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Thermal degradation of two liquid fuels and detonation tests for pulse detonation engine studies

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Abstract The use of liquid fuels such as kerosene is of interest for the pulse detonation engine (PDE). Within this context, the aim of this work, which is a preliminary study, was to show the feasibility to initiate a detonation in air with liquid-fuel pyrolysis products, using energies and dimensions of test facility similar to those of PDEs. Therefore, two liquid fuels have been compared, JP10, which is a synthesis fuel generally used in the field of missile applications, and decane, which is one of the major components of standard kerosenes (F-34, Jet A1, ...). The thermal degradation of these fuels was studied with two pyrolysis processes, a batch reactor and a flow reactor. The temperatures varied from 600°C to 1,000°C and residence times for the batch reactor and the flow reactor were, respectively, between 10–30 s and 0.1–2 s. Subsequently, the detonability of synthetic gaseous mixtures, which was a schematisation of the decomposition state after the pyrolysis process, has been studied. The detonability study, regarding nitrogen dilution and equivalence ratio, was investigated in a 50 mm-diameter, 2.5 m-long detonation tube. These dimensions are com-

patible with applications in the aircraft industry and, more particularly, in PDEs. Therefore, JP10 and decane were compared to choose the best candidate for liquid-fuel PDE studies.

Keywords Pyrolysis · Batch reactor · Flow reactor · Decane · JP10 · Pulse detonation engine (PDE) · Deflagration to detonation transition (DDT)

PACS 82.33.Vx · 82.30.LP

1 Introduction

The choice of fuel for Pulse Detonation Engine (PDEs) applications must take into account two opposing criteria: a good detonability with a high energetic content, and a low reactivity when ignited accidentally (IM requirements for military applications, or safety requirements in civil applications). Much work has been carried out in the field of hydrocarbons to develop high density energetic kerosene for aeronautical applications under safe conditions. Unfortunately, it is difficult to initiate a detonation with such fuels. Kerosenes are the subject of many studies in this field [1–3].

Within kerosenes, it is possible to distinguish from those that are obtained from crude oil (F34, jet A1...) and those that are made by synthesis, like JP10. The latter are used more often in the field of missiles for military applications. This is why detonability studies of JP10 fuel are more common in the PDE propulsion field. One important parameter to take into account is the critical detonation energy. There is much work being carried out with the aim of decreasing this energy; for example, this can be done by reducing the lengths of transition

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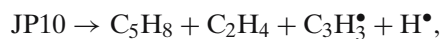
from deflagration to detonation. Generally these studies are carried out on kerosene sprays; however, kerosene originating from cracking could also be used for this kind of application, which could be for F34 fuel. Unfortunately, the complex nature of this liquid makes the studying of fundamental detonability extremely complex and difficult. Decane is one of the major components of this fuel and it can be used as a model for laboratory studies of detonation. The aim of this work is to compare the performances of two liquid fuels, a JP10 kerosene and decane, as possible candidates to supply PDEs with energy after a pyrolysis process. This preliminary study was carried out in the laboratory with a representative composition of gaseous products which were obtained after the pyrolysis of the two tested fuels.

The strategy of the Laboratoire Energétique, Explosions and Structures (LEES) and Roxel Company is to sensitise the detonation by means of the pyrolysis of the fuel before it is introduced into the detonation chamber [2,3]. It is this experimental method that will be used for the work presented in this article. The experimental device developed and used within the framework of this study will be briefly described and followed by a presentation of the principal results of pyrolysis for decane and JP10 fuel types. A parametric study, according to the temperature of pyrolysis T_f and the residence time τ , will be carried out with two different experimental devices. For each device, the thermal degradation process will be optimised according to the residence time and temperature values. The objective of this optimisation is to increase the probability of deflagration to detonation transition (DDT) in the detonation tube.

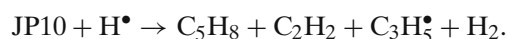
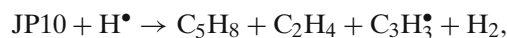
A study of detonation tests conducted in a tube will then be made to determine the detonation limits using a Schelkin spiral. Finally a comparison of the results for both hydrocarbons derived in this study will help to ascertain the best candidate for a future fuel that can be used in an embarked PDE application.

2 Bibliography

Several studies have been carried out on the degradation mechanism of JP10 during a pyrolysis. Among them, Davidson et al. [4] show that the initial major product is cyclopentene and summarise the different hypotheses relating to this subject. Williams et al. [5] and Li et al. [6] suggest that in a second step the final products are acetylene, ethylene and 1.3-butadiene. According to Li et al. [6] the degradation mechanism in the second step is the following:



Initially the products resulting from the JP10 decomposition are cyclopentene, ethylene, acetylene, and three radicals $\text{C}_3\text{H}_3^\bullet$, $\text{C}_3\text{H}_5^\bullet$ and H^\bullet . Afterwards the hydrogen radical reacts with the JP10 molecule and gives dihydrogen as another product:



Green and Anderson [7] postulate that benzene is the major product of the reaction.



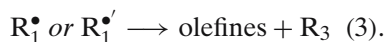
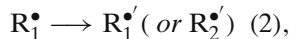
The thermal decomposition of JP10, in the context of a PDE application, has been the subject of several studies. Green et al. [7] studied the pyrolysis of JP10 in a flow reactor with a 2 ms residence time. They observed that the major product was cyclopentadiene for $T < 980^\circ\text{C}$ and benzene for $980^\circ\text{C} < T < 1,230^\circ\text{C}$. Brabbs and Merritt [8] studied the thermal degradation of JP10 using a fuel-rich catalytic combustion. The part of the fuel which had not reacted with oxygen was converted by pyrolysis. The combustion temperature of JP10/oxygen mixture, with an equivalence ratio of 5.06, reaches 950°C . The major species resulting from the pyrolysis are hydrogen (42.3% in mole fraction), ethylene (22.4%), hydrocarbons with three or more carbon atoms (16%) and methane (15.2%). Another method investigated to decompose the JP10 is a catalytic reaction. Cooper and Shepherd [9,10] studied the JP10 pyrolysis in a catalytic reactor with zeolite at 500°C . The flow reactor was a stainless steel tube with a 0.5-inch internal diameter. With a 2.3 g/h mass flow rate, the conversion of JP10 was 34% with zeolite and 3% without. The inclusion of zeolite was to produce lighter molecules and, more particularly, species with five carbon atoms at a low pyrolysis temperature. Galligan et al. [11] examined the catalytic decomposition of JP10 with three zeolites (ZSM-5, nanocrystalline ZSM-5 (nZSM-5), and UL-ZSM-5) and two Sulphur Aluminium Phosphate (SAPO-5 and SAPO-11) catalysts. The reactor consists of a catalyst mixed with quartz wool, heated between 250 and 650°C at 25 PSI of pressure. The reaction time is controlled with the helium carrier gas flow rate. The reaction time for 1.5, 2, and 5 mg catalysts are, respectively, 0.5, 0.8, and 1 s. This analysis was achieved by using a gas chromatographer/mass spectrometer. The results concerning hydrogen are not reported since the columns used do not have the compability to observe this light gas. The ZSM-5 Zeolite is not efficient due to the small pore size (10 \AA) when compared to the size of the JP10 molecule ($>9 \text{ \AA}$). With nZSM-5 and ULZSM-5, the decomposition products are xylene,

toluene, benzene, C₄, C₃ and C₂ species. Lighter products are more abundant at lower temperatures than at the higher temperatures where benzene, toluene, and xylene increase. The decomposition products with SAPO-5 are xylene, toluene, benzene, 1,2-divinylbenzene, butene, propyne, propylene and ethylene. SAPO-11 is less efficient than SAPO-5. Using SAPO-11, the decomposition products are C₅ and greater species, mainly toluene and xylene, even at 600°C. Methane was not observed in the decomposition products.

