

1 Rapid Compression Machine

1.1 Experimental Procedure

The studies in this dissertation were conducted using the Rapid Compression Machine (RCM) constructed by Mittal around 2005 and described in the work of Mittal and Sung [1] and Mittal [2]. This RCM has been used to study the autoignition behavior of a number of fuels, including *n*-decane, methylcyclohexane, hydrogen, syngas, dimethyl ether, methanol, toluene, benzene, diisobutylene, iso-octane, jet fuel, and gasoline [3–18].

A modern RCM operates by rapidly compressing (hence the name) a test gas mixture to targeted pressure and temperature conditions. The compression is effected by either a single piston or dual, opposed pistons. Upon reaching the targeted state, the piston is stopped and fixed in place so that the reactions proceed in a constant volume reactor. When studying autoignition with an RCM, the primary data are the measured pressure traces during and after the compression stroke. These pressure traces are processed to derive information such as the pressure and temperature at the end of compression (EOC) and the ignition delay that are typically reported. It is also possible to employ laser diagnostics or extract gas samples from the reactor to examine reaction pathways in more detail.

The present RCM is a pneumatically-driven/hydraulically-stopped single-piston arrangement. A schematic of the RCM is shown in ???. The RCM consists of four chambers and three pistons that are used to control machine. The chambers are called the reaction chamber, the hydraulic chamber, the pneumatic chamber, and the driving tank; similarly, the pistons are called the reactor, hydraulic, and pneumatic pistons and are each installed in the chamber of the same name. The rear of the reaction chamber is bolted to the front of the hydraulic chamber; seals in the face of the hydraulic chamber prevent oil from leaking and contaminating the reaction chamber. The driving tank and the rear of the pneumatic chamber are connected by a union; a seal around the circumference of the pneumatic piston seals gas in the driving tank from the front of the pneumatic chamber. Thus, the pneumatic piston can be driven by pressure from the driving tank on its rear and pressure from the

pneumatic chamber on its front. The three pistons are connected by a rod running from the front of the pneumatic piston to the rear of the reactor piston so that they move as one; this will be referred to as the piston assembly.

At the start of an experimental run, with the piston in the EOC position, the reaction chamber is vacuumed to less than one Torr. Next, the piston assembly is retracted pressurizing the front face of the piston in the pneumatic chamber. For safety, and to prevent damage to the RCM, the driving tank should be filled to limit the acceleration of the piston assembly during this retraction. The pressure on the front of the pneumatic piston pulls the piston assembly rearward and seats the rear of the hydraulic piston onto an o-ring in the rear of the hydraulic chamber. Then the hydraulic chamber is filled with oil to a pressure of approximately 800 psi, providing a rearward force on the front face of the hydraulic piston. The pressure is then released from the front of the pneumatic chamber and the driving tank is filled to the desired driving pressure. The force on the hydraulic piston opposes the force on the pneumatic piston from the driving tank and the piston assembly remains at rest. Then, the reaction chamber is filled with the required initial pressure of test gas mixture from the mixing tank. Finally, compression is triggered by releasing the hydraulic pressure through an electrically operated solenoid valve. The piston assembly is driven forward by the unbalanced force from the pressure in the driving tank on the pneumatic piston to compress the test mixture. The gases in the reaction chamber are brought to the compressed pressure (P_C) and compressed temperature (T_C) conditions in approximately 30-50 milliseconds.

The required driving pressure for a given EOC pressure can be estimated from a force balance between the force on the pneumatic piston from the driving tank and the force on the reactor piston from the reaction gases, as shown in Eq. (1c).

$$P_{d,\min} \cdot A_p = P_{r,\text{EOC}} \cdot A_r \quad (1a)$$

$$P_{d,\min} \cdot \frac{\pi d_p^2}{4} = P_{r,\text{EOC}} \cdot \frac{\pi d_r^2}{4} \quad (1b)$$

$$P_{d,\min} = P_{r,\text{EOC}} \cdot \frac{d_r^2}{d_p^2} \quad (1c)$$

In Eq. (1), $P_{d,\min}$ is the minimum driving pressure, A_p is the cross-sectional area of the pneumatic piston, $P_{r,\text{EOC}}$ is the pressure in the reactor at the EOC (i.e. P_C), A_r is the cross-sectional area of the reactor piston, d_p is the diameter of the pneumatic piston, and d_r is the diameter of the reactor piston.

