Ignition delay of 3-carene: single pulse shock tube study

N. Sharath[1], K. P. J. Reddy[1], P. K. Barhai[2] and E. Arunan[3,*]

[1]Department of Aerospace Engineering, Indian Institute of Science, Bengaluru 560 012, India
[2]Department of Applied Physics, Birla Institute of Technology, Mesra 835 215, India
[3]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bengaluru 560 012, India

Ignition delay experiments of 3-carene, a biofuel, have been carried out in a single-pulse shock tube for three equivalence ratios, 0.5, 1 and 2. The temperature was varied from 1140 to 1606 K. In the above-mentioned conditions, ignition delay was found to vary from 1.180 ms to 144 μs. The ignition delay values of 3-carene were found to be lower than those of JP-10, a kerosene-based fuel being considered for hypersonic applications.

Keywords: Biofuel combustion, 3-carene, ignition delay, shock tube.

IGNITION delay studies are important in calculating the minimum residence time required by a fuel to efficiently combust inside a combustion chamber and also in characterizing a fuel. Ignition delay of endothermic fuels like JP-10, a kerosene-based fuel, has been well studied[1–5]. Figure 1 shows the molecular structure of 3-carene, a monoterpene compound consisting of two isoprene units. The molecular formula of 3-carene, $C_{10}H_{16}$, is the same as that of JP-10, which is being considered for hypersonic applications. In early 1920s, Simonsen and co-workers started to analyse the oil extracted from two grasses obtained in the Himalaya and hills ranging from Kashmir to Assam[6–8]. The oil from two grasses, namely *Andropogon jwarancusa* and *Pinus longifolia* had a new hydrocarbon with molecular formula $C_{10}H_{16}$; it was named d-carene. It was also found that oil from *Andropogon jwarancusa* consists of 4-carene and *Pinus longifolia* consists of 3-carene[7].

In 1986, Panda *et al.*[9] carried out ignition of 3-carene/cardanol (70 : 30) blend in Pino's ignition delay apparatus and reported smooth pressure–time curve. Red fuming nitric acid (RFNA; consists of 77% HNO_3, 21% N_2O_4 and 2% water) with 5% by weight concentrated sulphuric acid was used as an oxidizer for the above measurements. When oxidizer-to-fuel ratio was 3.34, the ignition delay was found to be 35 ms. In 2009, Kulkarni *et al.*[10] carried out ignition delay experiments for several blends of 3-carene (with RFNA as an oxidizer) and suggested that 25% 3-carene with 75% ethylidenenorbornene can be a promising fuel.

Recently, in 2014, Salem *et al.*[11] extracted 3-carene from *Pinus roxburghii* by hydrodistillation. The extracted essential oil from wood, bark and needles was found to contain 14.95%, 28.05% and 33.37% of 3-carene respectively. *P. roxburghii* is reported to be commonly used in the making of adhesive, timber, paper and printing ink. Saei-Dehkordi *et al.*[12] found 13.64% 3-carene in the essential oil extracted from the leaves and flowers of *Zeravschania membranacea*, an edible plant grown in Iran.

Clearly, 3-carene which can be extracted from easily available plant sources, can be used as a fuel. Although ignition delay experiments of 3-carene in the presence of other molecules (blends) have been carried out, experiments on pure 3-carene have not been reported in the literature. Hence, we carried out the ignition delay experiments of 3-carene/O_2/Ar mixture. The main aim of this work is to understand the behaviour of 3-carene as a fuel. In this communication we describe the experimental results of 3-carene/O_2/Ar ignition and compare the values with those of JP-10.