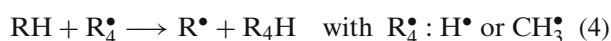
Several studies focused on determining the correct conditions to detonate JP10 in oxygen and air. Brophy et al. [1] obtained the detonation of JP10 fuel spray in oxygen in a 76.2 cm-long tube with an internal diameter of 3.96 cm. The ignition source was a spark that delivered power levels of approximately 4.9–16.2 kW. Akbar et al. [12] obtained detonation for JP10/O₂ and JP10/air mixtures with and without nitrate sensitisation. The experiments were performed at 1 atm and at 135°C in a 32 cm-internal diameter, 24 m-long heated test section and a 4 m-long H₂/O₂ driver. The JP10/air measured cell size was about 47 mm. Card et al. [13] studied flame acceleration and DDT in JP10-air mixtures at initial temperatures between 300 and 573 K for two initial pressures, 1 and 2 atm. These experiments were carried out in a 3.1 m-long, 10 cm -inner diameter heated tube equipped with equally spaced (10 cm) orifice plates. The blockage ratio of the obstacles is Br = 0.43. Ionisation probes located along the complete length of the tube, spaced 30.5 cm, are used to determine the flame velocity. JP10 is vapourised at 410K in a mixing chamber before it is introduced into the tube. No initiation of detonation has been observed for JP10-air mixtures at an initial pressure of 1 atm. Conversely, the initiation of detonation occurs over a range of mixture compositions (0.9–1.48% JP10 in air) at all tested temperatures. DDT limits have been studied at 2 atm for several temperatures according to the equivalence ratio. At 373 K the DDT occurs at equivalence ratios of JP10-air mixtures between ER = 0.77 and ER = 1.42. At 473 K the initiation of detonation occurs for equivalence ratios between ER = 0.8 and ER = 1.19, and between ER = 0.84 and ER = 1.19 at 538 K.

The fragmentation of alkanes can be explained by the Rice–Herzfeld–Kossiakoff mechanism. The reaction's initiation is made by an initial homolytic fission of the C–C bond since the energy of the C–H bond (approximately 400 kJ mol⁻¹) is higher than the C–C bond (approximately 350 kJ mol⁻¹). The initial molecule (RH) produces two radicals R₁[•] and R₂[•] (1), which can be fragmented by homolytic fission of the C–C bond to produce olefins and an inferior radical (3). An isomerisation is possible before the homolytic fission of the C–C

bond (3) concerning radicals with more than five carbon atoms:



Subsequently, the decomposition of the inferior radicals gives rise to hydrogen radicals (H[•]) and methyl radicals (CH₃[•]), which ensure that the reaction propagates (4):



Tieszen et al. [14] studied the detonability of decane in a heated detonation tube. The facility was 0.43 m inner diameter and 13.1 m long. The driver section contained a 40 g EL506C1 high density explosive to initiate the gaseous mixture. They obtained detonation of decane in air with an initial temperature of 100°C, an initial pressure of 1 atm and an equivalence ratio of 1. The measured cell width observed was 42 mm.

3 Experimental protocols

3.1 Batch reactor pyrolysis

A thermal degradation facility (Fig. 1) was built to analyse the pyrolysis products of kerosene as a function of the residence time and temperature.

It consists of an evaporator, a tubular quartz reactor inside an oven and a sample tank connected to a gas chromatograph (GC) Star 3800 provided by the Varian Company. The evaporator is heated to 100°C in order to evaporate the fuel contained in the tank. The vapour pressure of the fuel is approximately 12.4 kPa at this temperature. All the components are first heated to the selected temperature, and a primary vacuum ($P < 0.1$ kPa) is then achieved in the system up to valve 1. Then, all the valves are closed. Afterwards, the valve located at the outlet of the evaporator (valve 1) is manually opened for 2 s to allow the (equilibrium) kerosene

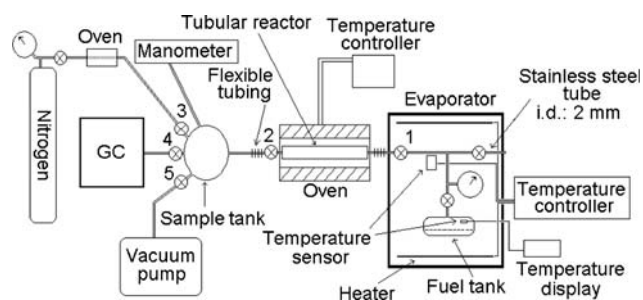


Fig. 1 Experimental device used for the batch reactor pyrolysis

vapours to flow into the reactor. This point is considered to be time zero and defines the residence time of the kerosene vapours in the reactor at the chosen pyrolysis temperature. The reactor temperature is determined with an uncertainty of $\pm 10^\circ\text{C}$. When the desired residence time is reached, the outlet valve of the reactor is opened (valve 2) for 5 s. Consequently, the gaseous mixture originating from the thermal degradation flows into the sample tank. Since the pressure of the sample must be above the atmospheric pressure before injection into the sample cell of the GC, nitrogen is introduced (via valve 3) into the sample tank until it reaches approximately 160 kPa. Finally, the gaseous mixture is injected into the GC (valve 4) for analysis. The maximal error in determining the mass fraction of each species is 5%. It is necessary to correct the molar fraction measurement according to the following relationship:

$$x_i = \frac{x_i^*}{1 - P_{N_2}/P_T^*},$$

where x_i and x_i^* are, respectively, the molar fraction before and after the addition of nitrogen, P_{N_2} is the partial pressure of N_2 and P_T^* is the total pressure with N_2 .

The residence times tested in this study are 10, 30 and 60 s. The maximum errors in determining the residence times are 5% for $\tau = 10$ s, 2% for $\tau = 30$ s and 0.8% for $\tau = 60$ s.

3.2 Flow reactor pyrolysis

A second experimental device (Fig. 2) was conceived to perform pyrolysis at atmospheric pressure with shorter residence times (between 0.1 and 1 s), which are closer with real applications. At first, the liquid fuel to be studied is evaporated at 400°C in the evaporator. Then the liquid fuel is introduced into the evaporator by flowing along a capillary tube ($150\ \mu\text{m}$ i.d.) from the fuel tank. The flow is controlled by the pressure of the nitrogen

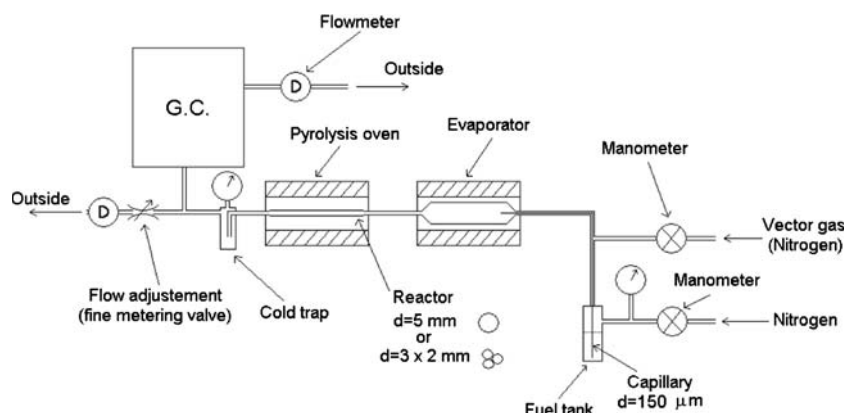
that resides above the liquid surface in the tank. Once evaporated, the gas flows into a quartz reactor by means of the carrier gas (nitrogen). The dilution ratio and the residence time in the reactor are controlled by the carrier gas flow and the fuel flow. The reactor temperature is determined with an uncertainty of $\pm 10^\circ\text{C}$. At the exit of the reactor a cold trap captures the heavy species, thus allowing them to be quantified and analysed. Afterwards, the gas flow is divided into two parts, a small amount of the gas flows into the GC Star 3800 and the other part flows out to the exit of the experimental apparatus. The maximum error in determining the mass fraction of each species is 5%. The flow can be adjusted by a fine metering valve to limit the pressure in the GC, which has to be lower than the working pressure in the sample injection valves. The values of the two flows are displayed by flow meters. The total flow allows to determine the residence time of the gas in the reactor. The maximum errors in determining the residence times are 0.7% for $\tau = 0.1$ s, 2% for $\tau = 0.3$ s and 6% for $\tau = 1$ s. All of the connections between each part of the facility are heated ($\sim 100^\circ\text{C}$) to avoid the condensation of heavy species.

