The fact that we have not systematically applied statistical methods to characterize the results of our ASTM-E659 testing (other than for n-hexane) should not be taken to mean that there is no intrinsic variability in the test outcome but rather that the limited temperature measurement resolution capabilities and apparently narrow region of overlap between ignition and non-ignition for many fuels makes statistical analysis challenging. This difficulty could potentially be overcome with a much larger data set produced under more well-controlled conditions (e.g. injection location, extent of residue buildup on the flask, etc.). In any case, the variability (e.g., confidence interval) as characterized by statistical analysis is of similar order to the temperature measurement uncertainty so all results are presented using the temperature measurement uncertainty to characterize the variability in the results.

Additionally, many of our early n-hexane tests did not make use of a data logger for thermocouple traces so peak temperature data is not available. Despite this issue, we find that for n-hexane, there is good agreement between the literature (NFPA, 1991) AIT value (236°C) and our result ($T = 235.3 \pm 3.1$°C) obtained for a slightly rich mixture.

In the case of n-decane, a 6°C difference is observed between the reported (NFPA, 1991; USCG, 1999) AIT of

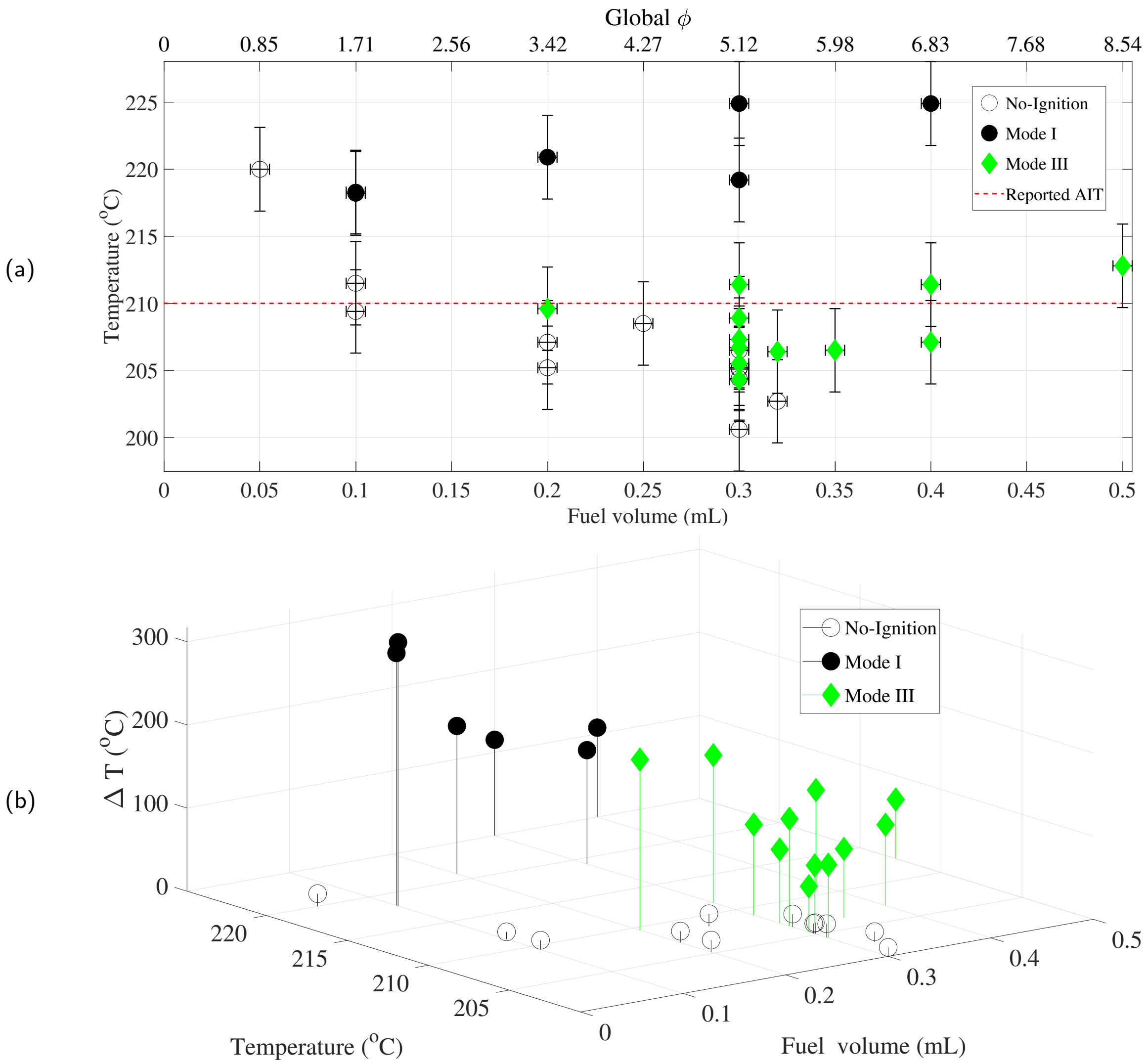


Figure 4: (a) n-Decane ignition testing results (b) Peak temperature rise

210°C and our experimentally determined value of 204.3 ± 3.1°C . In Fig. 4a we note some mode III ignition behavior near the AIT is also observed for globally rich mixtures with this behavior occurring over a rather broad range of temperatures near the AIT limit which seems to further broaden for even richer mixtures. In Fig. 4b we note that the peak temperatures in many of these cases are comparable to Mode I ignition temperatures with the exception of the slightly rich mixtures ($\phi = 1.71$) while n-decane rapidly becomes much harder to ignite closer to stoichiometric and in the lean regime.

Fig. 5 shows similar trends to those observed for n-decane with lean and near stoichiometric mixtures becoming harder to ignite and the rich regime producing some mode III events near the AIT limit. Fig. 5b also shows that these peak temperatures are comparable between mode I and mode III while the highest temperature rises are again seen occurring in the slightly rich regime ($2 < \phi < 4$) with a drop off in both leaner and richer conditions. The reported (NFPA, 1991) AIT value 203°C is quite close to our experimental value 202.2 ± 3.1°C. The is consistent with the small variation in the literature values as compared to many of the other fuels studied.