The minimum driving pressure is such that the piston does not rebound at the EOC due to pressure on the reactor piston. So that the driving pressure can be much lower than the EOC pressure, the diameter ratio of the reactor piston to the driver piston is 2/5, allowing a factor of 6.25 lower driving pressure than EOC pressure. The actual driving pressure should exceed the minimum by some safety margin so that the reactor remains at constant volume even if there is some pressure rise due to first stage ignition.

There is not a theoretical upper limit on the driving pressure. It is desired that the piston should reach the EOC conditions in as short a time as possible to minimize heat loss from the reactants to the reactor walls and minimize the time for reactions to occur during the compression stroke. This implies that the driving pressure should be made as high as possible so that the highest piston velocity is achieved. However, higher piston velocities require a higher deceleration at the EOC. In the present RCM, the deceleration is provided by venting the hydraulic oil between steps on the hydraulic piston and matched steps on the front of the hydraulic chamber. If the piston is overdriven—that is, the driving pressure is too high—the piston will not be sufficiently decelerated by the oil venting and will impact the front of the hydraulic chamber at high velocity. This can damage the RCM and cause the piston to rebound elastically. It also generates substantial noise in the pressure trace and should be avoided.

Typical driving gas pressures are between 50 psi for $P_C = 15$ bar experiments to $P_C = 125$ psi for 50 bar experiments. These driving pressures represent a good compromise between the minimum required for no rebound at EOC due to pressure and no rebound at EOC due to elastic reaction. Nonetheless, a small amount of piston rebound can be expected during/after the main ignition event. This small rebound may have an effect on the computation of ignition delay if it reduces the pressure rise rate during the ignition; it is expected that this effect will be very small relative to the typical random uncertainty in ignition delay experiments. Moreover, the driving pressures required to balance the full pressure rise during to ignition are more likely cause elastic rebound, especially for high P_C when the post-ignition pressure rise is greater.

The EOC conditions (P_C and T_C) can be independently varied. This is made possible by independent variation of the compression ratio, initial pressure and initial temperature, and the specific heat ratio of the test gases. The compression ratio can be increased by adding spacers onto the rear of the hydraulic chamber, increasing the stroke, and can be reduced by adding split shims onto the rear of the reaction chamber, increasing the EOC clearance length.

Fuel/oxidizer pre-mixtures are prepared in two mixing tanks, one approximately 17 L and the other approximately 15 L in volume. These large volumes allow many runs to be conducted from one mixture preparation. The mixing tanks are connected to the reaction chamber by flexible stainless steel manifold tubing. The tanks, reaction chamber, and connecting manifold are wrapped in heating tape and insulation to control the initial temperature of the mixture. Temperature controllers from Omega Engineering use thermocouples placed on the lid of each mixing tank, approximately in the center of each mixing tank, embedded in the wall of the reaction chamber, and near the inlet valve of the reaction chamber to control the preheat temperature of the mixture. A static pressure transducer (Omega Engineering, 0-5200 Torr) measures the pressure in the manifold and mixing tanks. This transducer is used during mixture preparation and to measure the initial pressure of a given experiment.

Most of the fuels studied in this work are liquids at room temperature and pressure and have relatively low vapor pressure. A similar procedure, outlined below, was used for all of the butanol

isomers, *iso*-pentanol, and methylcyclohexane. First mixing tanks are vacuumed to an ultimate pressure less than 5 Torr. The liquid fuel is massed in a syringe to a precision of 0.01 g prior to injection through a septum. Proportions of O₂, N₂, and Ar are added manometrically at room temperature. The preheat temperature of the RCM is set above the saturation point for each fuel to ensure complete vaporization. The vapor pressure as a function of temperature is calculated according to fits taken from Yaws [19]. A magnetic stirrer mixes the reactants. The temperature inside the mixing tank is allowed to equilibrate for approximately 1.5 hours.

This approach to mixture preparation has been validated in several previous studies by withdrawing gas samples from the mixing tank and analyzing the contents by GC/MS [20], GC-FID [3], and GC-TCD [7]. These studies have verified the concentration of *n*-butanol, *n*-decane, and water, respectively. In addition, both the work by Kumar et al. [3] on *n*-decane and the study of Weber et al. [20] on *n*-butanol confirmed that there was no fuel decomposition over the course of a typical set of experiments. Furthermore, within this study, each new mixture preparation is checked against previously tested conditions to ensure reproducibility.