The study also investigates the influence of the reactor geometry. The first tubular reactor is 150 mm long with a 5 mm inner diameter. It can be used for 0.3, 1 and 2 s residence time. The second reactor consists of three tubular pipes connected in parallel. Each tubular pipe is 150 mm long with a 2 mm inner diameter. This reactor has a greater thermal exchange area, when compared with the first one, and also has a smaller volume which thus decreases the residence time to 0.1 s while retaining a reasonable flow rate (roughly 14 ml/s).

3.3 Detonation tube

The detonation tube (Fig. 3) has been previously described [3]. Ignition is obtained by means of an exploding wire ($E_{\text{nom}} = 265$ J) with a Schelkin spiral to support

Fig. 2 Experimental device used for the flow reactor pyrolysis



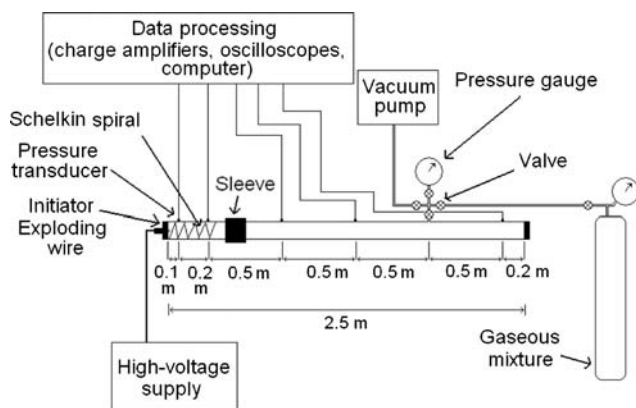


Fig. 3 Detonation tube used in this study

the DDT. The tube has an inner diameter of 49 mm and is 2.5 m long. The Schelkin spiral is 64 cm long with a 0.55 blockage ratio. The blockage ratio (Br) is defined by $Br = 1 - (d^2/D^2)$, where d is the inner diameter and D the outer diameter of the spiral. The spacing between the coils is nearly equal to the external diameter of the spiral. The choice of this spiral configuration has been discussed previously [2, 3].

The dimensions of the tube were chosen in order to be compatible with aircraft industry applications and more particularly the PDE. The tube is equipped with five pressure transducers (Kistler 603B) that are located, respectively, at 0.1, 0.3, 0.8, 1.3 and 2.3 m from the ignition source. These sensors are connected to charge amplifiers (Kistler 5011) which transmit the signal to oscilloscopes (Tektronix TDS 210). A personal computer records the signal from the oscilloscopes.

The detonation wave pressure can be measured and thus deduce its celerity. The measured pressures and celerity are compared with the Chapman–Jouguet values that are calculated with the NASA Chemical Equilibrium with Applications (CEA) computer code for each tested gaseous mixtures. The pressure measurements alone could not be used accurately to determine if the deflagration to detonation transition (DDT) occurred, and whether the detonation wave was at a steady state or not. This was due to the size of the pressure transducer (5 mm diameter). For the mixtures which present a large cell width, the measured pressures are influenced by the high pressures in the induction zone whose length increases with the cell size. Then the transducers measure pressures between P_{CJ} and a pressure near the Zeldovich, von Neumann and Döring value (P_{ZND}). For the more sensitive mixtures, the cell widths are small and the transducer measures an average pressure near the CJ value. For repeated similar experimental tests, a dispersion of pressure results are observed. To determine if the detonation is at a steady

state or not, wave velocity is more pertinent than pressure. Consequently, we focused our attention on the space–time diagrams defined by the distance between the transducers and the arrival time of the pressure wave on the transducers. The velocity is deduced from the gradient of the straight line on the space–time diagram. The maximum error by determining the wave velocity does not exceed 1%.

For information we have determined the DDT distances with the space–time diagrams. A DDT corresponds to a sudden change in the gradient of the straight line on the space–time diagram. The DDT distance is estimated by calculating the location of the intersection of the extrapolated straight lines. But the DDT occurs via “the explosion in the explosion” phenomenon and can be stochastic in nature. The uncertainty in the DDT location is large because the DDT occurs between two pressure transducers, that is to say $0.3 \text{ m} \leq L(\text{DDT}) \leq 0.8 \text{ m}$ in all tests.

An aluminium foil with a soot film is located at the end of the tube to observe the detonation cells. The cell width values mentioned in Sect. 4 are an average of the measurements carried out with several cells on one foil and for a series of tests with the same conditions. The cell widths are measured with a computer from pictures of the aluminium foil. The accuracy of this method is of the order of 1 mm.

Before each test the tube is evacuated by means of a primary vacuum pump. The gaseous mixtures are then introduced through a valve that is located at 1.8 m from the ignition system. The gaseous mixtures had been prepared by the method of partial pressures in a horizontal cylinder. The maximum error in determining the mass fraction of each species is about 0.3%. Before filling the tube, a sample is extracted from the cylinder and analysed with a GC to check that the gaseous mixture contains the correct composition. The measurement of the initial pressure of the gaseous mixture in the tube was carried out by a digital pressure gauge (accuracy of 0.1 kPa) that is connected to the filling valve. The reproducibility of the results is evaluated by several tests (between 3 and 5) on each mixture.

4 Results

4.1 Pyrolysis results with batch reactor

4.1.1 Experimental results of pyrolysis for decane

The influence of the residence time and furnace temperature T_f on the mass conversion rate for decane fuel is shown in Fig. 4.

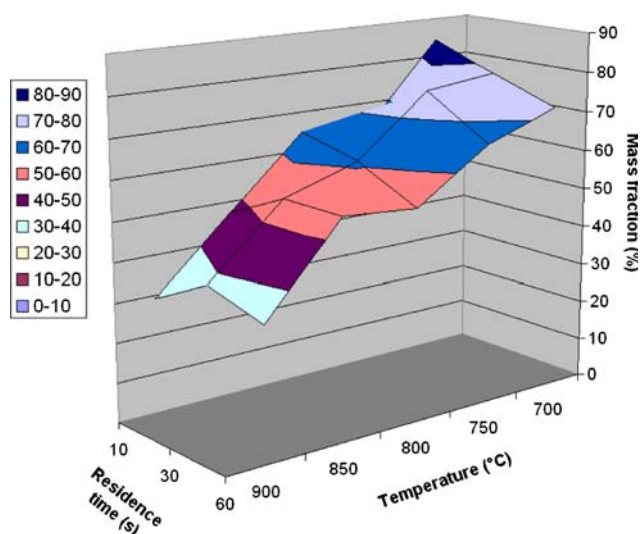


Fig. 4 Mass fraction of $C_{10}H_{22}$ not converted

Table 1 Detonation cell widths for various hydrocarbon-air mixtures with $P_i = 101.3$ kPa and $ER = 1$

| Gas species | Initial temperature (K) | λ (mm) | Reference |
|--------------------------|-------------------------|----------------|-----------|
| H_2 | 295 | 12 | [16] |
| CH_4 | 295 | 340 | [17] |
| C_2H_4 | 295 | 24 | [16] |
| C_3H_6 ($\beta = 3$) | 295 | 19 | [3] |
| C_3H_8 | 295 | 50 | [17] |
| C_6H_6 | 295 | 67 | [17] |
| $C_{10}H_{16}$ | 373 | 60 | [18] |
| $C_{10}H_{22}$ | 373 | 42 | [14] |

The detonation sensitivity of the gaseous mixtures can be characterised by their detonation cell widths (λ). Indeed, the critical energy to initiate a direct planar detonation with a reactive gaseous mixture is proportional to λ [15]. The aim of these experiments was to obtain a large amount of light gaseous products, such as, H_2 , C_2H_4 , C_3H_6 , etc., which have small detonation cell widths as reported on Table 1. Conversely the amount of CH_4 and fuel in the initial formula has to be minimised. The best conversion ratio in pyrolysed products will be investigated later in this study.

