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Donna Post Guillen

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EFFECT OF MATERIALS ON THE AUTOIGNITION OF CYCLOPENTANE

Donna Post Guillen

Idaho National Laboratory, Idaho Falls, ID 83415

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Abstract

Cyclopentane, a flammable hydrocarbon, is being considered as a working fluid for waste heat recovery applications using Organic Rankine Cycles with Direct Evaporators. A postulated failure mode consisting of a pinhole leak in a heat exchanger tube raises safety concerns due to autoignition of the working fluid. Experiments were conducted to determine the ignition delay time (IDT) of cyclopentane using an Ignition Quality Test™ (IQT™) device. Two sets of experiments were conducted per ASTM D6890 (with exception to charge pressure and temperature) to determine ignition delay of the fuel at atmospheric pressure for standard air (~20.95% oxygen) and vitiated air (13.3% oxygen) at a temperature of 803 K. Operation of the IQT device at a much lower pressure (1 bar) than normal operation (21.4 bar) with a standard injector led to very rich conditions and wetting of the stainless steel chamber walls. Catalytic effects are postulated to produce the small IDTs observed. Experiments were repeated with a modified injector to prevent wall wetting, resulting in average IDTs that are substantially longer.

Introduction

Cyclopentane is being considered for use as a working fluid in a Direct Evaporator of an Organic Rankine Cycle (ORC). In this configuration, the heat exchanger is placed directly in the flow of the hot exhaust gas, rather than using a secondary heat transfer loop to isolate the flammable working fluid from the heat source. This configuration offers the advantages of approximately 15% lower cost and improved efficiency over a standard ORC. However, placing a heat exchanger operating with a flammable hydrocarbon in the hot exhaust gas stream presents potential safety risks. If a pinhole leak were to occur in the heat exchanger, working fluid could leak into the hot exhaust stream. Gas turbine exhaust is provided to the Direct Evaporator at a temperature of approximately 803 K, whereas the autoignition temperature of cyclopentane is 634 K (Gallant and Yaws, 1993). Autoignition of the working fluid has been identified as the key risk for this type of system.

Autoignition occurs when sufficient self-heating by chemical reactions takes place to accelerate reaction rates to produce full-scale combustion. This is in contrast to forced ignition, in which an external source (e.g., spark) is employed to initiate the combustion process. For combustion to occur, the fuel to oxidizer concentration must be between the lower (lean) and upper (rich) flammable limits. The reaction rate depends on the species concentration of the fuel and oxidant, the local temperature and pressure. Ignition processes are comprised of steps that take a finite amount of time. This latent period prior to the start of combustion is referred to as ignition delay time (IDT).

Test Methods

There is currently very little autoignition data available in the public domain for cyclopentane covering the range of initial temperatures, pressures and oxygen concentrations relevant to ORCs with Direct Evaporators. Much of the data is either at too high of a temperature (>1000K), at too low or too high of a pressure, or for dilute concentrations. Sirjean et al. (2007) published ignition delay times for cyclopentane in the temperature range from 1300 to 1800 K. The general trend displayed is that IDT increases with decreasing temperature up to two orders of magnitude over this temperature range. Daley et al. (2008) measured ignition delay times for cyclopentane/air mixtures in a shock tube at temperatures of 847 to 1379 K, pressures of 11 to 61 atm, and equivalence ratios of 1.0, 0.5, and 0.25. Other published ignition delay data found are for relatively dilute mixtures of cyclopentane in argon, such as that by Sirjean et al. (2007) and Orme et al. (2005). Sirjean et al. (2007) measured ignition delay in a shock tube for cyclopentane/oxygen/argon mixtures with fuel concentrations of 0.5% and 1.0%, respectively, and equivalence ratios of 0.5 to 2.0 (O_2 concentrations of 1.875% to 9%), temperatures from 1230 to 1840 K, and pressures from 7.3 to 9.5 atm. Orme et al. (2005) made similar shock tube ignition measurements for cyclopentane/oxygen/argon mixtures with a cyclopentane concentration of 1.0%, equivalence ratios of 0.577 to 2.0 (O_2 concentrations of 3.5% to 13%), temperatures from 1370 to 1820 K, and pressures near 1 atm. Shock tube results with mixtures of cyclopentane, cyclopentene, cyclopentadiene and dicyclopentadiene in argon with a fuel concentration of 1.0 % and O_2 concentration of 13.0 %, displayed very similar IDTs. The researchers concluded that it is the concentration of O_2, rather than the equivalence ratio, that affects the IDT. Using a shock tube, Buda et al. (2005) measured IDTs of cyclopentane/oxygen/argon mixtures (0.5 or 1 % of hydrocarbon, equivalence ratios from 0.5 to 2) at temperatures from 1230 to 1800 K and pressures from 7.3 to 9.5 atm. Reitzer and Lamb (1955) used a rapid compression machine to obtain IDTs for stoichiometric mixtures of cyclopentane and air over the range of temperatures from 803 to 1033 K and pressure from 2.3 to 3.25 MPa.

