Experimental CO Time-History Study of the Pyrolysis of Pentan-1-ol, Neopentanol and 2-Methyl-butan-1-ol in a Shock Tube

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1 Introduction

In anticipation of the effects of climate change, a shift towards cleaner forms of energy has been with the recent rise in battery technology and cleaner fuels that can be incorporated into current infrastructure and designs. Following this shift, the look to more energy-rich biofuels has gained popularity in the literature [1, 2]. One of the most viable biofuels is alcohol-based fuels such as ethanol which is sourced using biomass and converted directly into liquid fuel [3]. Ethanol has now been blended with gasoline to improve emissions and efficiency of internal combustion engines. Building on this use of ethanol, there are other primary alcohols with longer carbon chains and multiple isomers that have higher energy content per molecule and have potential to reduce emissions and present a solution for sustainability in fuels. This study looks at three isomers of C5 alcohol family, i.e. pentan-1-ol, neopentanol, and 2-methyl-butan-1-ol. An experimental study is described herein where the pyrolysis of all three isomers is initiated using a shock-tube to initiate high temperatures, monitoring the process with the use of laser diagnostics, to measure CO, an intermediate species of alcohol pyrolysis. The time-history CO profiles are presented with comparisons between the isomers highlighted.

2 Methodology

2.1 Shock-Tube Facility

Experiments were conducted in the Aerospace Shock Tube at the TEES Turbomachinery Laboratory, Texas A&M University (TAMU). The stainless-steel apparatus has a driver section measuring 3.25 m

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in length and 7.62 cm in inner diameter, and a driven section 7.88 m in length and 16.2-cm inner diameter. The schematic shown in Fig. 1 shows the layout of the tube and its respective dimensions. To create a shock wave, the driver and driven section are separated by a polycarbonate diaphragm with a thickness of 0.25 mm, allowing for post reflected shock pressures to reach approximately 1.3 atm. The rupture of the diaphragm is kept consistent by the use of a cross-shaped cutter downstream of the diaphragm, giving consistently reliable measurements. To detect the shock wave through the tube, five piezoelectric pressure transducers are placed near the end wall, detecting both the incident and reflected shock wave. These measurements of shock position, and hence velocity, allow for the normal shock relations to be implemented, giving the velocity of the reflected shock wave as well as the temperature and pressure behind it, i.e. T_5 and P_5. These reflected-shock conditions are calculated within an uncertainty level of $\pm$1% and $\pm$0.8%, respectively [4]. Prior to each test, the experimental apparatus is well-vacuumed using a rotary vane pump coupled with a turbomolecular pump reducing initial pressures to, at most, 10^{-8} atm. Mixtures for all three alcohols are highly diluted in argon, minimizing temperature changes during the test time due to chemical reactions taking place [5] and ensuring minimal boundary-layer effects [6]. The level of dilution is maintained at 99.75% with 79.75% Argon and 20% Helium to accelerate vibrational relaxation of CO allowing for higher sensitivity laser absorption measurements [7]. Table 1 shows the mixture compositions for each compound tested as well as the temperature and pressure range for the experimental results. Helium is also used as the driver gas which, along with the specific geometry of the apparatus, allows for test times to reach 3 ms [8].

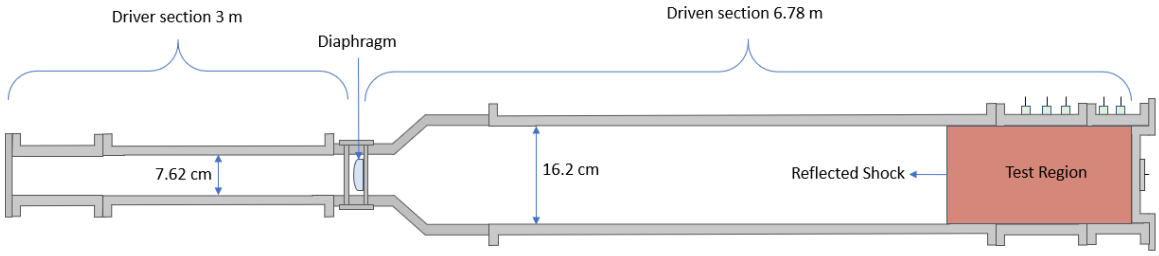

Figure 1: Schematic of Aerospace Shock Tube at TAMU used for experiments in this study.

Table 1: Mixture compositions, temperature and pressure ranges for the three pentanol isomers studied.

Fuel	X_{Fuel}	X_{He}	X_{Ar}	Temperature (K)	Pressure (atm)
Pentan-1-ol	0.0025	0.2	0.7975	1300 – 1546	1.19 – 1.36
Neopentanol	0.0025	0.2	0.7975	1197 – 1482	1.23 – 1.36
2-methyl-butan-1-ol	0.0025	0.2	0.7975	1185 -1530	1.24 – 1.33

2.2 Laser Diagnostics

CO time-history measurements were obtained using a tunable quantum cascade laser producing light near 4.8 µm, centered to the peak of the P(20) line of the 1 ← 0 band for CO. The conditions for this were 30°C and ~196 mA and were checked before each test using a removeable cell containing CO and Ar at a 10/90% concentration level to simulate the highly diluted mixture. This check allowed for the maximum absorption strength to be found by fine tuning. The specific wavelength used allows for CO measurements to be isolated from other absorbing species such as CO_2 and H_2O. The laser absorption setup is shown in Fig. 2.