In Fig. 6, mode II events begin to dominate the rich compositional space for the iso-cetane samples which is in stark contrast to the mode I and broadening mode III regimes observed for the n-alkanes studied. Additionally it is

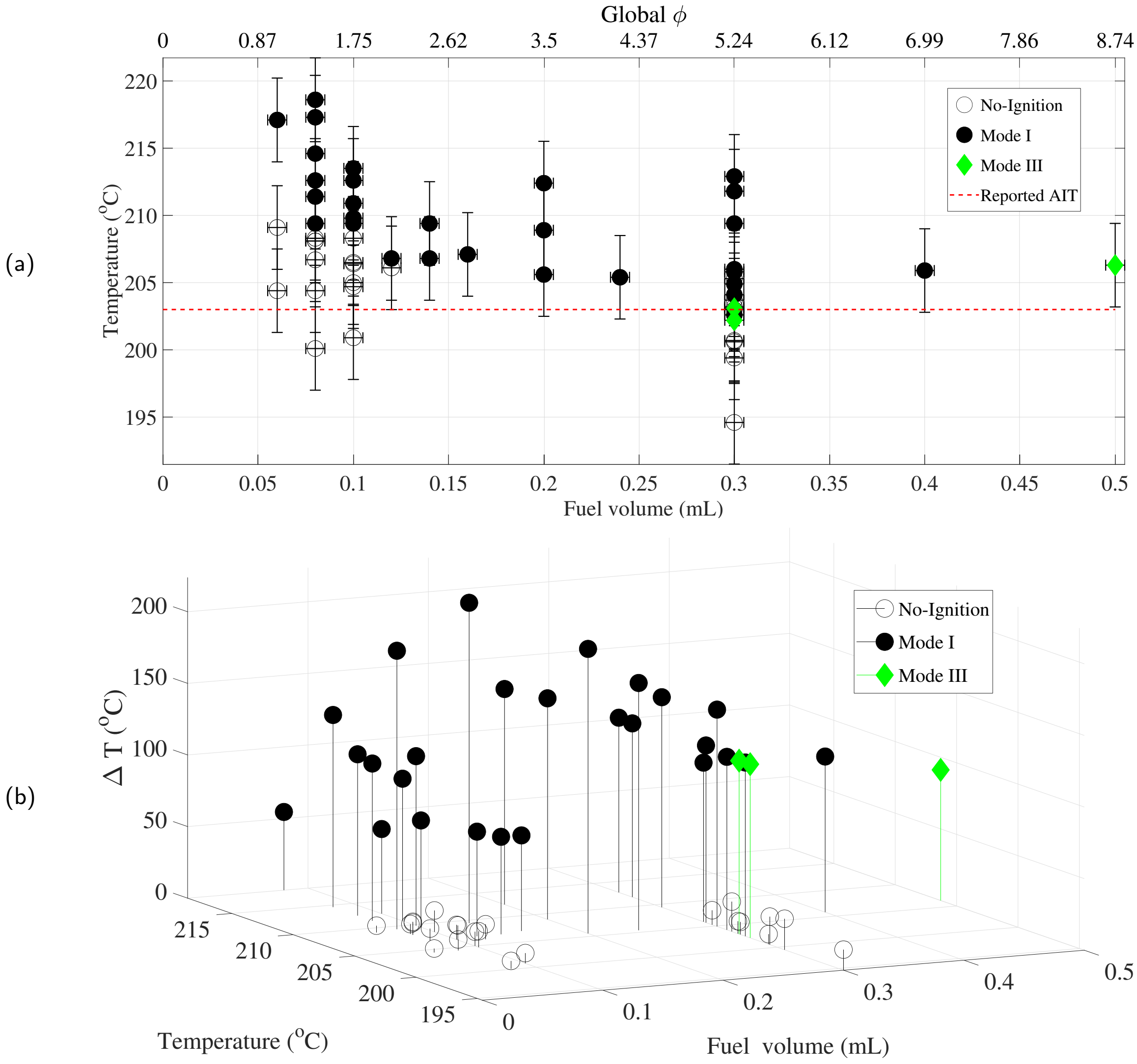


Figure 5: (a) n-Dodecane ignition testing results (b) Peak temperature rise

clear that the iso-cetane sample has a much higher ignition temperature than the n-alkanes which is consistent with the connections made between chemical structure (branching) and AIT as laid out in the literature (Affens et al., 1961). Fig. 6b shows that the mode II events result in much lower peak temperature rises making them easily distinguishable despite the luminosity present in both modes. As with the n-alkanes, the trend in ignition temperature with composition shows that the richer compositions are capable of ignition at much lower temperatures than the lean and near stoichiometric mixtures. An absolute minimum AIT of 395.2±4.1°C was observed but we did not locate any experimental AIT values. The only literature source found for iso-cetane AIT was the DIPPR database (as noted by Sund), which reported an AIT of 705°C based on a numerical study.

Some tests were indeed performed at these temperatures with very rapid ignition observed, however it was also found that these conditions lead to accelerated deformation of the test flask likely due to a transition to viscoelastic behavior of the borosilicate glass at these elevated temperatures. Under the flasks own self weight, this led to a "flowing" of the glass and elongation to a non spherical geometry. In this way the standardized conditions of the test are not consistent for substances with AIT above a certain threshold ($T > 600$°C) where in fact a different geometry of the combustion vessel becomes unavoidable. As discussed in the introduction, the apparatus has a significant impact on the ignition testing results so the elongation effect will in part lead to very different results from that expected for the

