Comparison between two liquid fuels for Pulse Detonation Engines

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1. Introduction

The choice of a fuel for pulse detonation engines 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 and energetic kerosene for aeronautical applications in safe conditions. Unfortunately, it is difficult to initiate a detonation with such fuels. Kerosenes are the subject of many studies in this field (Brophy 1998, Rocourt 2003, 2005)

Among kerosenes, it is possible to distinguish those which are obtained from crude oil (F34, jet A1…) from those made by synthesis like JP-10. The latter are used more often in the field of the military aviation. This is why the detonability studies of JP-10 fuel are more common in the field of the propulsion by PDE. Taking into account important critical energies in detonation, much work aims at decreasing these energies for example, by reducing the lengths of transition from deflagration to detonation. Generally these studies are carried out on kerosene sprays. However, kerosene resulting from oil thermal degradation could be used for this kind of application. That could be for F34 fuel, unfortunately the complex nature of this liquid makes the studies of fundamental detonability extremely complex and difficult. The 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 JP-10 kerosene and decane, as possible candidates to supply PDE with energy after a pyrolysis process.

The strategy of the L.E.E.S. laboratory and Roxel company is to sensitize the detonation by means of the pyrolysis of the fuel before its introduction into the detonation chamber (Rocourt 2003-2005). This is why this method will be used for the work presented in this article. The experimental device developed and used within the framework of this study will briefly be described and followed by a presentation of the principal results of pyrolysis for decane and JP-10 fuels type. A parametric study, according to the temperature of pyrolysis $T_f$ and the residence time $\tau$, will be carried out for two different experimental devices. For each of them, we have tried to optimize the thermal degradation process according to the values of residence time and temperature. The objective of this optimization is to increase the probability of DDT transition in our detonation tube.

A study of detonation tests in a tube will then be made in order to determine the detonation limits with the use of a Schelkkin spiral. Finally comparison of the results for both hydrocarbons retained for this study should help us to define the best candidate for a future fuel which can be used in an embarked application of PDE.

2. Previous studies
Several works have been carried out about the degradation mechanism of JP-10 during a pyrolysis. Among them, Davidson et al. (2001) show that the initial major product is the cyclopentene. They sum up the different hypothesis about this subject. Williams et al. (1999) and Li et al. (2001) suggest that in a second step the final products are acetylene, ethylene and 1,3-butadiene. According to Li et al. (2001) the mechanism of degradation in the second step is the following:

\[
\text{JP-10} \rightarrow C_5H_8 + C_2H_4 + C_3H_5 + H
\]

\[
\text{JP-10} \rightarrow C_3H_8 + C_2H_2 + C_3H_5^* + H^*
\]

In a first time, the products resulting from the JP-10 decomposition are cyclopentene, ethylene, acetylene, and three radicals \( C_3H_5^* \), \( C_3H_6^* \) and \( H^* \). Afterwards the hydrogen radical reacts with the JP-10 molecule that give dihydrogen as other product.

\[
\text{JP-10} + H^* \rightarrow C_3H_8 + C_2H_4 + C_3H_5^* + H_2
\]

\[
\text{JP-10} + H^* \rightarrow C_3H_8 + C_2H_2 + C_3H_5^* + H_2
\]

Green and Anderson (2000) think that benzene is the major product of the reaction.

\[
\text{JP-10} \rightarrow C_6H_6 + \text{other minority products}
\]

The thermal decomposition of JP-10 in the focus of a PDE application has been carried out by several workers. Green et al. (2000) have studied the pyrolysis of JP-10 in a flow reactor with a 2 ms residence time. They have observed that the major product was cyclopentadiene for T<980°C and benzene for 980°C<T<1230°C. Brabbs and Merritt (1993) have studied the thermal degradation of JP-10 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 JP-10/oxygen mixture with an equivalence ratio of 5.06 reaches 950°C. The majors species resulting from the pyrolysis were hydrogen (42.3% in mole fraction), ethylene (22.4%), hydrocarbons with three or more carbon atoms (16%) and CH₄ (15.2%). Cooper and Shepherd (2002 and 2003) have studied the JP-10 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, the conversion of JP-10 was 34% with zeolite and 3% without. The interest of zeolite was to produce light molecules and more particularly species with five carbons atoms with low pyrolysis temperature.