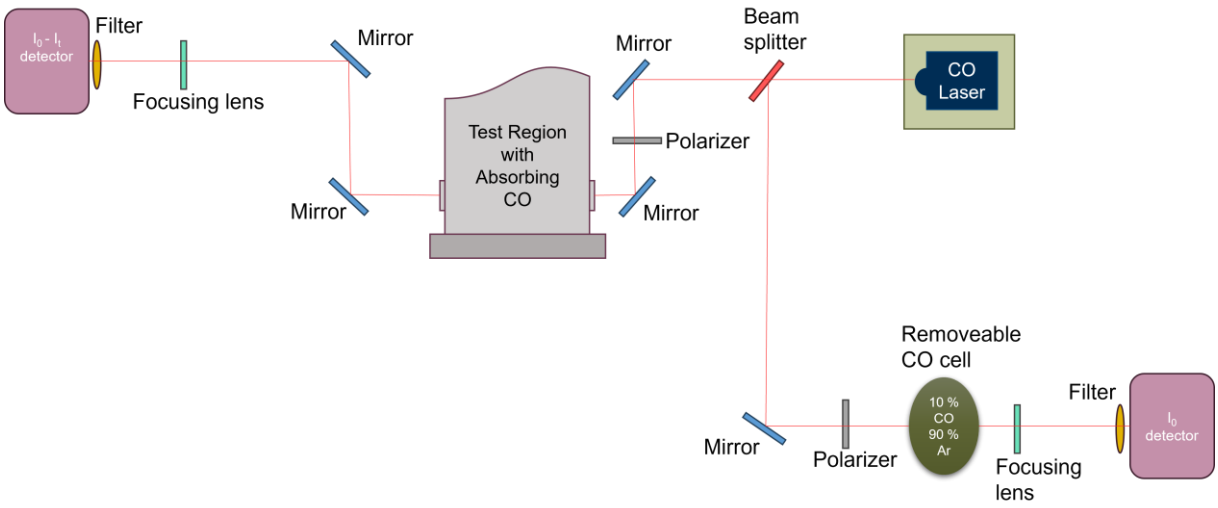

Figure 2: CO laser setup for experimental measurements.

For conversion of raw signal to a time history, the Beer Lambert Law is used, as shown below:

$$I_t/I_0 = exp(-k_\nu PL)$$

Where I_t = time-resolved transmitted beam intensity, I_0 = time-resolved incident beam intensity, k_ν = absorption coefficient (cm^{-1} atm^{-1}), P = partial pressure (atm), and L = path length (cm). The absorption coefficient follows the temperature dependent calibration equation:

$$k_\nu = 23.78\ exp^{-0.000646\ T}$$

This method of calibration was validated by Grégoire *et al.* [9].

3 Results

The CO time-history profiles for pentan-1-ol are presented in Fig. 3. There is an overall trend of a reduction in temperature causing a slower production of CO and the level of CO decreasing. However, for the highest temperature, the more intermediate temperatures give a higher level of CO.

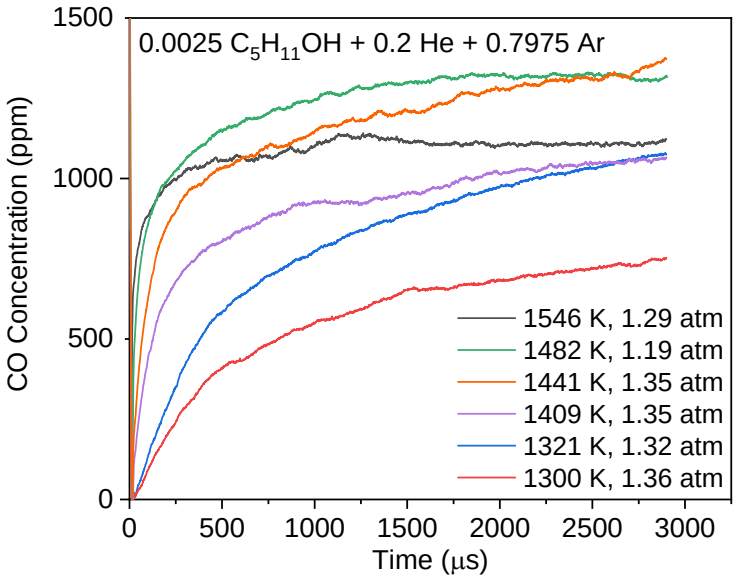

Figure 3: CO time-history profiles for pentan-1-ol for temperature range 1546 – 1300 K and pressure range 1.19 – 1.36 atm.