The ignition delay experiments of 3-carene/O_2/Ar mixture were carried out in chemical shock tube-2 (CST2). A brief description of the experimental set-up and procedure, the details of which have been given in our previous work[13,14], is given below. The lengths of the driver and driven sections of the shock tube are 2 m and 4.25 m respectively. The inner diameter of the shock tube is 39 mm. An ACTON (VM-502) VUV monochromator coupled with a photo-multiplier tube (DA-780-VUV) was used to obtain CH emission spectra. An ADIXEN (ATP-400) turbo molecular pump has been used to evacuate the shock tube before loading the sample into the sample section of the shock tube. Three PCB pressure transducers

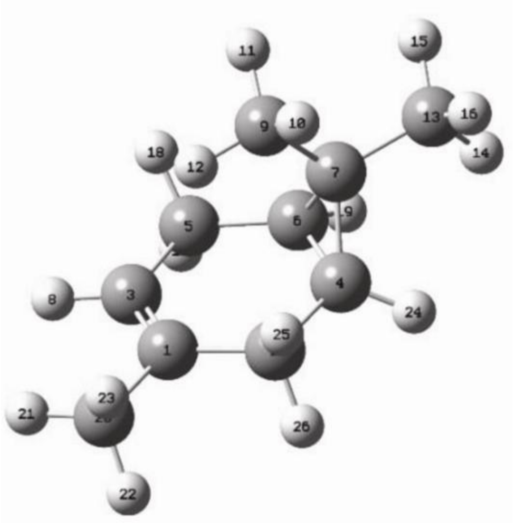

Figure 1. Molecular structure of 3-carene.

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*For correspondence. (e-mail: arunan@ipc.iisc.ernet.in) were used to obtain the pressure profile of the shock wave inside the shock tube. The shock Mach number calculated using two different sets of sensors was found to be the same. Two IRA pressure sensors of range 0–2 and 0–100 bar were used to measure pressure at the driven and driver sections of the shock tube respectively.

The sample section of the shock tube was heated and maintained at 70°C. It was evacuated to 10^{-4} mbar using the turbo molecular pump. The sample, 3-carene, was vapourized into the sample section of the shock tube. It was followed by pressuring the sample section with required amount of oxygen and dilution using argon to a total pressure of around 1866.5 mbar. The mixture was allowed to mix for 2 h. The pressure was reduced to the desired value and the mixture was subjected to reflected shock.

The pressure profiles obtained using the pressure transducers were used to calculate the shock Mach number. The obtained Mach number was then used in the *R*–*H* equation to calculate the reflected shock temperature, T_5. The pressure profile obtained at the pressure transducer mounted at a distance of 5 mm from the end wall was used to measure the ignition delay. The CH emission signal which was obtained using a vacuum monochromator tuned to 431.5 nm was also used to confirm the ignition delay of the fuel.

Ignition delay experiments of 3-carene/O_2/Ar were carried out for temperatures ranging from 1140 to 1606 K. The observed pressure was in the range 11–17.2 bar. The concentration of 3-carene was in the range 2.71×10^{-7}–7.83×10^{-7} mol/cm^3. The oxygen concentration was in the range 2.67×10^{-4}–1.38×10^{-5} mol/cm^3. In the above-mentioned conditions, ignition delay of 3-carene was found to vary from 1180 to 120 μs. At moderate and high temperatures, there is a sudden jump in the pressure profile due to ignition of fuel and hence one can easily measure the value of ignition delay, defined as the time difference between the arrival of reflected shock and ignition of fuel. An example of the pressure profile which shows ignition delay is displayed in Figure 2. At lower temperatures, the pressure rise will be gradual and one can define ignition delay values ID1 and ID2 as shown in Figure 3. Here the definition of ID1 is the same as that of

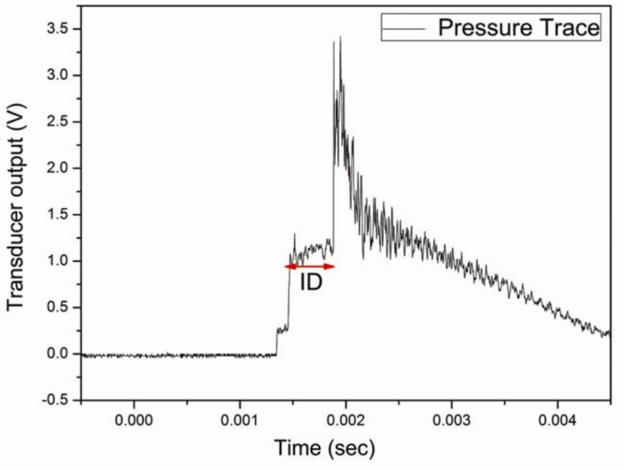

Figure 2. Typical pressure signal at moderate and high temperatures used to measure ignition delay. Sensitively of pressure transducer is 5.012 mV/psi.