The pressure in the reaction chamber during an experiment is monitored by a Kistler 6125B piezoelectric dynamic pressure transducer. The charge signal from the transducer is amplified and converted to a voltage by a Kistler 5010B charge amplifier. The voltage is sent to a National Instruments cDAQ equipped with the NI-XXXX module. The signal is recorded by LabView at 50 kHz.

1.2 Definition of Ignition Delay

?? shows a representative pressure trace from these experiments with methylcyclohexane at $P_C = 50$ bar, $T_C = 761$ K, and $\phi = 1.5$ (See ??). Note that ?? shows a case with two stages of ignition; not all of the fuels studied had conditions that showed two-stage ignition. Nonetheless, the ignition delay is consistently defined in all the work in this study. The definitions of the EOC and the ignition delays are indicated on the figure. The end of compression time is defined as the time when the pressure reaches its maximum before first stage ignition occurs, or for cases where there

is no first stage ignition, the maximum pressure before the overall ignition occurs. The first stage ignition delay is the time from the end of compression until the first peak in the time derivative of the pressure. The overall ignition delay is the time from the end of compression until the largest peak in the time derivative of the pressure.

Each unique P_C and T_C condition is repeated at least 5 times to ensure repeatability of the experiments. The experiment closest to the mean of the runs at a particular condition is chosen for analysis and presentation. The standard deviation of all of the runs at a condition is less than 10% of the mean in all cases.

1.3 Non-Reactive Experiments

?? also shows a non-reactive pressure trace. Due to heat loss from the test mixture to the cold reactor walls, the pressure and temperature of the gas in the reaction chamber will decrease after the end of compression. A non-reactive pressure trace is measured that corresponds to each unique P_C and T_C condition studied to quantify the effect of the heat loss on the ignition process and to verify that no heat release has occurred during the compression stroke. The non-reactive pressure trace is acquired by replacing the oxygen in the oxidizer with nitrogen, so that the specific heat ratio of the initial mixture is maintained, but the heat release due to exothermic oxidation reactions is eliminated. Maintaining a similar specific heat ratio ensures that the non-reactive experiment faithfully reproduces the conditions of the reactive experiment. A representative non-reactive pressure trace is shown in ?? corresponding to the experimental conditions in the figure.

1.4 New section

An RCM to be used for studies of homogeneous chemistry—as in this study—must ensure that homogeneous conditions exist inside the reaction chamber for the duration of the experiment. Due to the high piston velocities required to minimize heat loss and reaction during the compression stroke, complex fluid mechanical effects can strongly affect the state of the reactants at the EOC. The most important of these effects is caused by the motion of the piston itself, where the piston

pushes the wall boundary layer into a roll-up vortex [21]. This cold vortex mixes with the hotter gases near the center of the reaction chamber and causes large spatial inhomogeneities of temperature and species.

To facilitate spatially homogeneous conditions in the reactor and reduce the effect of the roll-up vortex, it is necessary to trap the boundary layer. This is accomplished on the present RCM by a crevice machined into the crown of the piston, shown in cross-section in ???. The boundary layer enters the crevice through the converging section as the piston moves forward and is trapped within the crevice. The dimensions of the crevice were optimized by **Mittal2006a** through CFD simulations for high-pressure conditions. Subsequently, Mittal and Sung [22] experimentally showed that the optimized crevice design provides homogeneous conditions in the reaction chamber up to approximately 150 milliseconds after the EOC. By using PLIF measurements of acetone-seeded mixtures, Mittal and Sung [22] showed that there was a core region of gases near the center of the reactor whose temperature remained spatially homogeneous.

1.5 Determination of Reactant Temperature

Two independent thermodynamic properties are required to fix the thermodynamic state of the reactants in the reaction chamber at a given time. The first property is the pressure, measured by the dynamic pressure transducer, as discussed previously; the second property is chosen to be the temperature.

In general, it is rather difficult to directly measure the temperature of the gases in the reaction chamber during and after compression. Intrusive methods such as thermocouples may introduce inhomogeneities into the reaction chamber and non-intrusive optical techniques are difficult to set up and require extensive calibration at the pressures of interest in RCM studies. Thus, the temperature is determined indirectly by applying an assumption called the "adiabatic core hypothesis" to the reaction chamber [1, 21].