For neopentanol, the profiles are shown in Fig. 4 and indicate an increase in the level of CO produced when compared to pentan-1-ol. At a similar high temperature, such as 1482 K, the level of CO produced at the end of the test time for neopentanol is approximately 20% higher than pentan-1-ol. At a lower temperature of 1300 K for pentan-1-ol and 1306 K for neopentanol, the neopentanol produces approximately 40% more CO at the end of the test time.

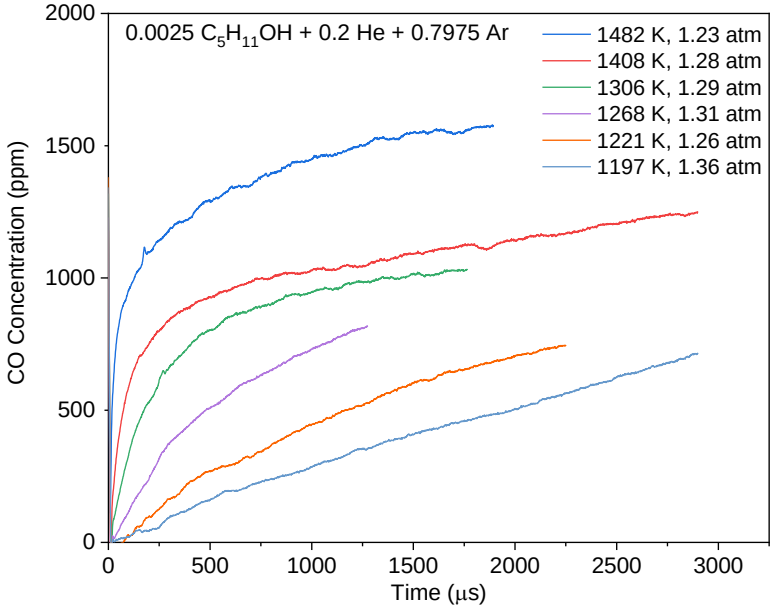

Figure 4: CO time-history profiles for neopentanol for temperature range 1482 – 1197 K and pressure range 1.23 – 1.36 atm.

Figure 5 shows the time-history profiles for the isomer, 2-methyl-butan-1-ol. The overall profiles are similar to neopentanol in regards to the amount of CO produced, where the highest temperature of 1391 K is within 50 ppm of what is measured for neopentanol at 1408 K. However, both of these are approximately 150 ppm higher than pentan-1-ol, indicating an approximately 15% increase compared to pentan-1-ol. At 1 ms, for temperatures of 1268 K and 1273 K for neopentanol and 2-methyl-butan-1-ol, respectively, the neopentanol has produced approximately 25% more CO than 2-methyl-butan-1-ol. This difference indicates a faster rate of production of CO for neopentanol in intermediate temperatures than the other isomers investigated. At the end of the test time (3 ms), for 1197 K, neopentanol had approximately 700 ppm of CO, which is consistent with the approximately 600 ppm produced from 2-methyl-butan-1-ol at 1185 K.

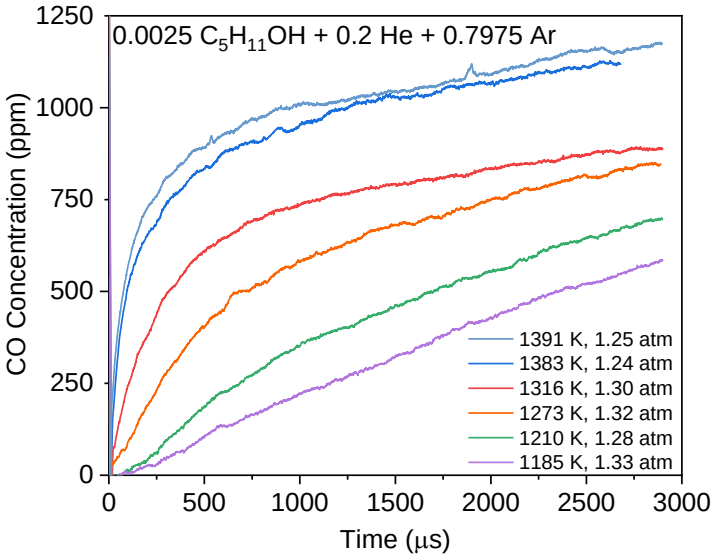

Figure 5: CO time-history profiles for 2-methyl-butan-1-ol for temperature range 1391 – 1185 K and pressure range 1.24 – 1.33 atm.

4 Conclusion

To conclude, this study presents the experimental results of the pyrolysis of three primary isomers of pentanol. Pentan-1-ol showed the least amount of CO produced over the test time when looking at similar temperatures between all three isomers. Additionally, neopentanol and 2-methyl-butan-1-ol showed similar amounts of CO at similar temperatures, however at intermediate temperatures, neopentanol still showed a clear faster rate of CO production. This disparity was reduced at higher and lower temperatures, indicating a region where the underlying kinetics have a dominant channel, favoring CO production for neopentanol over the other two isomers.

Acknowledgments

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