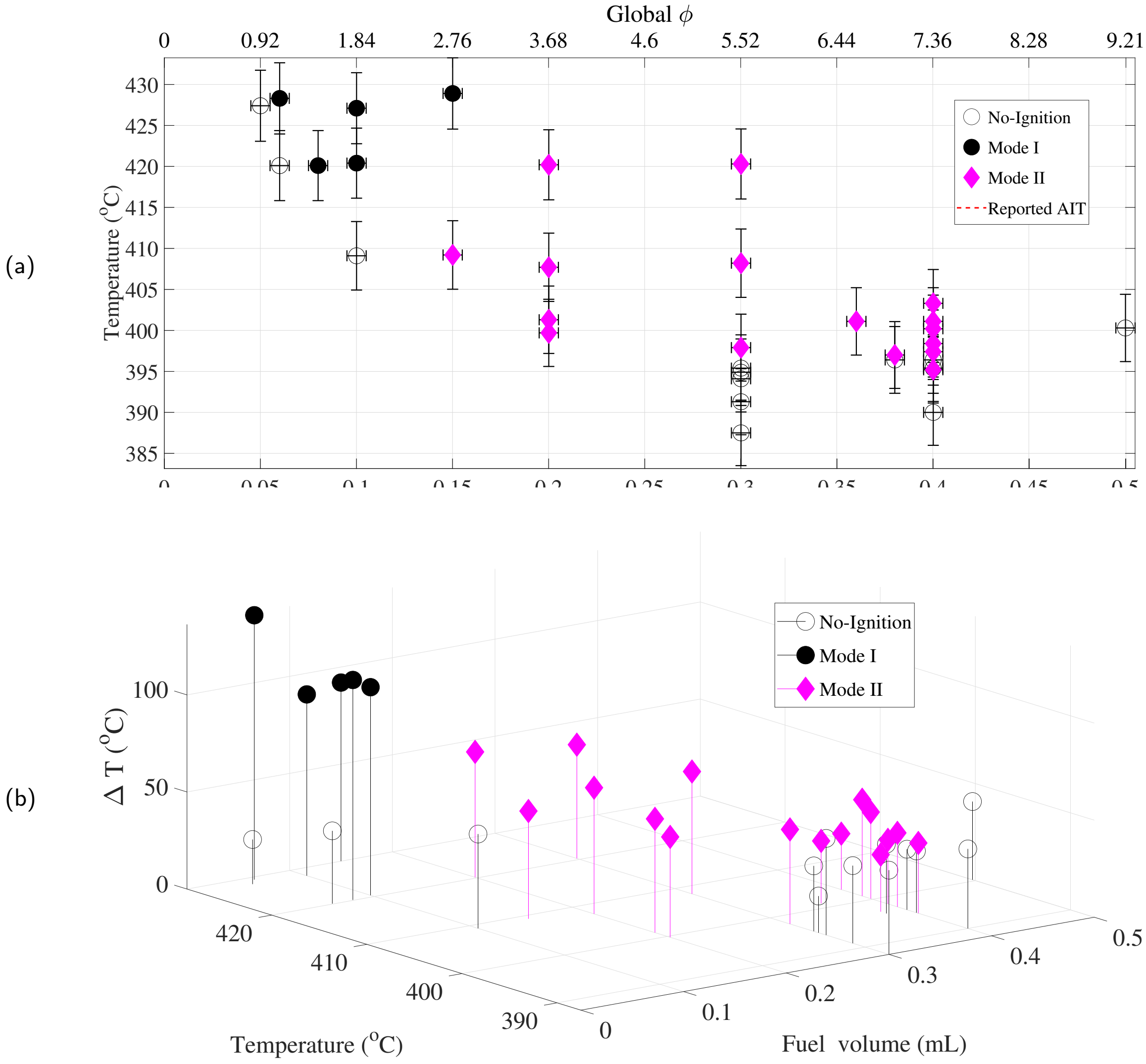


Figure 6: (a) iso-Cetane ignition testing results (b) Peak temperature rise

specified test conditions. Indeed this was observed here after the deformed flask was removed and some test conditions were repeated and showed that the deformed vessel actually allowed for ignition at lower temperatures than the spherical flask. It is not immediately clear why this is the case but it may be related to ignition behavior dependence on residence time which would be longer in the case of an elongated vessel as compared to a spherical one. The elongated geometry should allow for naturally convecting fluid particles to spend more time in the thermal boundary layer of the vessel leading to more rapid heating and perhaps accelerated low temperature chemistry leading more quickly to thermal runaway and ultimately ignition which is consistent with recent studies (Coronel et al., 2019; Jones and Shepherd, 2020).

3.3. Aromatics

The aromatic compounds studied here were also chosen based on their relevance to literature surrogate fuels with two alkylbenzenes (1,2,4-trimethylbenzene or TMB and trans-decalin or trans-decahydronapthalene) as well as one cycloaromatic (toluene). It is expected based both on reported values and literature discussed in the introduction that the minimum AITs of aromatic compounds should be far greater than n-alkanes which indeed is the case here in

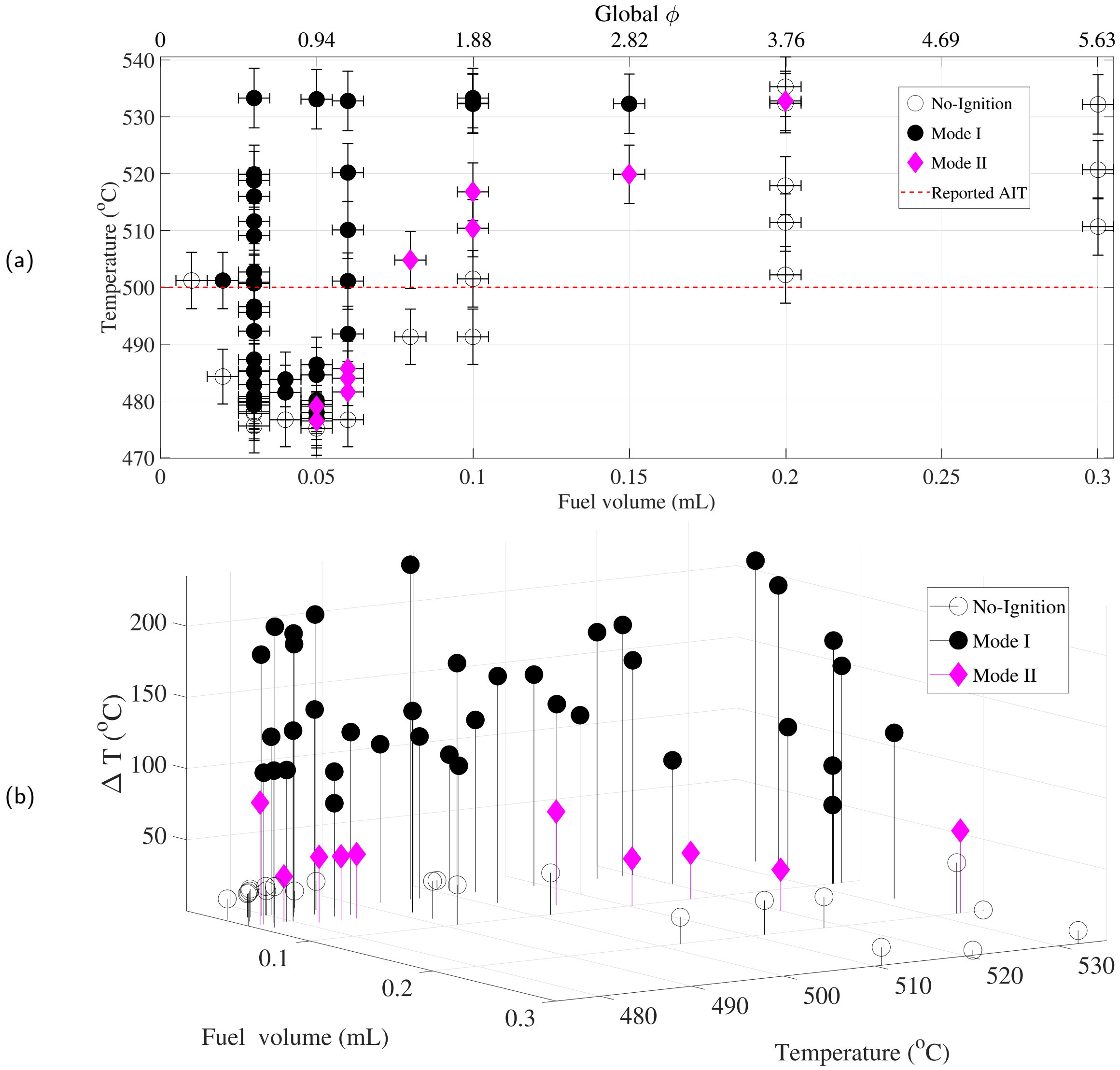


Figure 7: (a) 1,2,4-Trimethylbenzene ignition testing results (b) Peak temperature rise

general. Additional ignition modes were also observed for these fuels and far different trends in the parameter space as compared to those seen for alkanes.