Several studies aimed at determining the proper conditions to detonate JP-10 in oxygen and air. Brophy et al. (1998) have obtained the detonation of JP-10 fuel spray in oxygen in a 76.2 cm long tube with an internal diameter which was 3.96 cm. The ignition source was a spark delivering a power levels of approximately 4.9 kW to 16.2 kW. Akbar et al. (2000) have obtained detonation for JP-10/O₂ and JP-10/air mixtures with and without nitrate sensitisation. The experiments were performed at 1 atm and 135°C in a 32 cm internal diameter, 24 m long heated test section and a 4 m long H₂/O₂ driver. The JP-10/air measured cells size was about 47 mm.

The fragmentation of alcanes can be explained by the Rice-Herzfeld-Kossiakoff mechanism. The initiation reactions are made by an initial C-C bond-scission, the energy of the C-H bond (nearly 400 kJ.mol⁻¹) being higher than C-C bond (about 350 kJ.mol⁻¹). The initial molecule (RH) products two radicals \( R_1^* \) and \( R_2^* \) (1) which can be fragmented by a C-C bond-scission to product olefins and an inferior radical (3). Concerning the radicals with more than five carbon atoms an isomerization is possible before the C-C bond-scission (3).

\[
\text{RH} \rightarrow R_1^* + R_2^* \quad (1)
\]

\[
R_1^* \rightarrow R_1^* \text{ (or } R_2^* \text{) } \quad (2)
\]

\[
R_1^* \text{ or } R_1^* \rightarrow \text{olefins } + R_3 \quad (3)
\]

Then the decomposition of inferior radicals gives hydrogen radicals (H°) and methyl radicals (CH₃°) which ensure the propagation reaction (4).
\[
R H + R_4^+ \rightarrow R^- + R_4H \quad \text{with } R_4^+ : H^- \text{ or } CH_3^+ (4)
\]

Tieszen et al. (1991) have studied the detonability of decane in a heated detonation tube. The facility was 0.43 cm in diameter and 13.1 m long. The driver section contains 40 g EL506C1 detasheet explosive to initiate the gaseous mixture. They have obtained detonation of decane in air with a temperature of 100°C, an initial pressure of 1 atm and an equivalence ratio of 1. The measured cells size observed was 42 mm.

3. Experimental protocols
3.1 Batch reactor pyrolysis

A thermal degradation facility (figure 1) was built to analyse the pyrolysis products of kerosene as a function of 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 Varian Company. The evaporator is heated at 100°C in order to evaporate the fuel contained in the tank. The vapour pressure of the fuel is about 12.4 kPa at this temperature.

All the components are firstly heated to the selected temperature, a primary vacuum (P < 0.1 kPa) is 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 two seconds to allow the (equilibrium) kerosene vapours flowing into the reactor by depression. This point is considered as time zero to define the residence time of the kerosene vapours in the reactor at the chosen pyrolysis temperature. When the chosen residence time is reached, the outlet valve of the reactor is opened (valve 2) for five seconds. Consequently, the gaseous mixture stemming from the thermal degradation flows by depression 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 up to reach roughly 160 kPa. Finally the gaseous mixture is injected into the GC (valve 4) for analysis. A correction of the measurement of molar fraction is necessary according to the following relation:

\[
x_i = \frac{x_i^*}{1 - \frac{P_{N_2}}{P_T^*}}
\]

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

Figure 1. Experimental device used for the discontinuous pyrolysis of the fuels
3.2 Flow reactor pyrolysis

A second experimental device (Figure 2) was conceived to perform pyrolysis at atmospheric pressure with shorter residence times (between 0.1 s and 1 s) which are closer with the real application.

At first, the liquid fuel to be studied was evaporated at 400°C in the evaporator. The liquid fuel was introduced in the evaporator by flowing from the fuel tank in a capillary (150 μm i.d.). The flow was controlled by the nitrogen pressure over the liquid surface in the tank. Once evaporated, the gas was flowed into a quartz reactor by the mean of the vector gas (nitrogen). The dilution ratio and the residence time in the reactor were controlled by the gas vector flow and the fuel flow. At the exit of the reactor a cold trap captured the heavy species to allow their quantification and analyse. Afterwards, the gas flow was divided in two parts. A little amount of gas was flowed into the gas chromatograph (GC) and the other part was flowed to the exit of the experimental apparatus. The flow was adjusted by a fine metering valve to limit the pressure in the GC which has to be lower than the working pressure of the injection sample valves. The values of the two flows were displayed by flow meters. The total flow allowed us to accurately determine the residence time of the gas in the reactor.