With this criteria, the best conditions for the pyrolysis of decane are obtained with a residence time of $\tau = 10$ s and a furnace temperature of $900^\circ C$. The proportions of the different species concentrations are reported in Fig. 5. It may be observed that decane (26%), ethylene (44.5%) and methane (12.9%) are large contributors in the mass fraction. It can however be concluded that the pyrolysis products of decane should produce good results in detonation tests due to the high concentration of ethylene.

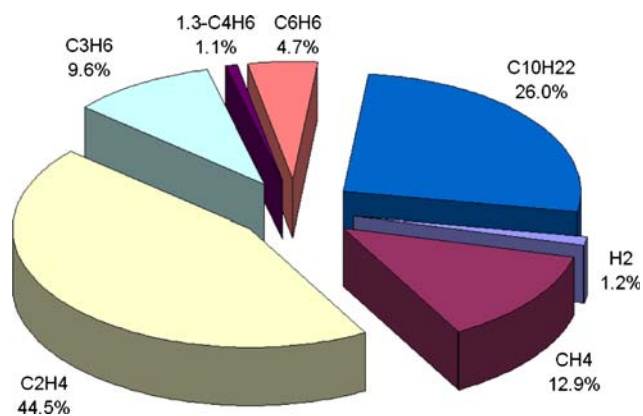


Fig. 5 Composition of pyrolysis products of decane in mass fraction ($T_f = 900^\circ C$ and $\tau = 10$ s)

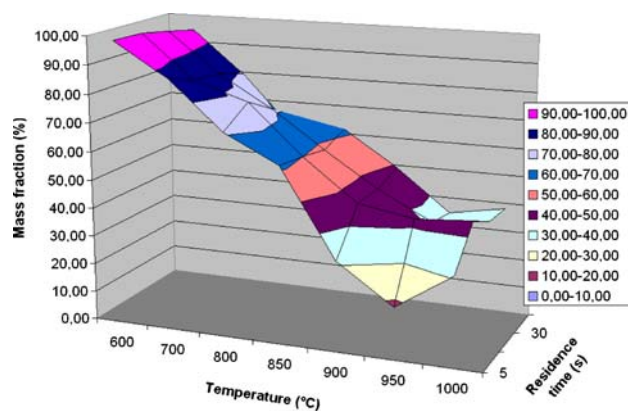


Fig. 6 Mass fraction of $C_{10}H_{16}$ not converted

4.1.2 Experimental results of pyrolysis for JP10

The influence of the residence time τ and furnace temperature T_f on the mass conversion rate of JP10 fuel is shown in Fig. 6.

As expected the conversion rate of the fuel to lighter molecules is improved by an increase of τ and T_f . Below $600^\circ C$ the thermal decomposition of this fuel is very low and also undetectable in our case. For the highest temperature ($T_f \approx 1,000^\circ C$) and longest residence time ($\tau \approx 30$ s), the decomposition conversion rate is about 61% wt, so that 39% wt of the original fuel is present in the mixture at the exhaust of the pyrolysis device. Mass fractions of the major species (H_2 , CH_4 , C_2H_4 , C_6H_6 , $C_{10}H_{16}$) rise as the temperature is increased. Conversely the concentration of propylene and 1.3-butadiene exhibit a maximum ($800 - 950^\circ C$ for propylene) or a plateau ($800 - 1,000^\circ C$ for 1.3-butadiene). These two species are thus revealed to be intermediate products. The conditions for optimal pyrolysis of JP10 are achieved with a residence time of 30 s and a temperature of $1,000^\circ C$. Figure 7 shows the main results

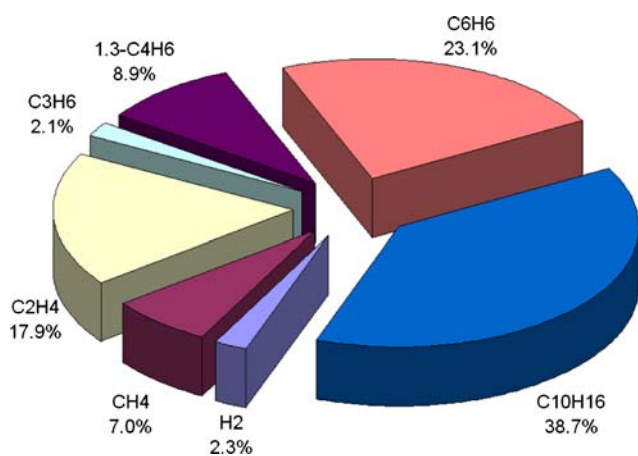


Fig. 7 Composition of pyrolysis products of JP10 in mass fraction ($T_f = 1000^\circ\text{C}$ and $\tau = 30\text{s}$)

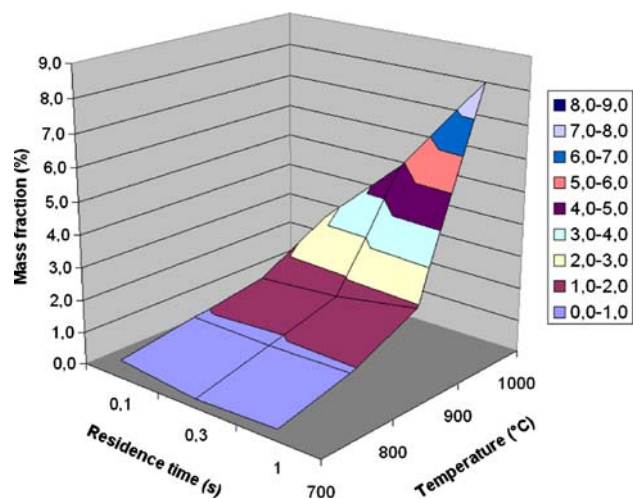


Fig. 8 Mass fraction of H_2 from the pyrolysis of decane with the $3 \times 2\text{ mm}$ reactor

given in mass percentage. The highest obtained mass fractions are C_2H_4 , C_6H_6 and $\text{C}_{10}\text{H}_{16}$. This result corresponds to a very low degradation of the fuel, which is not satisfactory.

As explain in the next section, the pyrolysis results with the flow reactor give better results in terms of conversion rate and produce more detonation-sensitive species. For these reasons, the detonability study focussed on gaseous mixtures originating from the flow reactor pyrolysis.