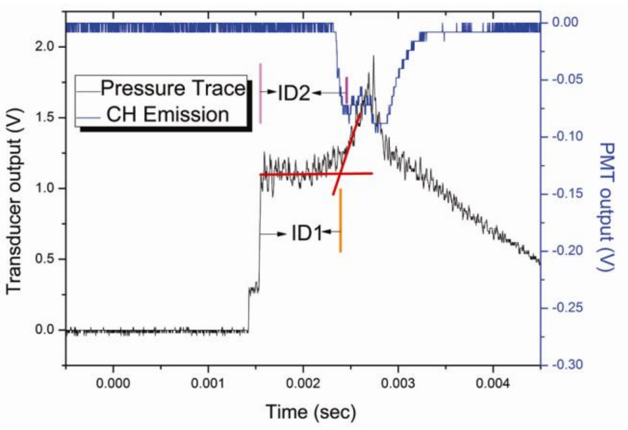

Figure 3. Typical pressure signal at low temperatures used for measuring ignition delay, where the pressure rise due to combustion is gradual. The definition of ID1 is the same as that of ID in Figure 2. PMT, Photo multiplier tube.

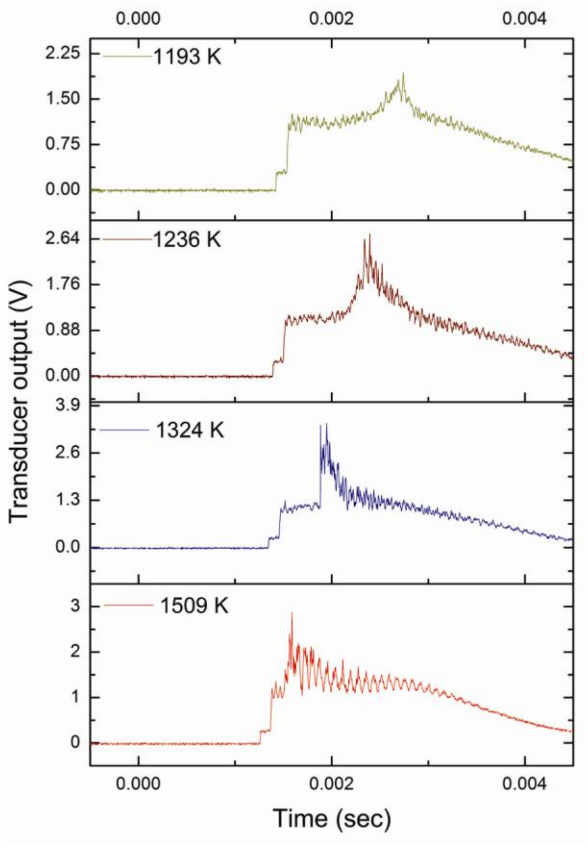

Figure 4. Pressure signals showing the variation in ignition delay of stoichiometric 3-carene/O_2/Ar mixture at different temperatures.

Table 1. Summary of results obtained in the ignition delay experiments of 3-carene