In Fig. 7a this difference is immediately obvious as there is a much sharper dependence on the composition with lean mixtures now proving to ignite much more readily than rich mixtures for 1,2,4-trimethylbenzene (TMB). Some mode II cool flame behavior is also seen here again with far lower peak temperature rises as compared to the mode I events again allowing them to be easily distinguished in Fig. 7b. The difference between the measured minimum AIT 476.5 ± 4.8°C and the literature (NFPA, 1991; USCG, 1999) value AIT of 500°C is significant in this case.

Fig. 8a shows that for trans-decalin there is not as sharp of a dependence on composition as seen for the TMB but rather a very weak compositional dependence. However it is interesting that trans-decalin exhibits the widest variety of ignition modes in any of the fuels studied. The mode IV events are present near stoichiometric and lean conditions while both mode II and III are present in the rich regime. The distinction to be made between all of these modes can begin to be seen in Fig. 8b where the temperature rise for mode IV events are much lower than other modes while the mode II and III are still significantly less than mode I. Further distinction is also made from luminosity observations and reaction timescales determined by the temperature traces as alluded to in Table 3. The minimum AIT determined

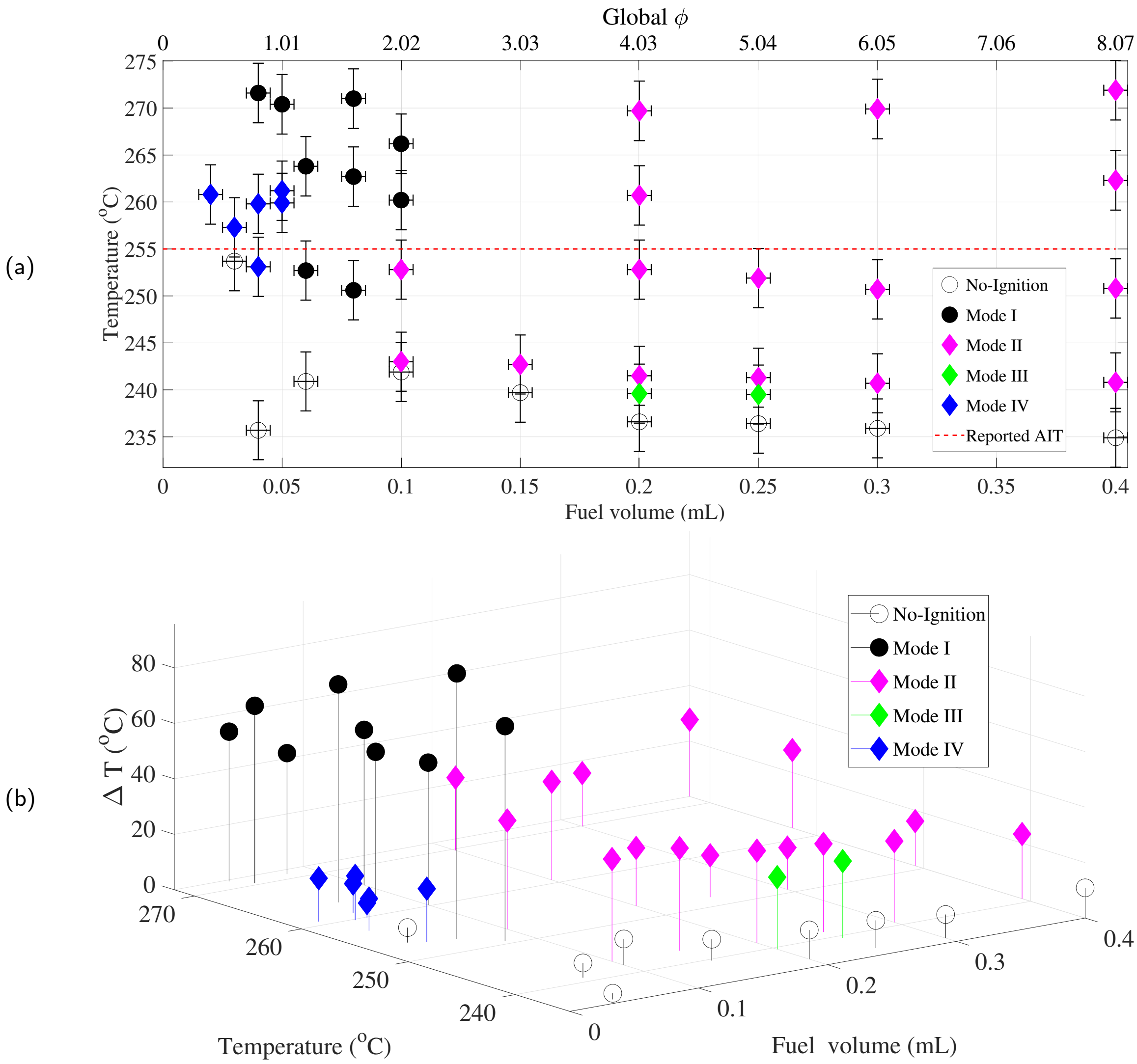


Figure 8: (a) trans-Decalin ignition testing results (b) Peak temperature rise

in our tests is $T = 239.5 \pm 3.1$°C and the NFPA (1991) value is 255°C.

Fig. 9a shows similar dependencies exist for toluene as for TMB. Namely the sharp compositional dependence is evident here again with samples much more readily ignited near stoichiometry than in the very rich or lean regimes. The mode II events seen here are again only present in the rich regime as with the other simple fuels. Fig. 9b illustrates the distinction between mode I and II events with lower temperature rises clearly evident for mode II events. There is a significant differnce between the reported (NFPA, 1991; USCG, 1999) AIT value of 480°C and our experimental result of 508.2 ± 5.0°C.