4.2 Pyrolysis and detonation tests with flow reactor device

4.2.1 Experimental results of pyrolysis for decane

The influence of furnace temperature T_f and residence time τ on the concentration of the gaseous molecules at

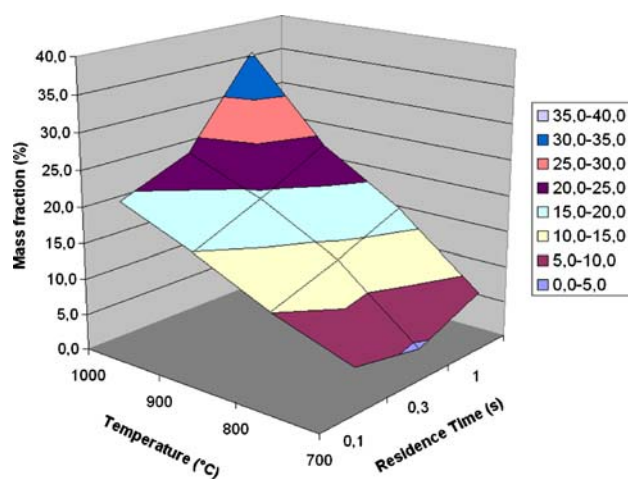


Fig. 9 Mass fraction of CH_4 from the pyrolysis of decane with the $3 \times 2\text{ mm}$ reactor

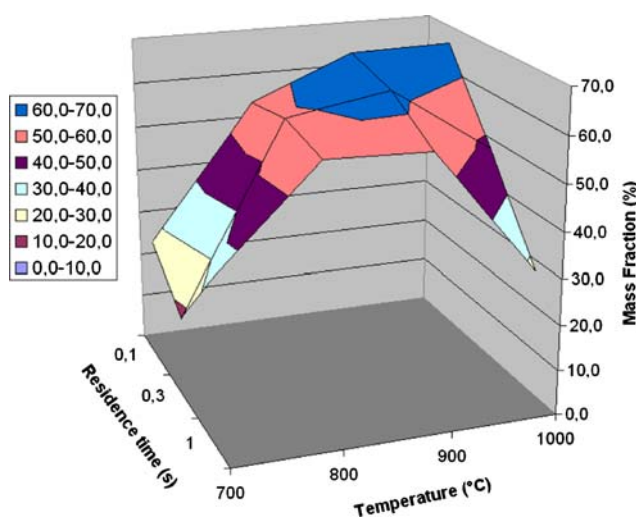


Fig. 10 Mass fraction of C_2H_4 from the pyrolysis of decane with the $3 \times 2\text{ mm}$ reactor

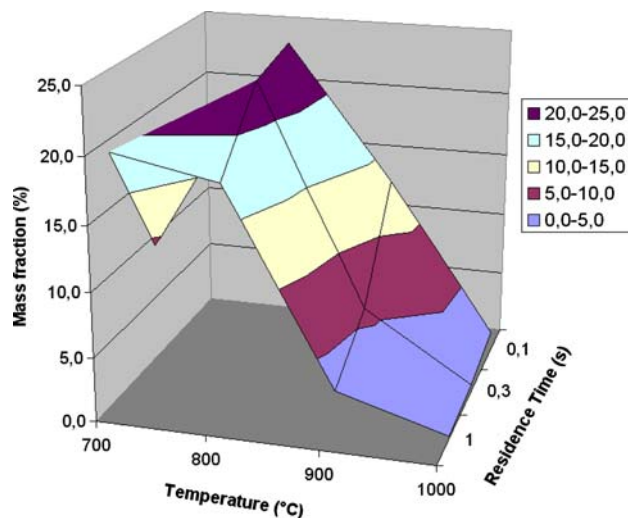


Fig. 11 Mass fraction of C_3H_6 from the pyrolysis of decane with the $3 \times 2\text{ mm}$ reactor

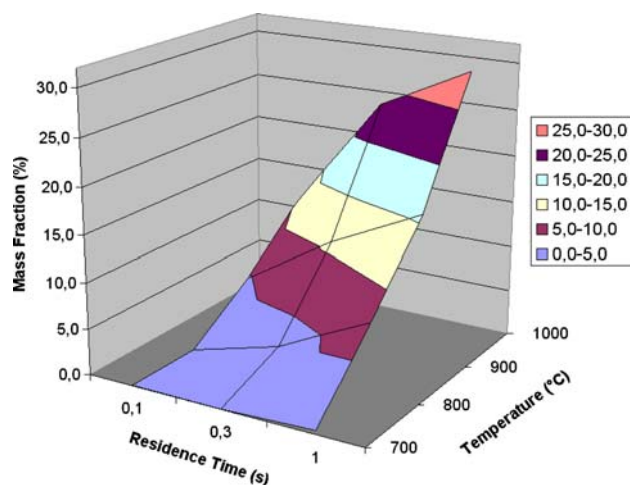


Fig. 12 Mass fraction of C_6H_6 from the pyrolysis of decane with the 3×2 mm reactor

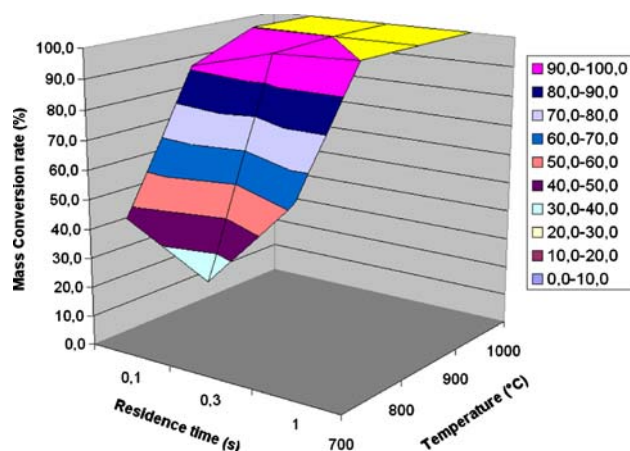


Fig. 13 Mass conversion rate of decane with the 3×2 mm reactor

the output of the experimental device is presented in Figs. 8, 9, 10, 11, 12 and 13.

The results are given for the 3×2 mm reactor, which has a higher conversion ratio than the 1×5 mm reactor. Firstly, it is easy to verify that the mass conversion rate for decane is higher when pyrolysis is achieved in the flow reactor device (100% against 70% for $T_f = 900^\circ\text{C}$) even if the residence time τ is shortened (0.3 s against 30 s). For this reason the flow reactor device should be considered as an improvement. The first analysis of the proportions of the product decomposition allows one to believe that the most favourable condition for DDT could be obtained with such a device. The presence of higher concentrations of “detonable” species, such as H_2 , C_2H_4 , C_3H_6 , etc., and low concentrations of inhibitor (CH_4 , $C_{10}H_{22}$) is, in fact, advantageous to the DDT process. The best conditions for decane pyrolysis are chosen for a 800°C temperature and a 0.3 s

Table 2 Decomposition of decane for $T_f = 800^\circ\text{C}$ and $\tau = 0.3$ s, for study of detonation (conversion rate is 98.8)

| Species | $C_{10}H_{22}$ | H_2 | CH_4 | C_2H_4 | C_3H_6 | C_6H_6 |
|---------|----------------|-------|--------|----------|----------|----------|
| %wt | 1.2 | 0.9 | 13.4 | 58.9 | 22.9 | 2.7 |

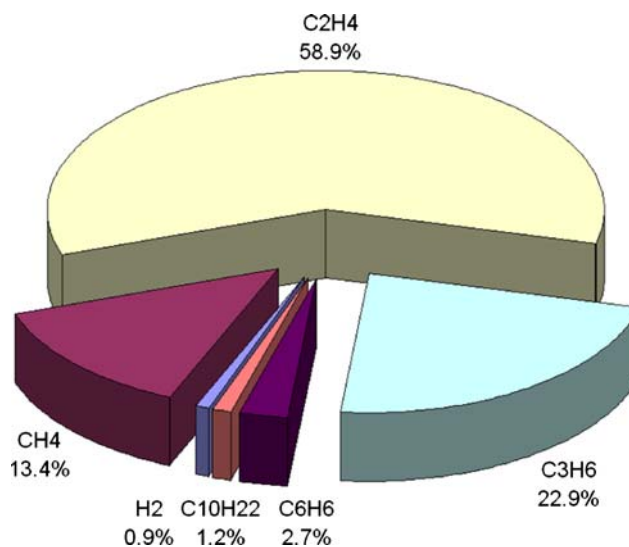


Fig. 14 Composition of pyrolysis products of decane in mass fraction ($T_f = 800^\circ\text{C}$ and $\tau = 0.3$ s)

residence time. The composition of the pyrolysis products are shown for this condition in Table 2 and Fig. 14.