T_5 (K)	P_5 (atm)	i.d (τ) (μs)	[3-carene] (mol/cm^3)	$[O_2]$ (mol/cm^3)
Equivalence ratio = 1				
1392	15.75	280	7.83E-07	1.10E-05
1335	13.1	432	4.06E-07	5.68E-06
1509	16.84	196	4.42E-07	6.19E-06
1324	13.41	428	5.02E-07	7.02E-06
1324	14.39	460	4.05E-07	5.67E-06
1236	13.81	772	4.49E-07	6.28E-06
1279	16.26	572	4.75E-07	6.65E-06
1279	15.38	484	6.60E-07	9.23E-06
1346	14.73	420	3.84E-07	5.37E-06
1279	15.09	568	4.34E-07	6.08E-06
1193	14.19	1010	4.22E-07	5.90E-06
1225	10.74	716	3.20E-07	4.49E-06
1140	11.5	1180	3.54E-07	4.95E-06
1392	14.41	436	2.96E-07	4.14E-06
1346	13.46	408	3.75E-07	5.25E-06
1346	12.65	424	3.41E-07	4.78E-06
1450	14.58	200	3.64E-07	5.09E-06
1301	12.04	444	3.28E-07	4.59E-06
1509	13.93	176	3.11E-07	4.35E-06
1438	17.65	328	4.44E-07	6.21E-06
1403	14.55	328	3.57E-07	4.99E-06
1214	14.18	950	3.24E-07	4.54E-06
1301	11.71	528	3.60E-07	5.04E-06
1438	12.58	272	2.72E-07	3.60E-06
1485	13.38	200	4.23E-07	5.92E-06
1403	11.05	324	2.92E-07	4.08E-06
1669	17.64	136	3.69E-07	5.17E-06
1594	17.93	148	4.32E-07	6.04E-06
1509	18.59	180	5.26E-07	7.37E-06
1606	18.87	144	4.29E-07	6.00E-06
1557	18.09	220	4.35E-07	6.09E-06
Equivalence ratio = 0.5				
1182	11.83	752	3.27E-07	9.16E-06
1279	13.47	436	3.49E-07	9.77E-06
1335	13.85	340	3.28E-07	9.19E-06
1403	14.79	148	4.46E-07	1.25E-05
1392	15.84	212	4.96E-07	1.39E-05
1473	15.43	120	3.41E-07	9.56E-06
1335	13.09	332	3.34E-07	9.35E-06
1403	14.95	192	3.73E-07	1.05E-05
1485	16.46	180	3.75E-07	1.05E-05
1140	11.65	936	3.24E-07	9.08E-06
1279	14.71	452	3.98E-07	1.11E-05
1193	12.17	664	3.44E-07	9.64E-06
1290	15.59	436	3.94E-07	1.10E-05
1324	16.9	336	4.28E-07	1.20E-05
1335	15.25	296	3.83E-07	1.07E-05
1301	16	348	4.09E-07	1.15E-05
1403	15.79	224	3.68E-07	1.03E-05
1392	14.69	188	3.45E-07	9.65E-06
1257	12.94	380	3.30E-07	9.25E-06
1485	16.93	128	3.76E-07	1.05E-05
1392	15.65	192	3.80E-07	1.06E-05
1335	14.02	336	3.76E-07	1.05E-05
1403	16.97	188	3.90E-07	1.09E-05
1193	12.51	624	3.54E-07	9.91E-06
1225	12.89	540	3.74E-07	1.05E-05
1438	15.37	140	3.50E-07	9.80E-06
1438	17.13	176	3.97E-07	1.11E-05
1426	15.57	156	3.58E-07	1.00E-05
1140	12.38	960	3.87E-07	1.08E-05
Equivalence ratio = 2				
1438	15.1	468	4.46E-07	3.12E-06
1485	16.18	348	5.67E-07	3.97E-06
1450	14.47	440	4.02E-07	2.82E-06
1485	14.47	416	4.25E-07	2.98E-06
1569	16.45	316	4.42E-07	3.10E-06
1606	15.76	264	4.01E-07	2.81E-06
1426	13.76	520	3.89E-07	2.72E-06
1392	16.87	460	5.19E-07	3.63E-06
1301	13.22	864	4.43E-07	3.10E-06
1335	13.32	736	5.07E-07	3.55E-06
1380	14.57	596	4.98E-07	3.48E-06
1392	15.58	480	3.97E-07	2.78E-06
1533	14.29	324	3.82E-07	2.68E-06

ID in Figure 2. The process of obtaining ignition delay value ID1 using steepest pressure rise and extrapolating it to meet the P_5 plateau has been used by several research groups[15–17].