Autoignition data were not found in the literature for cyclopentane at the conditions of interest (e.g., 13.3% O_2 environment at 803 K and atmospheric pressure). A determination of the IDT for the actual ORC operating conditions was necessary in order to specify appropriate safety controls. The purpose of the testing described here is to establish the minimum IDT of cyclopentane in a hot gas turbine exhaust gas stream. The particular failure mode under consideration stems from a pinhole leak in a finned heat exchanger tube, producing a fine spray of fuel available to combust. Southwest Research Institute (SwRI, San Antonio, TX) was commissioned to perform ignition delay tests with cyclopentane using both a standard (20.95% O_2) air (CRC Handbook of Chemistry and Physics, 1997 Edition) and vitiated (13.3% O_2) gas turbine exhaust environment at 803 K and atmospheric pressure. SwRI has extensive experience analyzing fuels with various techniques for many different manufacturers. The test procedure employed the same methods used in previous projects conducted at SwRI. The Ignition Quality Test™ (IQT™) Laboratory Model from Advanced Engine Technology Ltd. (Ottawa, Ontario, Canada) was used to perform the testing (shown in Figure 1). This test equipment injects a small amount of fuel into a heated, temperature-controlled constant volume chamber charged with compressed air. The combustion chamber is equipped with external electrical heating elements, suitable insulation and pneumatically actuated intake and exhaust valves. A heated,

pneumatically actuated fuel injection system with pump, injector nozzle assembly, and associated sample reservoir provides the test fluid to the chamber. The coolant system has a liquid-to-air heat exchanger, filter, circulating pump and flow control valves. Ignition is sensed via temperature thermocouples, pressure gages and sensors, an injector nozzle needle motion sensor, compressed gas pressure regulators, control valves, pneumatic actuator components and solenoid valves.

Figure 2 illustrates the test procedure. Cyclopentane is injected into the 0.213 liter combustion chamber of the IQT^{TM} device. Each injection produces a single-shot, compression ignition combustion cycle. The fuel injection system is a Pintle-type, single-hole nozzle with an air-driven fuel injection pump. Fuel at 323K is sprayed into an initially quiescent environment, where it immediately vaporizes. Ignition delay is measured using sensors that detect the start of fuel injection and the start of significant combustion for each cycle. The onset of ignition is sensed by the output of both pressure and heat flux gauges, which were fed into an oscilloscope. Ignition delay is measured from the start of needle lift to the chamber pressure recovery point. Ignition is manifested by either a sudden rise in the plateau value of the traces or a marked change in their slope. A complete sequence is comprised of 15 preliminary cycles and 32 additional test cycles. The ignition delay measured for the last 32 cycles is averaged. Per ASTM D6890, the system was calibrated using a chemical (i.e., n-heptane) with known IDT (Ciezki, and Adomeit, 1993).