4.2.2 Detonation tests for decane

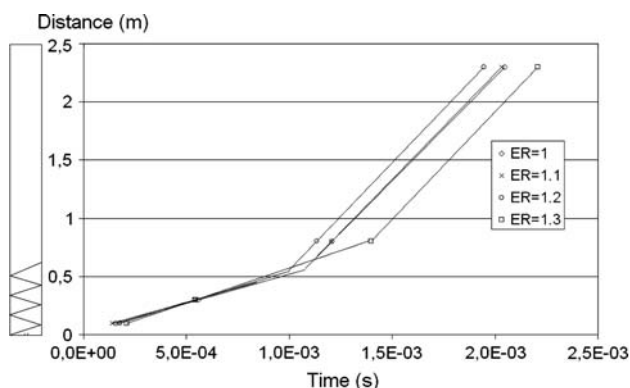
The detonability study concerns a gaseous mixture which is 100% representative in mass of the decane pyrolysis that generates the most detonation-sensitive products. For health and safety, the benzene has been replaced by propane which is very similar with regard to detonation sensitivity [17]. The tube was heated at 350 K to vaporise the decane introduced. The pyrolysis conditions are with a temperature of 800°C and a 0.3 s residence time. The product proportions that reside in the

Table 3 Composition of the representative mixture of decane pyrolysis (obtained with $T_f = 800^\circ\text{C}$ and $\tau = 0.3$ s)

| Gas species | Volume fractions | Mass fractions |
|----------------|------------------|----------------|
| H_2 | 11.3 | 0.9 |
| CH_4 | 21.0 | 13.4 |
| C_2H_4 | 52.9 | 58.9 |
| C_3H_6 | 13.7 | 22.9 |
| C_3H_8 | 0.9 | 2.7 |
| $C_{10}H_{22}$ | 0.2 | 1.2 |

Table 4 Influence of the equivalence ratio on the detonability for products of pyrolysis of decane with the 3×2 reactor, $P_i = 1$ bar, $T_i = 350$ K, $E_n = 265$ J, $\beta = 3.76$

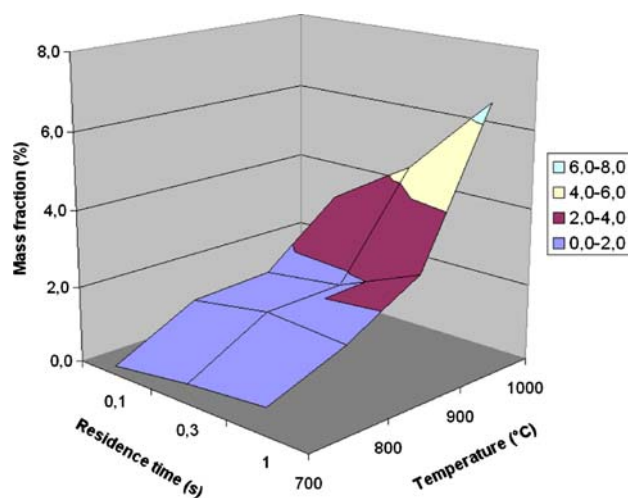
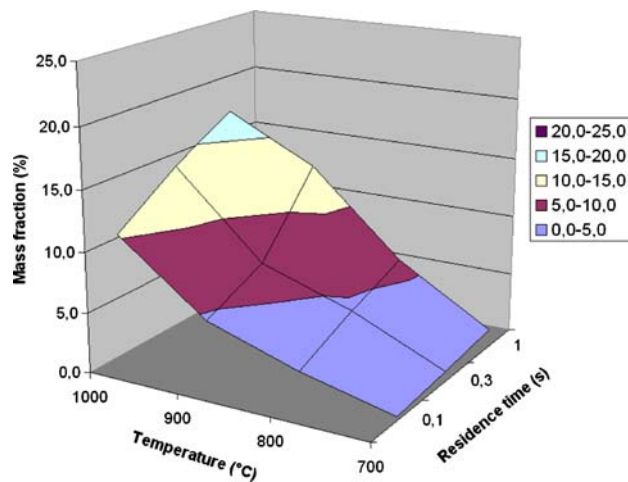
| Equivalence ratio | X_{DDT} (cm) | D (ms^{-1}) | D/D_{CJ} | D_{CJ} (ms^{-1}) | P (bar) | P/P_{CJ} | P_{CJ} (bar) |
|-------------------|----------------|--------------------------|------------|-------------------------------|-----------|------------|----------------|
| 1 | 57 | 1,786 | 0.92 | 1,949 | 30 | 1.49 | 20.2 |
| 1.1 | 56 | 1,810 | 0.93 | 1,938 | 29 | 1.46 | 19.9 |
| 1.2 | 54 | 1,845 | 1.04 | 1,927 | 29 | 1.47 | 19.7 |
| 1.3 | 70 | 1,852 | 0.97 | 1,914 | 28 | 1.44 | 19.4 |

**Fig. 15** Influence of the equivalence ratio on the detonability for products of decane pyrolysis with the 3×2 reactor, $P_i = 1$ bar, $T_i = 350$ K, $E_n = 265$ J, $\beta = 3.76$

representative mixture are given in Table 3. Detonation in the air (proportion $\beta = \frac{N_2}{O_2} = 3.76$) was obtained for this representative gaseous mixture of the pyrolysis. A parametric study, according to the equivalence ratio (ER) of this representative gaseous mixture with air ($\beta = 3.76$), varying from 1 to 1.3 was carried out. The results are reported in Fig. 15 and Table 4. The deflagration to detonation transition was observed with all the equivalence ratios tested. The measured detonation cell width for $ER = 1.3$ is about $\lambda = 36 \pm 2$ mm.

It can be noticed that the DDT length is at a minimum for $ER = 1.2$ and occurs at 54 cm away from the ignition source. The highest value of D/D_{CJ} (1.04) is reached with this equivalence ratio. It can thus be concluded that the optimal equivalence ratio to generate a detonation with the representative gaseous mixture of the decane pyrolysis equates to 1.2. This can certainly be explained by the minimum energy required to initiate a direct detonation for the three main species in the mixture in terms of mass fraction. These species are C_2H_4 (58.9%), C_3H_6 (22.9%) and CH_4 (13.4%). Knystautas et al. [19] investigated the minimum energy needed to initiate a direct detonation according to the equivalence ratio for these fuel–air mixtures with similar initial conditions ($P_i=1$ atm and $T_i = 298$ K). The optimum equivalence ratios are $ER \approx 1.3$ with C_2H_4 and C_3H_6 , and $ER \approx 1$

with CH_4 . It can then be predicted that the optimum equivalence ratio in our test is closer to $ER = 1.3$ than $ER = 1$. Indeed, the mass fraction of CH_4 is very small when compared to the mass fraction of C_2H_4 added with C_3H_6 .