Pressure signals showing the variation of ignition delay of 3-carene under stoichiometric conditions with temperature are displayed in Figure 4. This figure clearly shows the decrease in ignition delay with increase in reflected shock temperature. Results of 3-carene experiments are summarized in Table 1. In this study, definition of ignition delay at higher temperatures is the same as that of ID in Figure 2. At lower temperatures, we have used ID1 (which is the same as ID in Figure 2), shown in Figure 3, as the ignition delay. As seen from Figure 4, the three pressure signals show a constant pressure profile before the ignition of fuel. The facility effect and the pre-ignition effect described by Pang *et al.*[18] and Hong *et al.*[19] are not seen in these signals. However, the signals shown in Figure 2 and the one at 1324 K shown in Figure 4 show a gradual increase in profile before the ignition of fuel. On careful observation it was seen that the profiles around ~1350 ± 50 K, show similar trend. Since there is no facility effect in the rest of the temperature range, the rise in pressure in the range 1300–1400 K can be because of pre-energy release and not due to facility effect. A plot showing the variation of ignition delay with temperature for different equivalence ratios is displayed in Figure 5. The data in the plot were linear fitted to obtain A and E_a for eq. (1) below. Pre-exponential factor and activation energy for all the equivalence ratios are summarized in Table 2.

$$\tau = A \times e^{(E_a/RT)}. \tag{1}$$

Table 2. Activation energy and pre-exponential factors for 3-carene/O_2/Ar and JP-10/O_2/Ar ignition

Equivalence ratio	*A* (s) 3-carene	*A* (s) JP-10	E_a (kcal/mol) 3-carene	E_a (kcal/mol) JP-10
1	–6.14 ± 0.11	–6.54 ± 0.29	16.92 ± 0.66	20.54 ± 2.08
0.5	–6.69 ± 0.14	–7.50 ± 0.26	19.23 ± 0.86	25.08 ± 1.62
2	–5.66 ± 0.18	–5.45 ± 0.16	15.23 ± 1.20	14.57 ± 1.13

The value of E_a for JP-10 ignition (for $\phi = 1$) from Wang *et al.*[3] is 19.03 kcal/mol.

The values of *A* and E_a for JP-10 ignition (for $\phi = 1$) from Ryan *et al.*[20] are –5.38 s and 21.8 kcal/mol respectively.

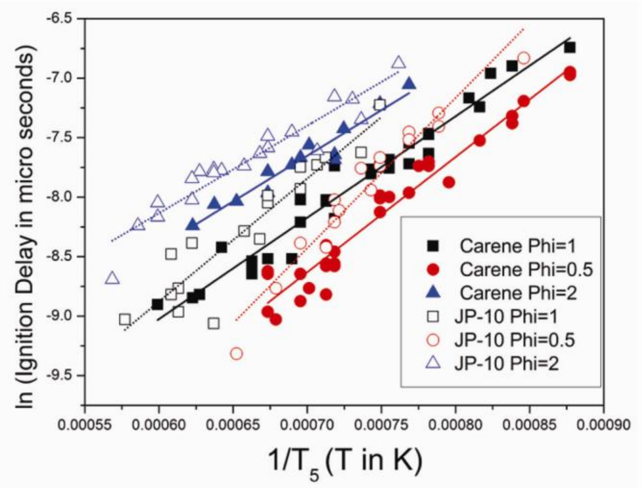

Figure 5. Plot showing the variation of ignition delay of 3-carene and JP-10 with temperature. Solid lines, Linear fit for 3-carene; dotted lines, linear fit for JP-10.

Here τ is ignition delay value, *A* the pre-exponential factor, E_a the activation energy for ignition, *R* the universal gas constant and *T* is the temperature.

There have been numerous reports on JP-10 ignition delay[1–4,20]. Our laboratory has measured ignition delay of JP-10 for equivalence ratio 1 and results have been reported[5]. A series of experiments for equivalence ratios 0.5, 1 and 2 was carried out and the results are given here. Results on JP-10 ignition are in broad agreement with recent reports. Our main objective in this work is to report the ignition delay for 3-carene and compare it with that of JP-10, measured under similar conditions.

The ignition delay experiments of JP-10 were carried out for three equivalence ratios of 0.5, 1, and 2, with the pressure ranging from 11 to 21 bar and temperature ranging from 1182 to 1733 K. The concentration of JP-10 was varied from 1.87×10^{-7} to 2.34×10^{-7} mol/cm^3, and the concentration of oxygen was varied from 1.31×10^{-6} to 5.34×10^{-6} mol/cm^3. In the above-mentioned experimental conditions ignition delay values of JP-10 were found to vary from 1080 to 116 μs.