All the connections between each parts of the facility were heated (~100°C) to avoid the condensation of heavy species.

We have studied the influence of the reactor geometry. The first tubular reactor was 150 mm long with a 5 mm inner diameter. It was used for the 0.3 s, 1 s and 2 s residence time. The second reactor consisted of three tubular pipes connected in parallels. Each tubular pipe was 150 mm long with a 2 mm inner diameter. This reactor has a greater thermal exchange area as compared to the first one and a more little volume which allowed decreasing the residence time at 0.1 s by keeping a reasonable flow (roughly 14 ml/s).

![Figure 2. Experimental device used for continuous pyrolysis](image)

3.3 Detonation tube

The detonation tube (Figure 3) has been previously described (Rocourt 2005). Ignition is obtained by means of an exploding wire (E_{nom} = 265 J) with a Schelkin spiral to support the DDT. The tube has an inner diameter of 49 mm and is 2.5m long. The Schelkin spiral is 64 cm long with a 0.55
The dimensions of the tube were chosen in order to be compatible with aircraft industry applications and more particularly the PDE. The tube was instrumented with five pressure transducers (Kistler 603B) respectively located at 0.1 m, 0.3 m, 0.8 m, 1.3 m and 2.3 m from the ignition source. These sensors were connected to charge amplifiers (Kistler 5011) which transmit the signal to oscilloscopes (Tektronix TDS 210). A personal computer recorded the signal from the oscilloscopes. We can measure the detonation wave pressure and deduce its celerity. The measured pressures and celerity are compared to the Chapman-Jouguet values calculated with the NASA Glenn’s computer program Chemical Equilibrium with Applications (CEA). An aluminium foil covered of soot film is located at the end of the tube to observe detonation cells. Before each shot the tube was evacuated by means of a primary vacuum pump. The gaseous mixtures were then introduced through a valve located at 1.8 m from the ignition system. The gaseous mixtures were prepared by the method of partial pressures in a horizontal cylinder. Before filling the tube, a sample was extracted from the cylinder and analyzed with a gas chromatograph to check that the gaseous mixture to check the correct composition of the gaseous mixture. 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) connected to the filling valve.

4. Results
4.1 Pyrolysis and detonation results with batch reactor
4.1.1 Decane
4.1.1.1 Experimental results of pyrolysis for decane

The influence of residence time $\tau$ and furnace temperature $T_f$ on the pyrolysis process of JP-10 fuel is shown in figure 4.

In this experiments, we have tried to obtain a large amount of light gaseous products such as $\text{H}_2$, $\text{C}_2\text{H}_4$, $\text{C}_3\text{H}_6$ … which are known to be sensitive in terms of detonation. On the contrary, the amount of $\text{CH}_4$ and fuel in its initial formula has to be minimised. The best conversion ratio in pyrolysed products is researched afterwards. With this criteria, the best conditions of pyrolysis for decane are obtained for a residence time $\tau = 10$ s and a furnace temperature of 900 °C. The repartition of the concentrations of different species is reported in figure 5 and it may be observed that decane, ethylene and methane are very important in mass fraction. We can
therefore conclude that decane should give good results for detonation tests. This assumption will be verified in a next section.

**Figure 4.** Mass fraction of pyrolysis products of decane
Mass fractions
(Decane T=900°C and τ=10 s)

Figure 5. Composition of pyrolysis products of decane

4.1.1.2 Detonation tests for Decane

The mixture tested is representative of about 92.5% in volume and 68.2% in mass of the real mixture produced at the output of the furnace of pyrolysis (see figure 5). The main pyrolysis products that have not been introduced is benzene due to the safety issues of its handling and gaseous decane not studied at this stage of the work. They are both poor detonation components that would reduce the detonability of the mixtures. The results for the detonation tests on mixtures 1, 2 and 3 are presented in figure 6 and table 2. It can be seen that detonation occurs only for an equivalence ratio of 1.1 and 1.2. For these two cases the experimental shock wave velocity is very close to the Chapman-Jouguet celerity of detonation (P/P_{CJ}=0.99) and we can observe detonation cells. The detonation wave celerity is about 1847 m.s\(^{-1}\) for an equivalence ratio (ER) of 1.1 and nearly 1860 m.s\(^{-1}\) for ER=1.2. A higher experimental pressure ratio P/P_{CJ} has also been observed. Indeed, for mixtures which are near the detonability limit, with large cells width, the measured pressures are influenced by the high pressures in the induction zone. The transducers measure pressures between P_{CJ} and a pressure near the Zeldovich, von Neumann and Döring value (P_{ZND}). The Deflagration to Detonation Transition (DDT) distance is approximately 36 cm for the two mixtures.