If all of the gases in the reaction chamber are compressed isentropically, the temperature at the end of compression can be found by the following relations:

$$\ln(\text{CR}) = \int_{T_0}^{T_{ic}} \frac{1}{T(\gamma - 1)} dT \quad (2a)$$

$$\ln\left(\frac{P_{ic}}{P_0}\right) = \int_{T_0}^{T_{ic}} \frac{\gamma}{T(\gamma - 1)} dT \quad (2b)$$

where CR is the volumetric compression ratio, T_0 is the initial temperature, T_{ic} is the temperature at the end of isentropic compression, γ is the temperature-dependent ratio of specific heats, P_{ic} is the pressure at the end of isentropic compression, and P_0 is the initial pressure.

However, experiments show that the measured pressure in the reaction chamber does not reach the value of P_{ic} calculated by using the geometric compression ratio. The difference is due to finite heat loss from the reactants to the reactor walls and the crevice volume during the compression. Under the adiabatic core hypothesis, it is assumed that the heat loss from the reactants only occurs in a thin boundary layer near the wall, and the central core region is unaffected by heat loss (i.e. it is the core is adiabatic) [23]. Thus, the heat loss is modeled as an effective reduction in the compression ratio, and the temperature during the compression stroke can be calculated by:

$$\ln\left(\frac{P_C}{P_0}\right) = \int_{T_0}^{T_C} \frac{\gamma}{T(\gamma - 1)} dT \quad (3)$$

where P_C is the measured pressure at the end of compression, T_C is the temperature at the end of compression, and the other variables are the same as in Eq. (2).

After the end of compression, the pressure in the reaction chamber decreases, as can be seen in ???. This pressure decrease is caused by heat loss from the constant volume reaction chamber and is accompanied by a decrease in the temperature of the reactants. To model the thermodynamic state after the end of compression, the adiabatic core hypothesis is again applied, and the heat loss is assumed to occur only in a thin boundary layer near the reactor walls. Thus, the core region is again modeled as adiabatic, and the heat loss from the boundary layer can be modeled as an isentropic

volume expansion.

1.6 Determination of Compressed Temperature

In general, the specific heat ratio is a function of temperature, so Eq. (3) cannot be integrated directly. If the specific heats are parameterized with a polynomial fit, it is possible to integrate Eq. (3) directly, but this process is quite tedious; nonetheless, it will be applied in Sec. 1.7 to determine the uncertainty of T_C . In general, the simplest method of calculating T_C is to use software numerically integrate Eq. (3).

In this work, the CHEMKIN-Pro [24] software is used to perform the numerical integration and calculation of T_C . The CHEMKIN-Pro software provides the facility for a user-specified volume as a function of time to be applied to a homogeneous, adiabatic reactor. Since the adiabatic core of the reaction chamber is modeled as undergoing an isentropic volumetric compression followed by an isentropic volumetric expansion, the user-specified volume functionality is used to compute the RCM reactor state as a function of time. A volume trace for simulation is computed from the measured pressure trace using the isentropic relation:

$$\frac{V_2}{V_1} = \left[\frac{P_1}{P_2} \right]^{\frac{1}{\gamma}} \quad (4)$$

where V_1 and V_2 are the volumes at consecutive time points, P_1 and P_2 are the pressures at consecutive time points, and γ is the temperature dependent specific heat. This equation is applied during and after the compression stroke to calculate the volume trace.

For use in Eq. (4), γ is tabulated for each time point. Thus, the temperature at each time point must also be computed by using the isentropic relation for temperature:

$$\frac{T_2}{T_1} = \left[\frac{P_2}{P_1} \right]^{\frac{\gamma-1}{\gamma}} \quad (5)$$

where T_2 and T_1 are the temperature at consecutive time points. Since T_2 depends on the value of γ , which in turn depends on T_2 , Eq. (5) is iterated until the temperature changes by less than one tenth of one percent on consecutive iterations. The temperature calculated by Eq. (5) is typically within 1K of the temperature calculated by CHEMKIN-Pro; the difference is due to differences in the time step used by CHEMKIN-Pro.

1.7 Uncertainty of Ignition Delay and Compressed Temperature