Table 2 gives a comparison of the activation energy and pre-exponential factor for ignition of JP-10 from the work carried out in our lab with those of 3-carene. The ignition delay values of 3-carene and JP-10 for all the three equivalence ratios are compared in Figure 5. It can be clearly seen that the barrier for ignition and the ignition delay of 3-carene are lower compared to that of JP-10. The ignition delay signals of stoichiometric, fuel-rich and fuel-lean JP-10/O_2/Ar mixture at different temperatures are given in Figures S1, S2 and S3 respectively (see Supplementary Information online). The experimental conditions and corresponding ignition delay values in JP-10 ignition delay studies are given in Table S1 (see Supplementary Information online). Similar to 3-carene, a rise in pressure before the ignition of fuel can also be seen in JP-10 for a small range of temperatures. However, in case of JP-10, the rise in pressure due to pre-ignition energy release was found to be at a higher temperature than that of 3-carene. This also confirms that the pressure rise seen in Figure 2 is due to the chemistry of the fuel and not because of facility effect. In the case of JP-10, the effect of pre-ignition energy release can be clearly seen from the pressure signal at 1497 K in Figure S1 (see Supplementary Information online).

Ignition delay experiments for 3-carene, a biofuel, were carried out in a single-pulse shock tube for three equivalence ratios of 0.5, 1 and 2, for temperature ranging from 1140 to 1606 K. Results showed that ignition delay values of 3-carene for all three equivalence ratios were less than those of JP-10, a kerosene-based well-characterized fuel. As seen from the present and previous studies, 3-carene can be used as an alternative biofuel for hypersonic application. A detailed study to understand initial pyrolysis and oxidation processes is in progress.

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Comparison of performance of solar photovoltaics on dual axis tracker with fixed axis at 13°N latitude

Roshan R. Rao, H. R. Swetha, J. Srinivasan and Sheela K. Ramasesha*

Divecha Centre for Climate Change, Indian Institute of Science,
Bengaluru 560 012, India

Tracking systems, that continually orient photovoltaic (PV) panels towards the Sun, are expected to increase the power output from the PV panels. Tremendous amount of research is being done and funds are being spent in order to increase the efficiency of PV cells to generate more power. We report the performance of two almost identical PV systems; one at a fixed latitude tilt and the other on a two-axis tracker. We observed that the fixed axis PV panels generated 336.3 kWh, and the dual-axis Sun-tracked PV panels generated 407.2 kWh during August 2012–March 2013. The tracked panels generated 21.2% more electricity than the optimum tilt angle fixed-axis panels. The cost payback calculations indicate that the additional cost of the tracker can be recovered in 450 days.

Keywords: Cost payback time, dual axis Sun tracker, energy conversion, solar panel.

THE annual average growth rate of solar photovoltaic (PV) operating capacity in the world was the highest at 55% during 2008 through 2013 followed by concentrated solar power at 48% and wind power at 21% (ref. 1). The amount of solar energy incident on the surface of the Earth is several times more than the global energy consumption[1]. The major source of electricity in India as of November 2014 is from thermal sources (69%), followed by nuclear and hydroelectric sources (17%) and the renewable energy sources (14%)[2]. Currently, among the renewable energy sources, wind power share is 66%, biomass and bagasse cogeneration is 12.7%, small hydro and others is 12.3% and solar energy is 9% (ref. 3). India receives an annual average global horizontal insolation (GHI) of about 5 kWh/m^2/day (ref. 2) and nearly 58% of the geographical land area has the potential for solar energy production, which translates to a solar potential of nearly 9 million GWh per day[4]. PV panels have a great potential in meeting the energy demand of the country and at the same time protecting our environment by reducing CO_2 emissions in their life cycle[5]. In this scenario, it is necessary to utilize as much solar energy as possible to generate electricity.

If the conventional flat PV panel systems with a fixed tilt angle are used, during the course of the day the sunlight incident will be along the surface in the morning

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*For correspondence. (e-mail: sheela@caos.iisc.ernet.in)