**Fig. 16** Mass fraction of H_2 from the pyrolysis of decane with the 3×2 mm reactor**Fig. 17** Mass fraction of CH_4 from the pyrolysis of decane with the 3×2 mm reactor

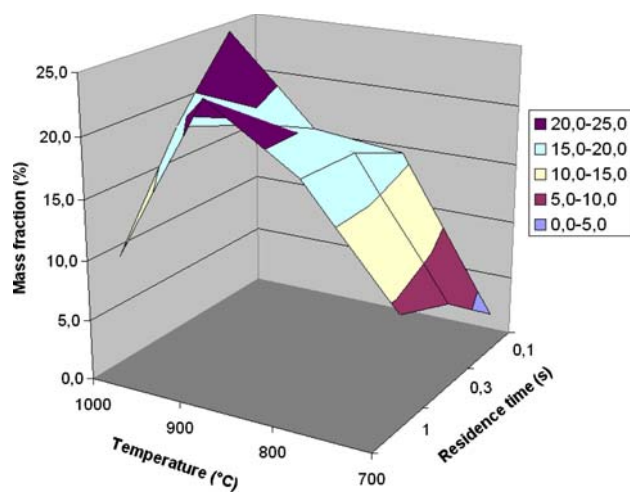


Fig. 18 Mass fraction of C_2H_4 from the pyrolysis of decane with the 3×2 mm reactor

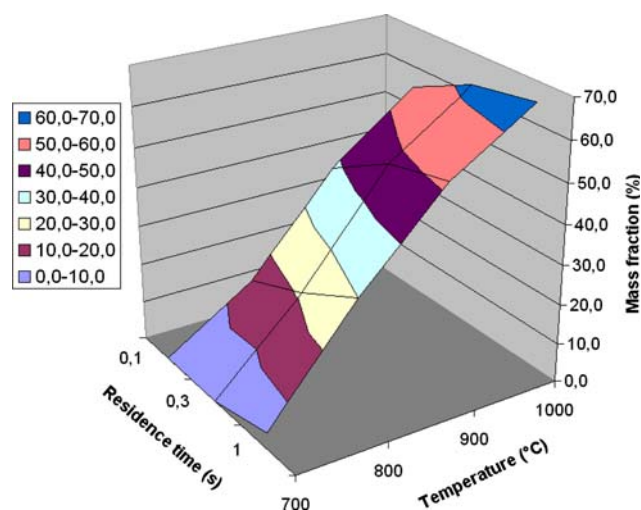


Fig. 21 Mass fraction of C_6H_6 from the pyrolysis of decane with the 3×2 mm reactor

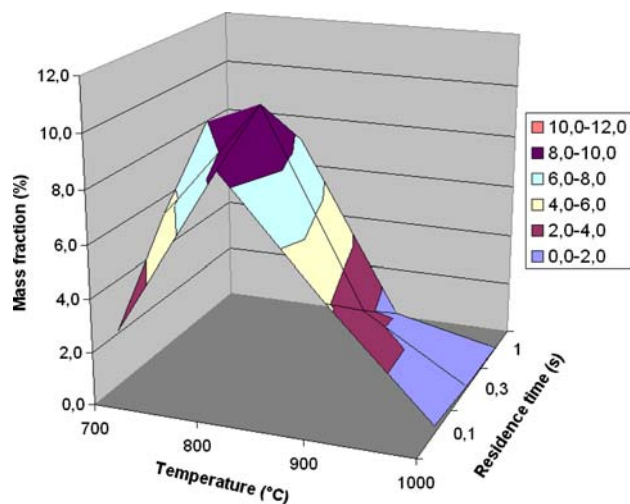


Fig. 19 Mass fraction of C_3H_6 from the pyrolysis of decane with the 3×2 mm reactor

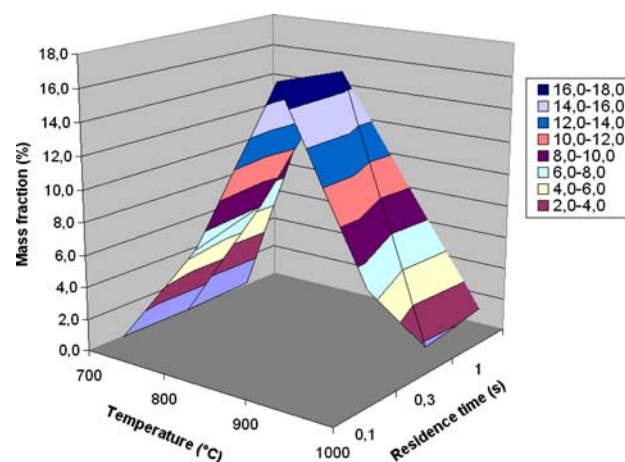


Fig. 22 Mass fraction of C_7H_8 from the pyrolysis of decane with the 3×2 mm reactor

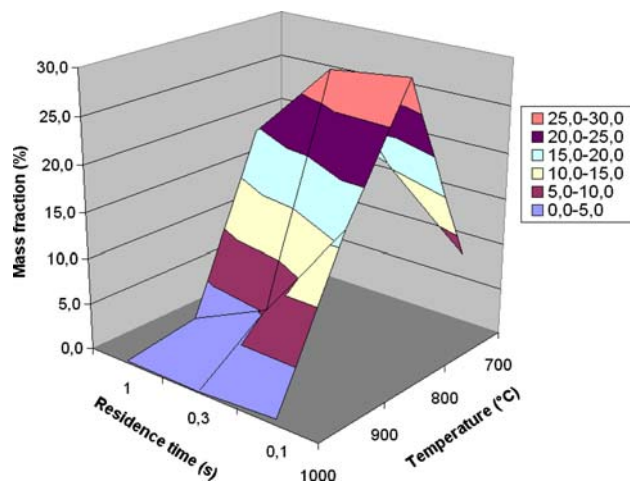


Fig. 20 Mass fraction of 1,3- C_5H_6 from the pyrolysis of decane with the 3×2 mm reactor

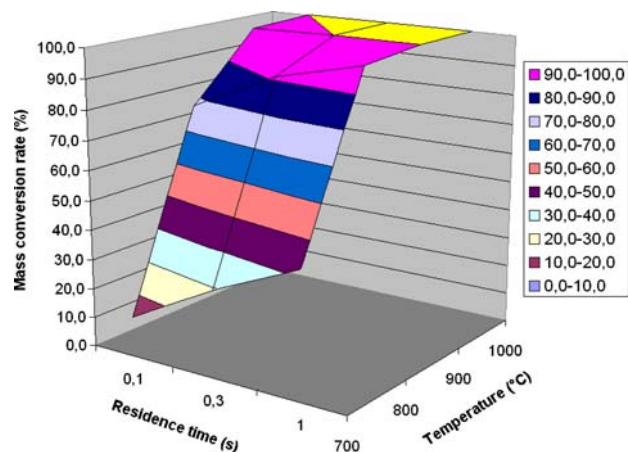
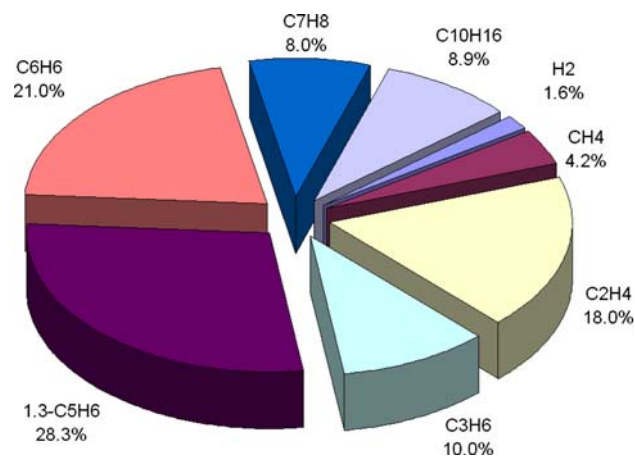
4.2.3 Experimental results of pyrolysis for JP10

The thermal degradation of JP10 to lighter molecules is much improved by the use of a flow reactor when compared with a batch reactor. It can be seen, in Figs. 16, 17, 18, 19, 20, 21, 22 and 23 that the mass conversion rate is nearly 100% when $T_f = 1,000^\circ\text{C}$ and τ is in the range of 0.1 – 1 s. In the case of a batch reactor the residual JP10 mass fraction is 38.7 and 8.9% with a flow reactor. This is a very important result since the presence of JP10 in the mixture considerably increases the DDT delay. The proportion of the species is also favourable in the use of a flow reactor.