3.4. Single-component fuels summary

The n-alkanes studied showed generally lower AITs than iso-cetane and the aromatics which is consistent with the connections made between chemical structure (branching, unsaturation) and AIT as laid out in Affens et al. (1961). The n-alkanes also generally exhibited lower ignition temperatures at more fuel rich conditions where mode III ignition events became dominant. iso-Cetane also followed this trend but with mode II ignition becoming dominant at fuel rich conditions. The TMB and toluene showed an opposite trend in that the minimum AIT was generally observed at near

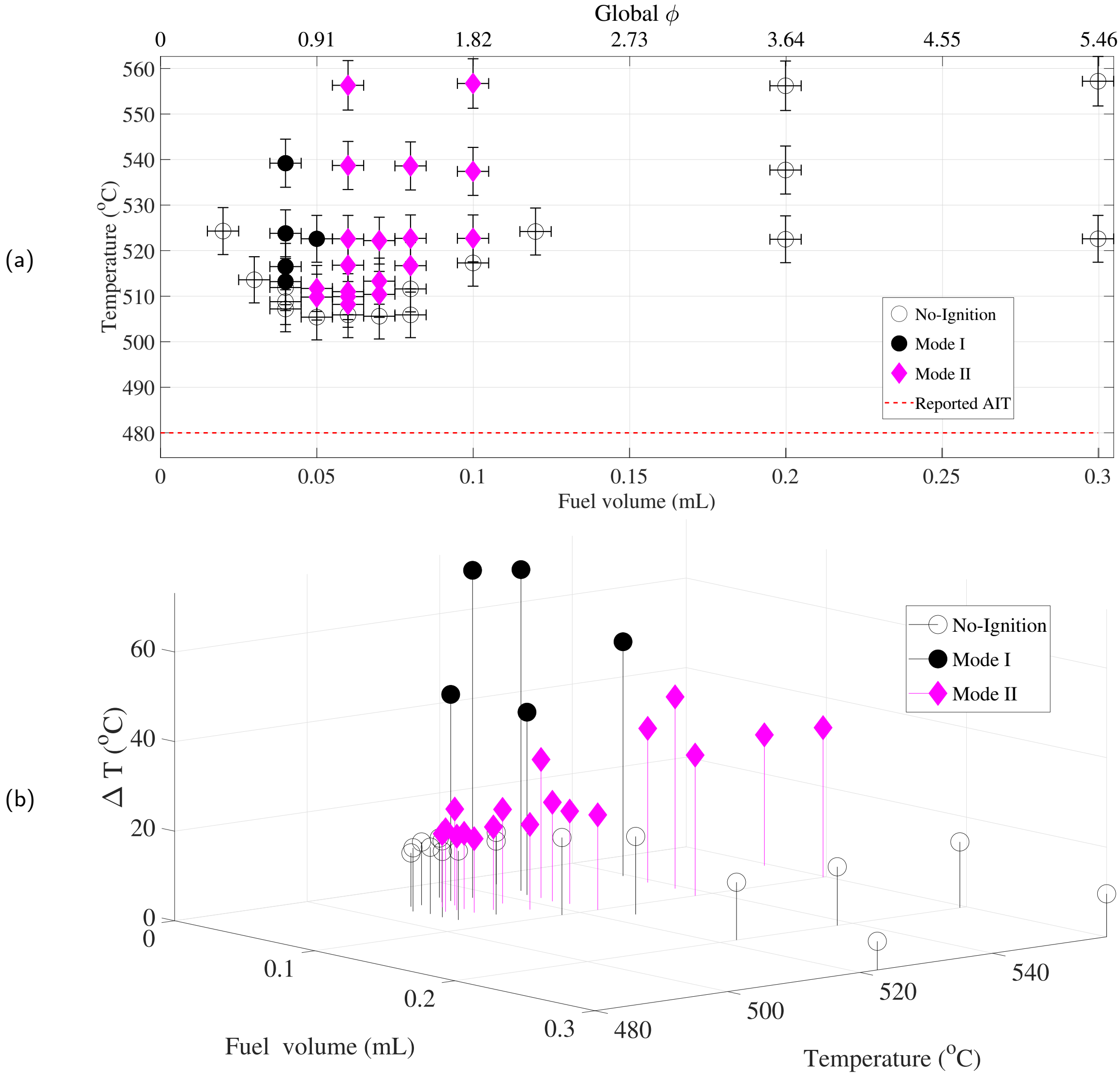


Figure 9: (a) Toluene ignition testing results (b) Peak temperature rise

stoichiometric or slightly lean conditions with increasingly great difficulty igniting at rich conditions. Additionally mode II ignition rapidly became dominant at even slightly rich conditions for both of these aromatics. The exception to these trends for the aromatic fuels was the trans-decalin which became more easily ignited at rich conditions with a far lower AIT around 240°C. In addition trans-decalin exhibited all four ignition modes with mode II and III both becoming dominant at rich conditions and mode IV ignition being observed only at lean conditions near the ignition threshold. The temperature rises measured were also far higher for the n-alkanes than iso-cetane or any of the aromatics.

3.5. Multi-component fuels

The multi-component fuels examined in this study were Jet A fuel standards (POSF-4658 and POSF-10325) and surrogate jet fuels from the literature (Aachen and JI). Some of the observed ignition behaviors of these fuels can be attributed to characteristics of their molecular components. As summarized in Table 1, these fuels are effectively entirely composed of alkane and aromatic compounds with the alkanes making up the bulk of the fuels which indicates that the alkane ignition behavior is expected to dominate.

POSF-4658 is a Jet A blend which has been examined extensively by a number of researchers, see Edwards (2017).