Table 1. Composition of the mixture tested in the detonation facility for decane after pyrolysis (obtained for T=900°C and τ=10 s):

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Volume fractions</th>
<th>Mass fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>19.6</td>
<td>1.9</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>24.7</td>
<td>18.9</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>48.7</td>
<td>65.2</td>
</tr>
<tr>
<td>C(_6)H(_6)</td>
<td>7</td>
<td>14</td>
</tr>
</tbody>
</table>
Table 2

<table>
<thead>
<tr>
<th>Mixture</th>
<th>equivalence ratio</th>
<th>$X_{DDT}$ (cm)</th>
<th>D(m.s$^{-1}$)</th>
<th>D/D$_{CJ}$</th>
<th>D$_{CJ}$ (m.s$^{-1}$)</th>
<th>P (bar)</th>
<th>P/P$_{CJ}$</th>
<th>P$_{CJ}$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>/</td>
<td>814</td>
<td>0.44</td>
<td>1825</td>
<td>6.1</td>
<td>0.34</td>
<td>18.2</td>
</tr>
<tr>
<td>2</td>
<td>1.1</td>
<td>36</td>
<td>1847</td>
<td>0.99</td>
<td>1851</td>
<td>32.1</td>
<td>1.73</td>
<td>18.6</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>36</td>
<td>1860</td>
<td>0.99</td>
<td>1868</td>
<td>29.8</td>
<td>1.58</td>
<td>18.9</td>
</tr>
</tbody>
</table>

Figure 6 and table 2. Influence on the equivalence ratio on the limit of detonability for pyrolysis products of decane, $P_i$=1 bar, $T_i$=295 K, $E_n$=265 J, $\beta_{N_2/O_2}$=3.76.

4.1.2 JP-10

4.1.2.1 Experimental results of pyrolysis for JP-10

The influence of residence time $\tau$ and furnace temperature $T_f$ on the pyrolysis process of JP-10 fuel is shown in figure 7. As expected the conversion rate of the fuel in higher molecule is favored by an increase of $\tau$ and $T_f$. Beneath 600 °C, the thermal decomposition of this fuel is very low and also undetectable in our case. For the highest temperature ($T_f$ = 1000 °C) and long residence time ($\tau$ = 30 s), the conversion rate of decomposition is about 61 %wt, so that 39 %wt of original fuel is present in the mixture at the exhaust of the pyrolysis device. Mass fractions of major species (H$_2$, CH$_4$, C$_2$H$_4$, C$_6$H$_6$, C$_{10}$H$_{16}$) rise when temperature is increasing. On the contrary the concentration of propylene and 1.3 butadiene exhibits a maximum (800 - 950 °C for propylene) or a plateau (800 – 1000 °C for 1.3 butadiene). These two species are thus revealed to be intermediate products.

The conditions of optimum pyrolysis for JP-10 are achieved for a period of 30 s and a temperature of 1000 °C. Figure 8 shows the main results, given in mass percentage. The higher mass fractions obtained are C$_2$H$_4$, C$_6$H$_6$ and C$_{10}$H$_{16}$. This result corresponds to a degradation of the fuel which is not satisfactory.
Figure 7. Mass fraction of the pyrolysis products according to residence time and temperature.
**Figure 8.** Composition of pyrolysis products for JP-10 pyrolysis (batch reactor T=1000°C, \( \tau =30 \) s)

### 4.1.2.2 Detonation tests with JP-10

The first mixture tested is representative of nearly 75% in volume and 29% in mass of the pyrolysis which generates the more sensitive to detonation gaseous mixture, and this composition is obtained with a residence time of 30 s and a temperature of 1000°C in the batch reactor. The products selected from this pyrolysis for the detonation tests are given on table 3.