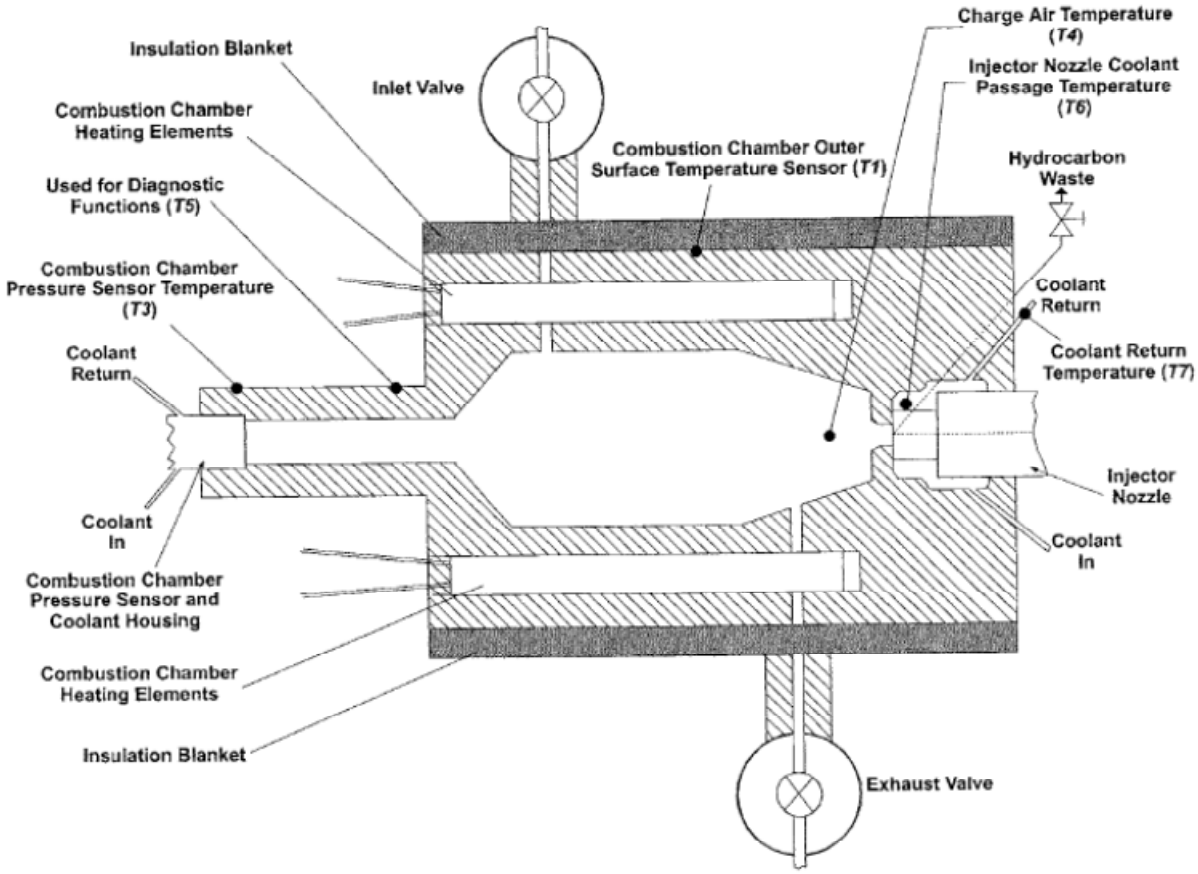

Figure 1. IQT^{TM} Combustion Chamber Schematic (courtesy of SwRI).