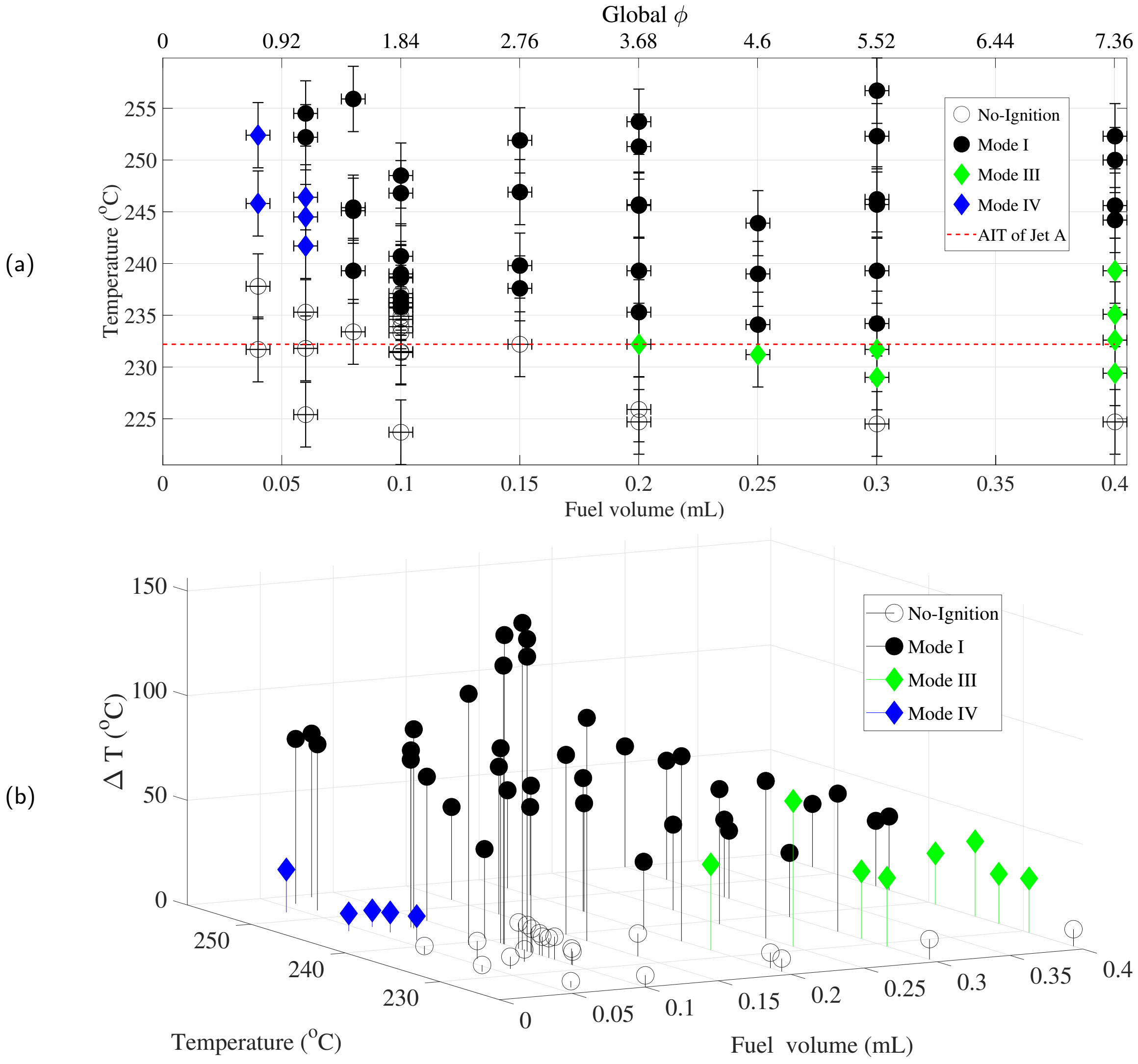


Figure 10: (a) POSF-4658 (Jet A) ignition testing results (b) Peak temperature rise

Fig. 10a shows the ignition results obtained in this study for this blend. Mode III and mode IV events are observed in the rich and lean regimes respectively which is similar to the behavior of the simple fuels. There is a good agreement between our experimental AIT of 229.0±3.1°C and the accepted FAA (2018) Jet A AIT value of 232°C. This relatively low AIT can likely be attributed to the alkane dominant composition of Jet A since alkanes generally exhibit AITs in this range while aromatic compounds tend to be much higher. Fig. 10b shows temperature rises around 100°C while the mode III and IV events exhibit far lower temperature increases.

POSF-101325 shows substantially similar ignition behavior to POSF-4658, which is consistent with the modest differences in composition between the two fuel blends (Fig. 1). The POSF-10325 ignition data shown in Fig. 11a is similar to Fig. 10a but has a few minor differences. One of these differences is in the lean regime where the mode IV ignition occurs at slightly lower temperatures than for the POSF-4658. Similar to POSF-4658, the mode III events are seen in the rich regime and occur at higher temperatures for increasingly high compositions while the minimum AIT levels off for very rich mixtures. Fig. 11b shows that peak temperature rises for all ignition modes are similar to those seen for POSF-4658. The minimum AIT of 225.3 ± 3.1°C for POSF-4658 and agrees reasonably well with the accepted FAA (2018) Jet A AIT of 232°C.

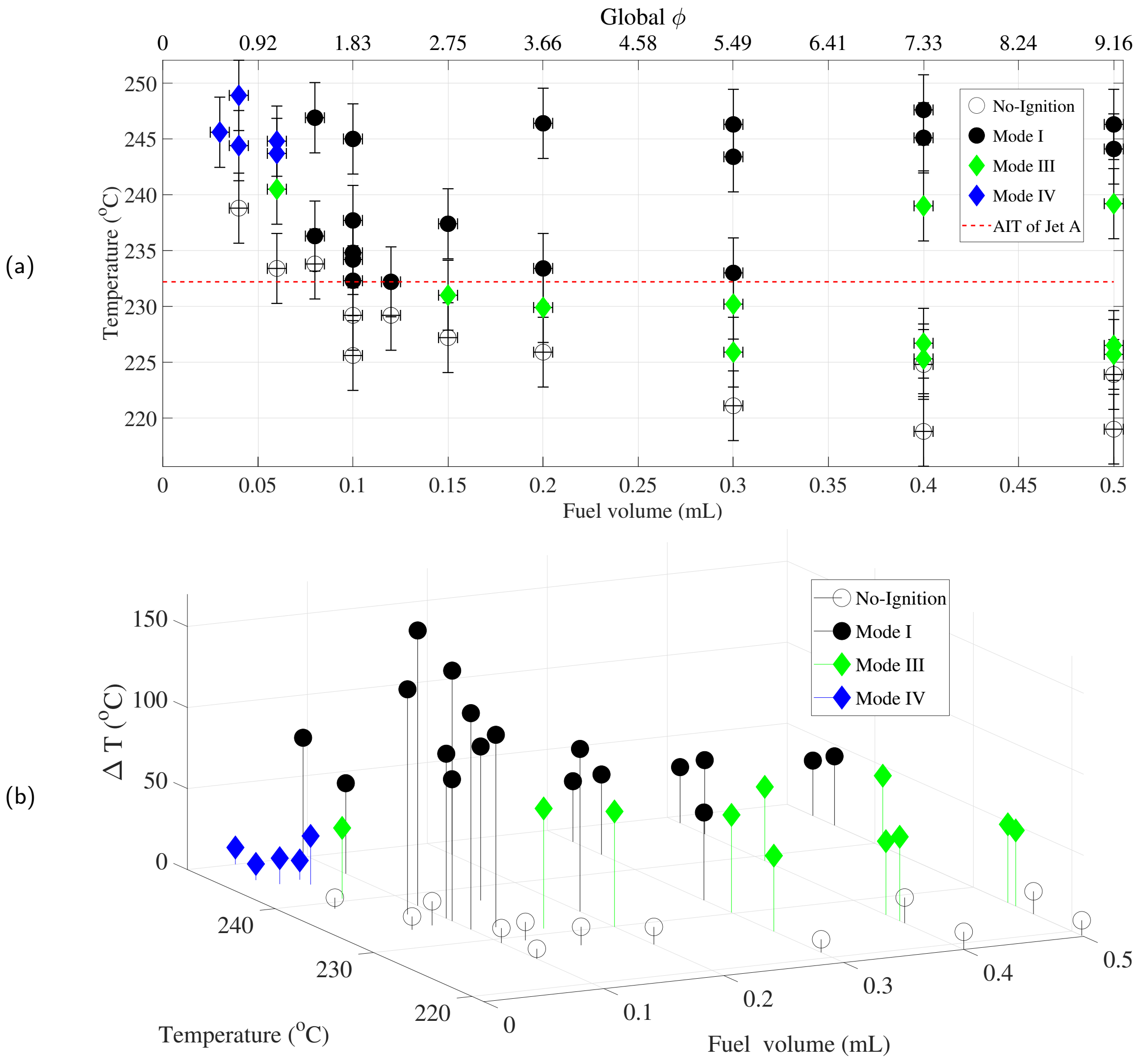


Figure 11: (a) POSF-10325 (Jet A) ignition testing results (b) Peak temperature rise