A detonation of this representative mixture was obtained in air (\( \beta =3.76 \)) and was confirmed by the presence of detonation cells (\( \lambda \sim 27 \) mm). The results of the detonation tests are reported on table 4 and figure 9. The DDT occurs at 36 cm from the ignition source. The celerity of the detonation wave is 1829 m.s\(^{-1}\), very close to the Chapman-Jouguet value (\( D/D_{CJ}=0.99 \)). Concerning the measured pressure, it reaches 30.4 bar at the end of the tube. This value is high comparing to the theoretical value \( P_{CJ} \) (\( P/P_{CJ}=1.71 \)) for the same reasons mentioned for the decane detonation tests.

![Figure 9 and Table 4](image)

**Table 3.** Composition of the mixture tested in the detonation facility of JP-10 (obtained for T=1000°C and \( \tau =30 \) s):

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Volume fractions</th>
<th>Mass fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>49.9</td>
<td>7.6</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>19.3</td>
<td>23.7</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>28.5</td>
<td>61.3</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_6 )</td>
<td>2.3</td>
<td>7.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>equivalence ratio</th>
<th>( X_{TDD} ) (cm)</th>
<th>( D ) (m.s(^{-1}))</th>
<th>( D_{CJ} ) (m.s(^{-1}))</th>
<th>( D/D_{CJ} )</th>
<th>( P ) (bar)</th>
<th>( P_{CJ} ) (bar)</th>
<th>( P/P_{CJ} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>36</td>
<td>1829</td>
<td>1842</td>
<td>0.99</td>
<td>30.4</td>
<td>17.8</td>
<td>1.71</td>
</tr>
</tbody>
</table>

In this second part, we have tried to test the detonation for a more representative mixture than previously. To reach this objective, JP-10 vapours have been added in the heated detonation tube...
(50°C). This mixture is representative of about 84.6% in volume and 68% in mass of the real mixture produced at the output of the furnace of pyrolysis (mainly due to the omission of benzene for the reasons discussed above). The main proportions of the components of the pyrolysis products selected for the detonation tests of JP-10 are given on table 5. The thermal degradation conditions of the fuel are the same as previously, a residence time of 30 s and a temperature of 1000 °C.

As presented on figure 10, detonation is obtained in the mixture for a scale of equivalence ratio from 1 to 1.3 with diluted oxygen and nitrogen in a ratio of $\beta=3.0$. The DDT length is the minimum for an equivalence ratio of 1.2. However, the detonation of this mixture has not been obtained in the air ($\beta=3.76$) with an equivalence ratio of 1.

Table 5. Composition of the mixture tested in the detonation facility of JP-10 (obtained for $T=1000^\circ\text{C}$ and $\tau=30$ s):

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Volume fractions</th>
<th>Mass fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>44.3</td>
<td>3.4</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>17.1</td>
<td>10.3</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>25.3</td>
<td>26.3</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>2.1</td>
<td>3.1</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{16}$</td>
<td>11.2</td>
<td>56.9</td>
</tr>
</tbody>
</table>

Table 6

<table>
<thead>
<tr>
<th>equivalence ratio</th>
<th>$X_{TDD}$ (cm)</th>
<th>D (m.s$^{-1}$)</th>
<th>D/D$_{CJ}$</th>
<th>D$_{CJ}$ (m.s$^{-1}$)</th>
<th>P (bar)</th>
<th>P/P$_{CJ}$</th>
<th>P$_{CJ}$ (bar)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>1827</td>
<td>0.90</td>
<td>2039</td>
<td>27.5</td>
<td>1.23</td>
<td>22.4</td>
</tr>
<tr>
<td>1.1</td>
<td>64</td>
<td>1850</td>
<td>0.91</td>
<td>2029</td>
<td>23.3</td>
<td>1.05</td>
<td>22.1</td>
</tr>
<tr>
<td>1.2</td>
<td>44</td>
<td>1850</td>
<td>0.92</td>
<td>2017</td>
<td>23.3</td>
<td>1.07</td>
<td>21.8</td>
</tr>
<tr>
<td>1.3</td>
<td>58</td>
<td>1840</td>
<td>0.92</td>
<td>2003</td>
<td>25.1</td>
<td>1.17</td>
<td>21.5</td>
</tr>
</tbody>
</table>

Figure 10 and table 6. Influence of the equivalence ratio on the limit of detonability for products of pyrolysis of JP-10, $\beta=3.0$.