For example, the mass fractions of H_2 , C_2H_4 , C_3H_6 are greatly increased when a flow reactor is used. Unfortunately, the presence of methane (undesirable species) is aided by the use of a flow reactor. In order to increase

Table 5 Decomposition of JP10 for $T_f = 800^\circ\text{C}$ and $\tau = 0.3$ s, for study of detonation (conversion rate is 91.8%wt)

| Species | $\text{C}_{10}\text{H}_{16}$ | H_2 | CH_4 | C_2H_4 | C_3H_6 | 1.3- C_5H_6 | C_6H_6 | C_7H_8 |
|---------|------------------------------|--------------|---------------|------------------------|------------------------|-----------------------------|------------------------|------------------------|
| %wt | 8.9 | 1.6 | 4.2 | 18.0 | 10.0 | 28.3 | 21.0 | 8.0 |

**Fig. 23** Mass conversion rate of JP10 with the 3×2 mm reactor**Fig. 24** Composition of pyrolysis products of JP10 in mass fraction ($T_f = 800^\circ\text{C}$ and $\tau = 0.3$ s)

the chance of obtaining the DDT transition, the following conditions for the test are chosen: $T_f = 800^\circ\text{C}$ and $\tau = 0.3$ s. Under such conditions, the proportion of the species is given in Table 5 and in Fig. 24.

4.2.4 Detonation tests for JP10

The detonability of a representative gaseous mixture resulting from the thermal degradation of JP10 in a flow reactor is presented in this section. The mass fractions of each species in the representative gaseous mixture reported in Table 6 are the same as in the original mixture originating from the pyrolysis (see Table 5).

Table 6 Composition of the mixture tested in the detonation facility for JP10 after pyrolysis (obtained for $T_f = 800^\circ\text{C}$ and $\tau = 0.3$ s)

| Gas species | Volume fractions | Mass fractions |
|------------------------------|------------------|----------------|
| H_2 | 24.2 | 1.6 |
| CH_4 | 7.9 | 4.2 |
| C_2H_4 | 19.4 | 18.0 |
| C_3H_6 | 7.2 | 10.0 |
| C_3H_8 | 39.3 | 57.3 |
| $\text{C}_{10}\text{H}_{16}$ | 2.0 | 8.9 |

The 1.3-cyclopentadiene, benzene and toluene mass fractions have been replaced with propane. Indeed, benzene has the same order of magnitude of detonation sensitivity as propane [17]. It has been suggested that 1.3-cyclopentadiene and toluene, which are also aromatic molecules, should be similar to benzene with regard to detonation sensitivity. The tube was heated to 350 K to vaporise the JP10 introduced. Firstly, it was attempted to obtain a detonation with the representative gaseous mixture in the air (proportions $\beta = 3.76$) with the range of equivalence ratios varying from 1 to 1.3. No detonation was observed for $\text{ER} = 1, 1.1$ and 1.3 . But for $\text{ER} = 1.2$, three tests out of eight transitioned into detonation. This work allows the determination of the optimal equivalence ratio for the combustion with respect to the flame front celerity, and is found to be $\text{ER} = 1.2$. The minimum energy required to initiate a direct detonation can be compared for the three main species in the mixture in terms of mass fraction, that is to say, for C_3H_8 (57.3%), C_2H_4 (18%) and C_3H_6 (10%). Knystautas et al. [19] investigated the minimum energy needed to initiate a direct detonation according to the equivalence ratio for these fuel–air mixtures with similar initial conditions ($P_i = 1$ atm and $T_i = 298$ K). The optimum equivalence ratios are $\text{ER} \approx 1.1$ with C_3H_8 , and $\text{ER} \approx 1.3$ with CH_4 and C_3H_6 . The optimum equivalence ratio in our test is between these optimum values. Consequently the detonability limit of the mixture, according to the dilution ratio β , has been investigated at a fixed $\text{ER} = 1.2$. The results are reported in Fig. 25 and Table 7.

The detonability limit is reached with $\beta = 3.6$ where two tests out of four produced a detonation at the end of the tube. The DDT occurs 61 cm away from the ignition source, that is to say, at the end of the Schelkin spiral (length = 64 cm). The celerity of the shock wave is

Table 7 Detonability limit according to the dilution ratio β for products of pyrolysis of JP10, $P_i = 1$ bar, $T_i = 350$ K, $E_n = 265$ J, ER=1.2

| β | X_{DDT} (cm) | D (m s ⁻¹) | D/D_{CJ} | D_{CJ} (m s ⁻¹) | P (bar) | P/P_{CJ} | P_{CJ} (bar) |
|---------|----------------|--------------------------|------------|-------------------------------|-----------|------------|----------------|
| 3.50 | 61 | 1,863 | 0.96 | 1,934 | 27 | 1.34 | 20.1 |
| 3.60 | 61 | 1,807 | 0.94 | 1,920 | 27 | 1.36 | 19.8 |
| 3.65 | – | 814 | 0.43 | 1,913 | 4 | 0.20 | 19.7 |

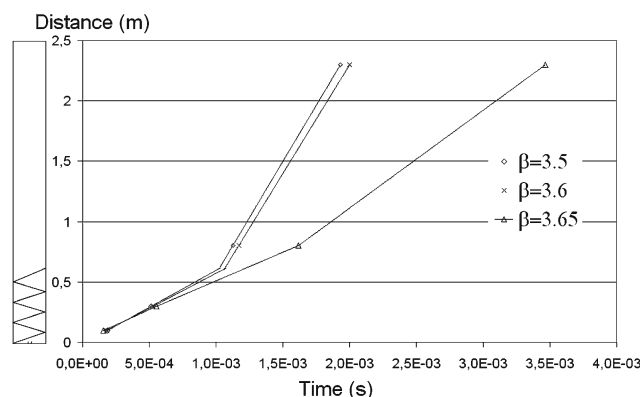


Fig. 25 Detonability limit according to the dilution ratio β for products of pyrolysis of JP10, $P_i = 1$ bar, $T_i = 350$ K, $E_n = 265$ J, ER = 1.2

just under the Chapman–Jouguet celerity with the value $D/D_{CJ} = 0.94$ if $\beta = 3.6$. The pressure measured at the end of the tube is higher than the P_{CJ} value because of the large induction zone in the detonation cells, which disturbs the transducer. The measured detonation cell width is nearly $\lambda = 46 \pm 2$ mm.

5 Conclusion

It can be concluded from the previous results that it is possible to obtain a DDT transition for the pyrolysis products of decane and JP10 with equivalence ratios ranging from 1.1 to 1.2. Unfortunately in the case of batch reactors the thermal degradation of JP10 is quite low (61% conversion in mass for $T = 1,000^\circ\text{C}$ and $\tau = 30$ s). Conversely, it is very easy to transform decane into H_2 , CH_4 and mainly into C_2H_4 (44.5%), with a very high percentage of degradation (74% in mass for $T = 900^\circ\text{C}$ and $\tau = 10$ s) in the batch reactor. This may be explained by the molecular structure of decane since it is a linear alkane with a high H_2/C ratio. The thermal decomposition of exo-tetrahydrodi(cyclopentadiene), the JP10 fuel, is difficult due to the cyclic structure of the molecule and the large amount of C–C bonds with a stronger binding energy than those of C–H bonds. An important improvement of mass conversion is possible if a flow reactor is used. In this case, for the mixture studied in Table 3 and 6, DDT is always obtained for products from the decomposition of decane, even in air ($\beta = 3.76$) and for equivalence ratios in the range

of 1 – 1.3. For the product decomposition of JP10, it is more difficult to obtain DDT in our detonation tube. It was necessary to decrease the nitrogen dilution down to $\beta = 3.6$ in order to have a probability of detonation of 50% at the end of our tube.

In conclusion, this work indicates that decane, or perhaps F34 kerosene, could be a suitable combustible after a pyrolysis process for feeding PDEs with energy. This assumption has to be verified by conducting detonation tests immediately proceeding the pyrolysis process to have the whole set of components. Finally, the last step of this project should be a direct connexion between the output of the pyrolysis device and the inlet of the PDE fuel supply at Roxel Company.

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