The Aachen surrogate is a simple two component blend which seems to capture the general trends from the Jet A batches while missing some details like mode IV events in the lean regime as seen in Fig. 12a. Mode III events are generally well captured in the rich regime with this mode extending to higher temperatures for richer compositions as was seen for Jet A. The Aachen surrogate has a lower AIT value (219.0 ± 3.1°C) than the accepted FAA (2018) Jet A value of 232°C. Fig. 12b shows that there is also some discrepancy in the peak temperature rise for both the mode I and III events as compared to those seen in both Fig. 10b and Fig. 11b.

The more complex JI surrogate consisting of 4 components does a much better job at reproducing the ignition behaviors found in the Jet A samples. Fig. 13a shows the existence of mode IV events in the near stoichiometric regime along with the mode III events being maintained in the rich regime. However, these mode IV events occur at slightly richer compositions than observed for Jet A. Fig. 13b shows another difference in that the temperature rises measured for JI are much lower than those seen in either of the Jet A samples as shown by Fig. 10b and Fig. 11b. The minimum AIT of 228.3 ± 3.1°C is also more consistent with the accepted FAA (2018) Jet A AIT value of 232°C.

The global minimum AIT measured from each of the fuels as well as the corresponding test conditions are summarized in Table 4 and compared to some values reported in the literature. The differences between present results

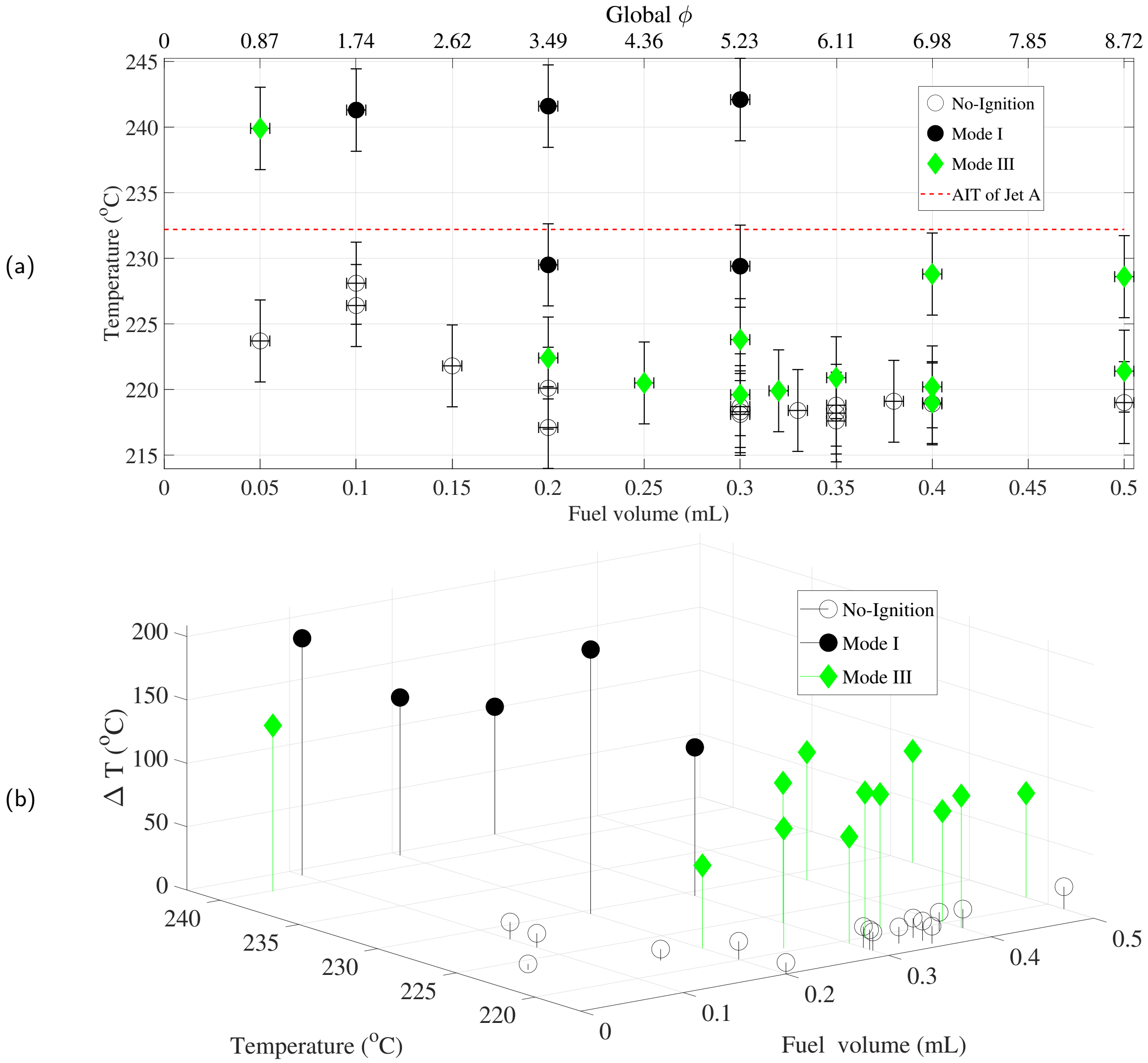


Figure 12: (a) Aachen surrogate ignition testing results (b) Peak temperature rise

and literature values range from 1 to 7%, comparable to or larger than the estimated uncertainty of ±1%.

4. Conclusions

The very low-temperature thermal ignition regime is important to industrial safety for commodity fuels but presents many challenges for combustion experimenters and modelers. In concert with related efforts in our laboratory, we have examined the potential for using surrogate fuels with simple and well-controlled composition rather than samples of Jet A which can have wide variability in properties. As a first step in determining the applicability of surrogates for very low temperature Jet A thermal ignition studies, we have examined the ignition behavior in the ASTM-E659 apparatus for two Jet A surrogates, their molecular components, and two standardized batches of Jet A. The origins of the ASTM-E659 method were examined along with various limitations and practical considerations associated with the empirical nature of the test.