4.2 Pyrolysis and detonation tests with flow reactor device
4.2.1 Decane
4.2.1.1 Experimental results of pyrolysis for decane

The influence of furnace temperature $T_f$ and residence time $\tau$ on the concentration of gaseous molecule at the output of the experimental device is presented in figure 11. The results are given for the 3x2 mm reactor which have an higher conversion ratio than the 2 mm reactor. Firstly, it is easy to verify that 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 $\tau$ is shortened (0.3 s against 30 s).

For this reason, flow reactor device should be considered as an improvement. The first analysis of the repartition of the product of decomposition allows us to think that more favourable condition for DDT could be obtained for such a device. The presence of higher concentration of “detonable” species, such as H$_2$, C$_2$H$_4$, C$_3$H$_6$ ...and low concentration of inhibitor (CH$_4$, C$_{10}$H$_{16}$) is, in fact, favorable to the DDT process.

The best conditions of pyrolysis for decane were chosen as indicated on the table 6.
Species | C\textsubscript{10}H\textsubscript{22} | H\textsubscript{2} | CH\textsubscript{4} | C\textsubscript{2}H\textsubscript{4} | C\textsubscript{3}H\textsubscript{6} | C\textsubscript{4}H\textsubscript{6} | % wt
\hline
          |          |          |          |          |          |          | 1.2 | 0.9 | 13.4 | 58.9 | 22.9 | 2.7
\hline
Table 7: Decomposition of decane for T\textsubscript{f} = 800 °C and \(\tau = 0.3\) s, for study of detonation (conversion rate is 98.8).

4.2.1.2 Detonation tests for Decane

The detonability study concerns a gaseous mixture which is representative of 100 % in mass of the decane pyrolysis generating the more sensitive to detonation products. For health security, the benzene has been replaced by propane which has the same order of sensibility of detonation. This
pyrolysis conditions are a temperature of 800°C and a 0.3 s residence time. The proportions of products making up the mixture are given on table 8.

The detonation in the air proportion (β=3.76) was obtained for this representative gaseous mixture of the pyrolysis. A parametric study, according to the equivalence ratio, varying from 1 to 1.3 was carried out in air (β = 3.76) as reported on figure 12 and table 9. The deflagration to detonation of the gaseous mixture was observed in all cases. The measured detonation cell width for ER=1.3 is about λ=36 mm.

![Figure 12 and table 9. Influence of the equivalence ratio on the detonability for products of pyrolysis of decane, β=3.76.](image)

<table>
<thead>
<tr>
<th>equivalence ratio</th>
<th>X_{DDT} (cm)</th>
<th>D(m.s⁻¹)</th>
<th>D/D_{CJ}</th>
<th>D_{CJ} (m.s⁻¹)</th>
<th>P (bar)</th>
<th>P/P_{CJ}</th>
<th>P_{CJ} (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>57</td>
<td>1786</td>
<td>0.92</td>
<td>1949</td>
<td>30.2</td>
<td>1.50</td>
<td>20.2</td>
</tr>
<tr>
<td>1.1</td>
<td>56</td>
<td>1810</td>
<td>0.93</td>
<td>1938</td>
<td>28.6</td>
<td>1.44</td>
<td>19.9</td>
</tr>
<tr>
<td>1.2</td>
<td>54</td>
<td>1845</td>
<td>1.04</td>
<td>1927</td>
<td>28.7</td>
<td>1.46</td>
<td>19.7</td>
</tr>
<tr>
<td>1.3</td>
<td>70</td>
<td>1852</td>
<td>0.97</td>
<td>1914</td>
<td>27.9</td>
<td>1.44</td>
<td>19.4</td>
</tr>
</tbody>
</table>

We can notice that the DDT length is minimal for ER=1.2 and it occurs at 54 cm from the ignition source. The highest value of D/D_{CJ} (1.04) is reached for this equivalence ratio. We can conclude that the optimal equivalence ratio equals to 1.2 to generate a detonation with the representative gaseous mixture of the decane pyrolysis.

4.2.2 JP-10

4.2.2.1 Experimental results of pyrolysis for JP-10

The thermal degradation of JP-10 in lighter molecule is highly improved by the use of low reactor when compared to the batch one.

It can be seen, in figure 13, that the mass conversion rate is nearly 100 % when T_f= 1000°C and τ in the range 0.1 to 1 s. The residual JP-10 mass fraction is 38.7 % in the case of batch reactor and 8.9 % for the second one. This is a very important result because the presence of JP-10 in the mixture increases considerably the DDT delay.