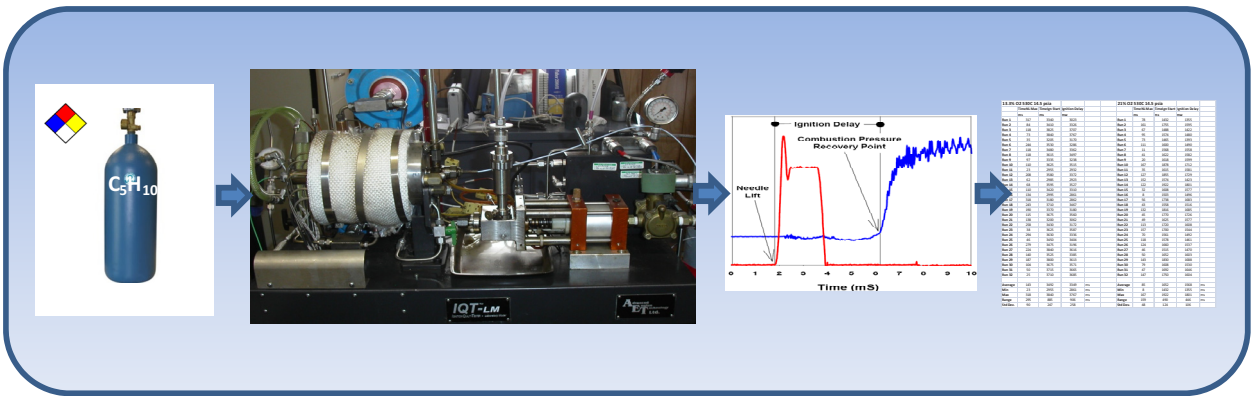

Figure 2. Ignition Delay Measurement Procedure.

Test Results

Experiments with Standard IQT™ Injector

This experiment involved testing cyclopentane in the IQT™ using ASTM D6890 (with exception to charge pressure and temperature) to determine ignition delay of the fuel at atmospheric pressure for both standard (20.95% oxygen) and vitiated air (13.3% oxygen). The IQT™ is normally operated at 21.4 bar initial pressure and 835K initial charge temperature. Two tests were performed to establish feasibility of the test procedure with cyclopentane. Both tests were performed with standard (20.95% oxygen) air at 21.4 bar. One test was run at the normal (835 K) charge temperature and the other test was run at a slightly lower temperature (781 K). The cyclopentane ignited and the IDT ranged from 90.1 to 184.5 ms.

Testing was then performed with an initial charge pressure and temperature of 1 bar and 803K. Using the IQT™ outside of its normal operating conditions caused a few issues. The standard software that runs the IQT™ system would not run with the low initial pressure, so the system had to be operated manually. Additionally, some of the ignition delay times were outside the recordable range for the software, so the ignition traces had to be recorded on an oscilloscope and post-processed. The fuel injector for the IQT™ injects a fixed mass into the chamber. Approximately 0.0974 grams of cyclopentane was injected per event. For the tests conducted at 1 bar, the combustion chamber had approximately 21 times less mass leading to very rich conditions (0.95:1 air-fuel ratio or approximately 15 times too much fuel). This injection scenario led to chamber wall wetting and erratic ignition due to low charge density.

Table I summarizes the results for the two feasibility tests and the two tests conducted at ORC operating conditions. The table lists the minimum, maximum and average IDT, along with the measurement range (i.e., maximum minus minimum) and standard deviation. The resulting ignition delays from the 13.3% and 20.95% O_2 runs varied greatly within the 32 run test. For the tests conducted with the chamber at atmospheric pressure, values for standard deviation are comparable to the quantity measured.

Table I. Ignition Delay Results with Standard IQT™ Injector.

Pressure (bar)		**1**	**1**	**21.4**	**21.4**
Temp (K)		**803**	**803**	**781**	**835**
O_2 (conc.)		**13.3%**	**20.95%**	**20.95%**	**20.95%**
IDT (ms)	**Average**	29	24.0	111.0	75.8
	Min	3.0	6.0	90.1	13.0
	Max	83.0	90.0	184.5	91.0
	Range	80.0	84.0	94.4	78.0
	Std Dev	24.0	23.9	21.4	13.2

These results indicate that if cyclopentane comes in contact with stainless steel at these oxygen concentrations, temperatures and pressures, it can ignite in the range of 3 to 90 ms from the time of injection. The large discrepancy in IDTs obtained from the tests conducted with a combustion chamber pressure of 21.4 bar and those where the combustion chamber was at atmospheric pressure prompted an investigation into the possible causes. It was postulated that this extremely small IDT could be the result of the extremely rich mixture and resultant catalytic reactions from wall wetting. The IQT™ is constructed of stainless steel, a material that contains nickel. Nickel is known to catalytically decompose cyclopentane (Ginosar, 2011). It appears that the catalytic effects of the IQT materials of construction influenced the IDTs for this set of tests.