Four distinct ignition modes were observed near the AIT threshold and were characterized using the limited diagnostic tools possible in the ASTM-E659 test. Experimental results were compared with reported minimum AIT numbers from literature sources with some data obtained showing significant discrepancies with reported AIT num-

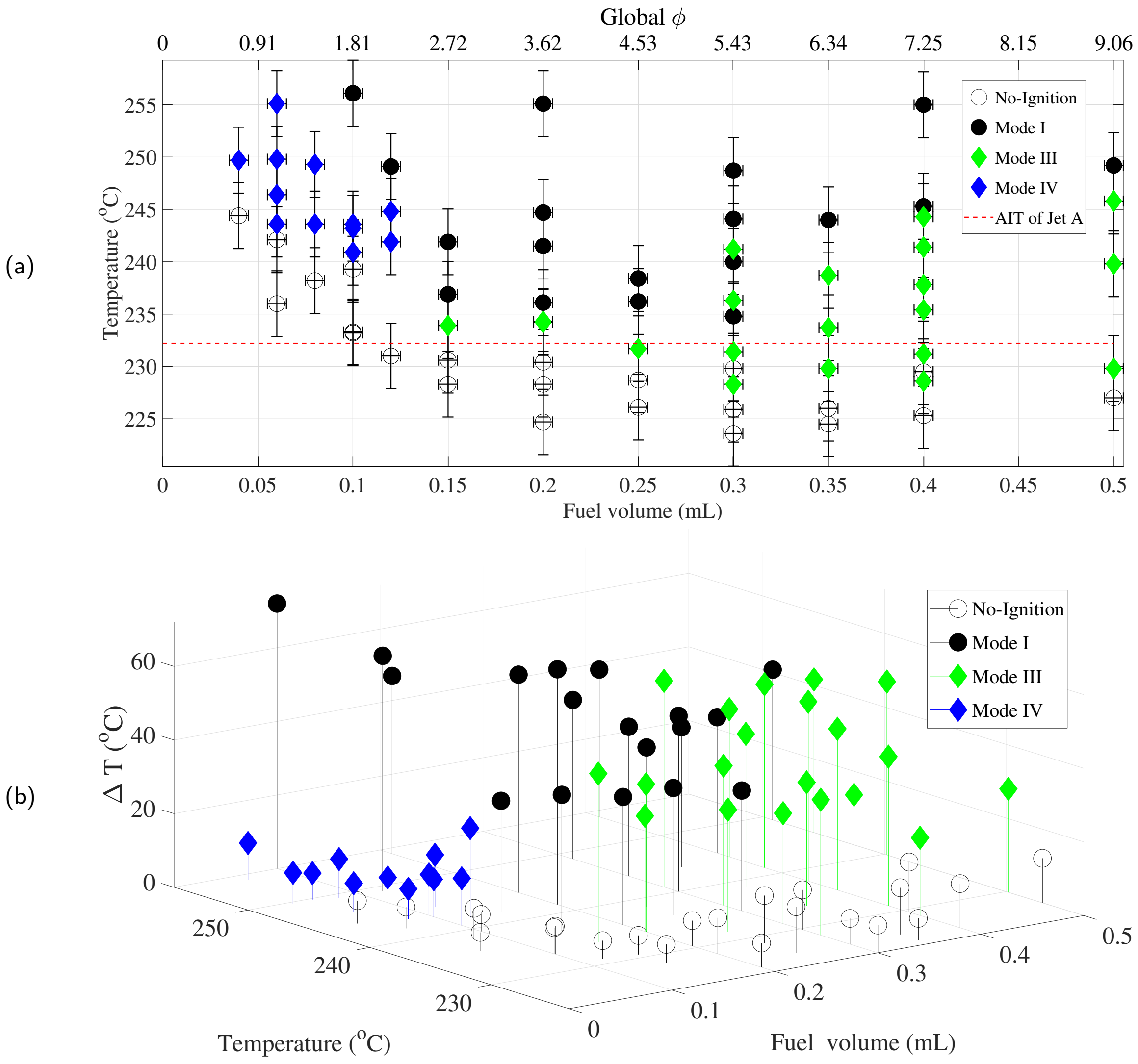


Figure 13: (a) JI surrogate ignition testing results (b) Peak temperature rise

Table 4
Summary of measured minimum AIT values and corresponding test conditions

		Measured			Literature
	Fuel	**Fuel Volume (mL)**	**Global ϕ**	**Minimum AIT (°C)**	**Reported AIT (°C)**
Alkanes	n-hexane	0.10	1.56	235.3 ± 3.1	225[a] (236[b])
	n-decane	0.30	5.12	204.3 ± 3.1	210[ab]
	n-dodecane	0.30	5.24	202.2 ± 3.1	203[a]
	iso-cetane	0.40	7.36	395.2 ± 4.1	-
Aromatics	1,2,4-trimethylbenzene	0.05	0.94	476.5 ± 4.8	500[ab]
	trans-decalin	0.25	5.04	239.5 ± 3.1	255[a]
	toluene	0.06	1.09	508.2 ± 5.0	480[ab]
Multi component	POSF-4658	0.30	5.52	229.0 ± 3.1	232[c]
	POSF-10325	0.40	7.33	225.3 ± 3.1	232[c]
	Aachen Surrogate	0.40	6.98	219.0 ± 3.1	-
	JI Surrogate	0.30	5.43	228.3 ± 3.1	-

[a] NFPA (1991) ; [b] USCG (1999) ; [c] FAA (2018)

bers. Branched alkanes and aromatics seemed to show more exotic ignition behavior, but overall showed higher AIT thresholds as compared to n-alkanes. The multi-component fuels exhibited ignition characteristics that appear to be dominated by n-alkanes which is consistent with the predominance of alkane components in these fuels. The two Jet A batches studied showed very similar ignition behavior across the parameter space while both the Aachen and JI surrogates were able to reasonably replicate most of the Jet A ignition trends with composition and temperature. The JI surrogate did however exhibit much better agreement for ignition thresholds in comparison with Jet A than the Aachen surrogate and was even able to reproduce the existence of mode IV ignition events which the Aachen surrogate could not.

Acknowledgements

This work was carried out in the Explosion Dynamics Laboratory of the California Institute of Technology and was partially supported by The Boeing Company (CT-BA-GTA-1). Conor Martin was also supported by the Department of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program. The GC-FID measurements were made in the Caltech Environmental Analysis Center with the guidance of Dr. Nathan Deleska.

CRediT authorship contribution statement

Conor D. Martin: Data Curation, Methodology, Investigation, Writing - Original Draft. **Joseph E. Shepherd:** Conceptualization, Funding Acquisition, Supervision, Writing - Review and Editing.

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