The repartition of species is also favourable to the use of flow reactor. By example, mass fraction of H₂, C₂H₄, C₃H₆ are greatly increased when the flow reactor is used.

Unfortunately, the presence of methane (undesirable specie) is aided by using the flow reactor. In order to increase the chance to obtain the DDT transition, the following conditions for the test was chosen: T_f = 800 °C and τ = 0.3 s. In such conditions, the repartition of the species is given in table 10.
Table 10: Decomposition of JP-10 for $T_f = 800$ °C and $\tau = 0.3$ s, for study of detonation (conversion rate is 91.8)
4.2.2.2 Detonation tests for JP-10

The detonability of a representative gaseous mixture resulting from the thermal degradation of JP-10 in the flow reactor is presented in this section. The 1.3-cyclopentadiene, benzene and toluene mass fractions have been replaced with propane which has the same order of sensibility to detonate. The composition of the representative gaseous mixture is given on table 11. Firstly we have tried to obtain a detonation in the air proportions (β=3.76) in the range of equivalence ratio varying from 1 to 1.3. No detonation was observed for ER=1, 1.1 and 1.3. For ER=1.2, three shots on eight were transit in detonation. This work allowed us to determine the optimal equivalence ratio, ER=1.2, for the combustion in term of flame front celerity. Then the detonability limit of the mixture according to the dilution ratio β has been looking for at a fixed ER=1.2. The results are reported on figure 14 and table 12.

**Figure 13**: Mass fraction of the pyrolysis products of JP-10 with the 3x2 mm reactor

**Table 11**: Composition of the mixture tested in the detonation facility of JP-10 (obtained for T=800°C and τ=0.3 s):

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Volume fractions</th>
<th>Mass fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>24.2</td>
<td>1.6</td>
</tr>
<tr>
<td>CH₄</td>
<td>7.9</td>
<td>4.2</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>19.4</td>
<td>18.0</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>7.2</td>
<td>10.0</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>39.3</td>
<td>57.3</td>
</tr>
<tr>
<td>C₁₀H₁₈</td>
<td>2.0</td>
<td>8.9</td>
</tr>
</tbody>
</table>

**Figure 14 and table 12**: Detonability limit according to the dilution ratio β for products of pyrolysis of JP-10, ER=1.2.

The detonability limit is reached for β=3.6 where 2 shots on 4 produce detonation at the end of the tube. The DDT occurs at 61 cm 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 near the Chapman-Jouguet celerity by inferior value D/Dₜ=0.94 if β = 3.6. The pressure measured at the end of the tube is higher than the Pₕ because of the large induction zone in detonation cell which perturbs the transducer. The
measured detonation cell width is nearly 46 mm.

5. Conclusion
Due to the previous result, we think that it is possible to obtain a DDT transition for pyrolysis products of decane and JP-10 in a range of equivalence ratios from 1.1 to 1.2. Unfortunately the thermal degradation of JP-10 is rather low (61% conversion in mass for T= 1000 °C and τ = 30 s), in the case of batch reactor. On the contrary, it is very easy to transform decane in H2, CH4 and mainly in C2H4 (44.5%), with a very high percentage of degradation (74% in mass for T = 900 °C and τ = 10 s) in batch reactor. This may be explained by the molecular structure of decane which is a linear alcan with a high H2/C ratio. The thermal decomposition of exo-tetrahydrodi (cyclopentadiene), the JP-10 fuel, is difficult because of the cyclic structure of the molecule and the large amount of C-C bond with a stronger binding energy than those of C-H bond.

An important improvement of mass conversion is possible if a flow reactor is used. In this case, for the mixture studied in this work (table 8 and 11), a DDT was always obtained for product of decomposition of decane, even in air (β = 3.76) and for equivalence ratios in the range 1 to 1.3.

For the product decomposition of JP-10, it is more difficult to obtain DDT in our detonation tube. It was necessary to decrease nitrogen dilution down to β = 3.6 in order to have a probability of detonation of 50% at the end of our tube.

In conclusion we think that this work indicates that decane, or perhaps F34 kerosene, could be a good combustible for feeding PDE with energy.

Acknowledgements: This work was achieved under contract with Roxel Company and with the help of the European community for FSE support.

REFERENCES