Experiments with Modified Injector

Due to the issues surrounding the use of the IQT™ outside of its design limits, Idaho National Laboratory requested that SwRI modify and re-calibrate the injection pump for the correct fuel mass at atmospheric pressure and re-run the tests. To correct the air-to-fuel ratio for each combustion gas, or more specifically, the oxygen to fuel ratio, the injector pump was removed and adjusted to allow for lower injected mass. The injector and pump assembly were then calibrated by injecting 100 shots into a container, which were weighed to determine the mass per injection. This process was repeated until the desired fuel mass for stoichiometric combustion was achieved and then repeated three times to determine repeatability. It was determined that 0.004 and 0.0063 grams of fuel would be needed to achieve stoichiometric combustion for the cyclopentane and gas with 13.3% and 20.95% O_2 concentration, respectively. The injector is open for approximately 7.5 ms, producing respective mass flow rates of 0.53 and 0.84 g/s into the chamber.

A new set of tests were run with the modified injector using combustion gas with either a 13.3% or 20.95% O_2 concentration at 803 K and 1 bar. The results of the tests with the modified injector are shown in Table II. The results exhibit the trend of a higher IDT at the lower oxygen concentration. As the oxygen content is reduced from 20.95% (essentially atmospheric) to 13.3%, the IDT increases by more than a factor of two. The minimum measured IDT is 2.861 seconds for the conditions present in the ORC Direct Evaporator (i.e., 13.3% O_2 concentration, 803 K and 1 bar) system. Based upon these results, cyclopentane can ignite in the range of 2.9 to 3.8 seconds from the time of injection at 13.3% oxygen concentration and 1.4 to 1.8 seconds at 20.95% oxygen concentration at 1 bar pressure and 803 K.

It should be noted that the standard deviations are slightly higher than optimal when testing a standard diesel fuel, but are expected when testing a fuel with octane ratings above 90

(cyclopentane has an octane rating of approximately 94). With the greatly reduced fuel mass injected, the observed fuel penetration distance appears to be very short, which would reduce the fuel-wall interaction. However, with the long ignition delay times, there might be sufficient time for some of the liquid fuel, if present, to settle onto the floor of the combustion chamber, increasing the standard deviation of the measurements.

Table II. Ignition Delay Results with Modified Injector.

O_2 (conc.)		13.3%	20.95%
IDT (ms)	Average	3349	1568
	Min	2861	1355
	Max	3767	1801
	Range	906	446
	Std Dev	258	106

The reader is cautioned not to extrapolate these results to other operating conditions. IDT results found in the literature typically plot the logarithm of the IDT (ms) against the reciprocal of temperature (K^{-1}). Experimental results for n-heptane-air mixtures by Ciezki and Adomeit (1993) over the range of temperature between 660 and 1350 K show a linear relationship between temperature and IDT in the high- and low-temperature regions, with IDT increasing with decreasing temperature. However, in the temperature range between 700 and 950 K, the dependence becomes strongly non-linear and the trend reverses, producing an S-shaped curve. In this intermediate temperature region, IDT decreases with decreasing temperature. This behavior, wherein a negative temperature coefficient is displayed at intermediate temperatures, has been observed for various hydrocarbons (Minetti et al., 1994; Cadman et al., 2000). This phenomenon is attributed to the transition from a low- to high-temperature kinetic mechanism.

Since the exhaust gas cools from the maximum temperature of 803 K as it travels from the inlet through the Direct Evaporator, a range of temperatures will be present. Also, a pinhole leak may produce air-to-fuel ratios other than stoichiometric to be present. Therefore, additional experiments at temperatures ranging from the autoignition temperature to the maximum temperature at different equivalence ratios are needed to establish a set of ignition delay curves. The conditions tested by the current set of experiments may not have captured the minimum IDT for this system.

Conclusions

IDTs measured with the standard IQT™ injector were likely affected by the extremely rich mixtures and reactions from wall wetting. Therefore, tests with the standard IQT™ injector were not representative of a small cyclopentane leak. The IDT data obtained with the modified injector conducted at the proper air-to-fuel ratio for stoichiometric combustion are more representative of a pinhole leak.

Acknowledgments

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