SUPPLEMENTARY MATERIAL

Analysis and modelling of flame speed in autoignitive mixtures of n-heptane and methane

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The supplementary material section contains:

1. Additional data for validation and comparison of chemical kinetic models
2. Flame speed data used in order to obtain the flame speed models
3. Additional data comparing alternative mixing-rules.

## Additional data for validation and comparison of chemical kinetic models

The 106 species Polimi-106 skeletal mechanism is selected for this study based on comparison against experimental ignition delay time and flame speed data for combustion of pure methane and pure n-heptane. Since ignition delay and flame speed measurements for combustion of methane/n-heptane blends are not generally available, the Polimi-106 model predictions for methane/n-heptane blends are also compared with predictions of more detailed chemical mechanisms. Data are presented for the chemical models summarised in Table 1.

Table 1. Summary of chemical models.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Mechanism name** | **Reference** | **Main fuel** | **Number of species** | **Type** |
| **Polimi-451** | [‎1] | n-heptane | 451 | detailed |
| **Mehl *et al.*** | [‎2] | n-heptane | 658 | detailed |
| **Polimi-106** | [‎3] | n-heptane | 106 | reduced |
| **Liu *et al.*** | [‎4] | n-heptane | 44 | reduced |
| **Lu *et al.*** | [‎5] | n-heptane | 52 | reduced |
| **Chalmers** | [‎6] | n-heptane | 42 | reduced |
| **GRI3.0** | [‎7] | methane | 53 | detailed |
| **San Diego** | [‎8] | methane | 50 | detailed |

The Polimi-106 skeletal scheme [‎3] is a sub-set of the Polimi-451 scheme [‎1]. The 44-species reduced mechanism by Liu *et al.* [‎4] is considered because it gives an adequate compromise between predictive accuracy and computational expense for engine calculations, and the 42-species Chalmers mechanism is considered because it performed best out of the mechanisms compared in a previous study of methane/n-heptane dual fuel combustion [‎6]. The 52-species reduced mechanism developed by Lu *et al.* [‎5] employs dynamic stiffness removal in order to achieve low computational cost, and it has been validated against its parent detailed mechanism in a perfectly-stirred reactor at ambient temperatures and for homogeneous autoignition at engine-relevant temperatures.

### Ignition delay

Constant volume ignition delay predictions are presented for pure methane and n-heptane in Figs. Figure S1 and Figure S2, in comparison with shock-tube measurements for stoichiometric methane-air at 30 atm [‎9], n-heptane–air at 55 atm [‎10] and n-heptane–air at 42 atm [‎11]. Ignition delay time predictions for the reduced n-heptane mechanisms are compared with the detailed n-heptane mechanisms for ignition of methane/n-heptane blends in Figure S3.

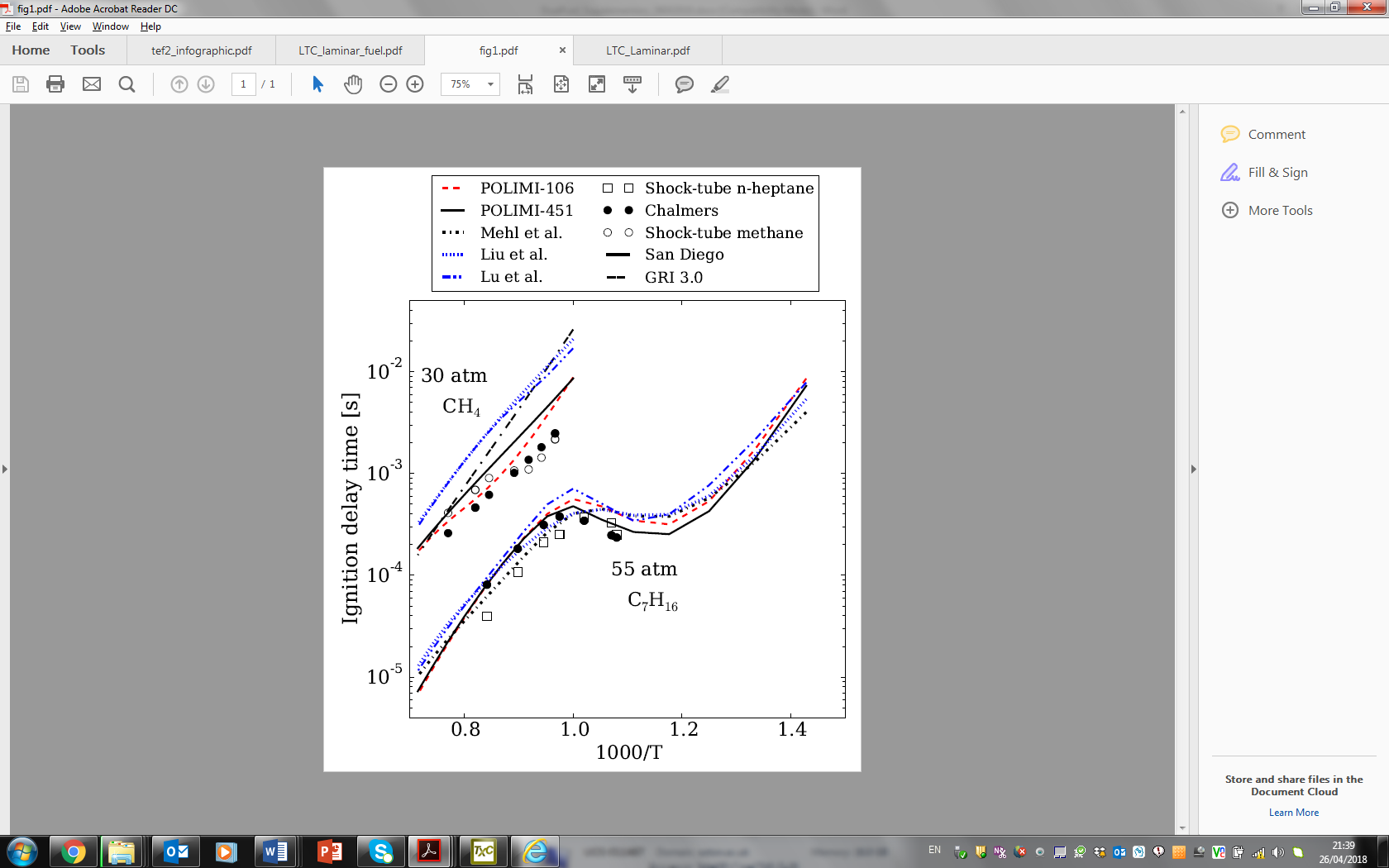


Figure S1. Constant-volume ignition delay times for stoichiometric methane–air at 30 atm and n-heptane/air at 55 atm. Shock-tube data: ○ [‎9], □ [‎10].

#### Figures/fig_S1.pdf

Figure S2. Constant-volume ignition delay times for stoichiometric n-heptane-air at 42atm for Polimi-451, Mehl *et al.,* Polimi-106, Liu *et al.* and Lu *et al.* (refer to Figure S1 for legend). Shock-tube data ▲[‎11].

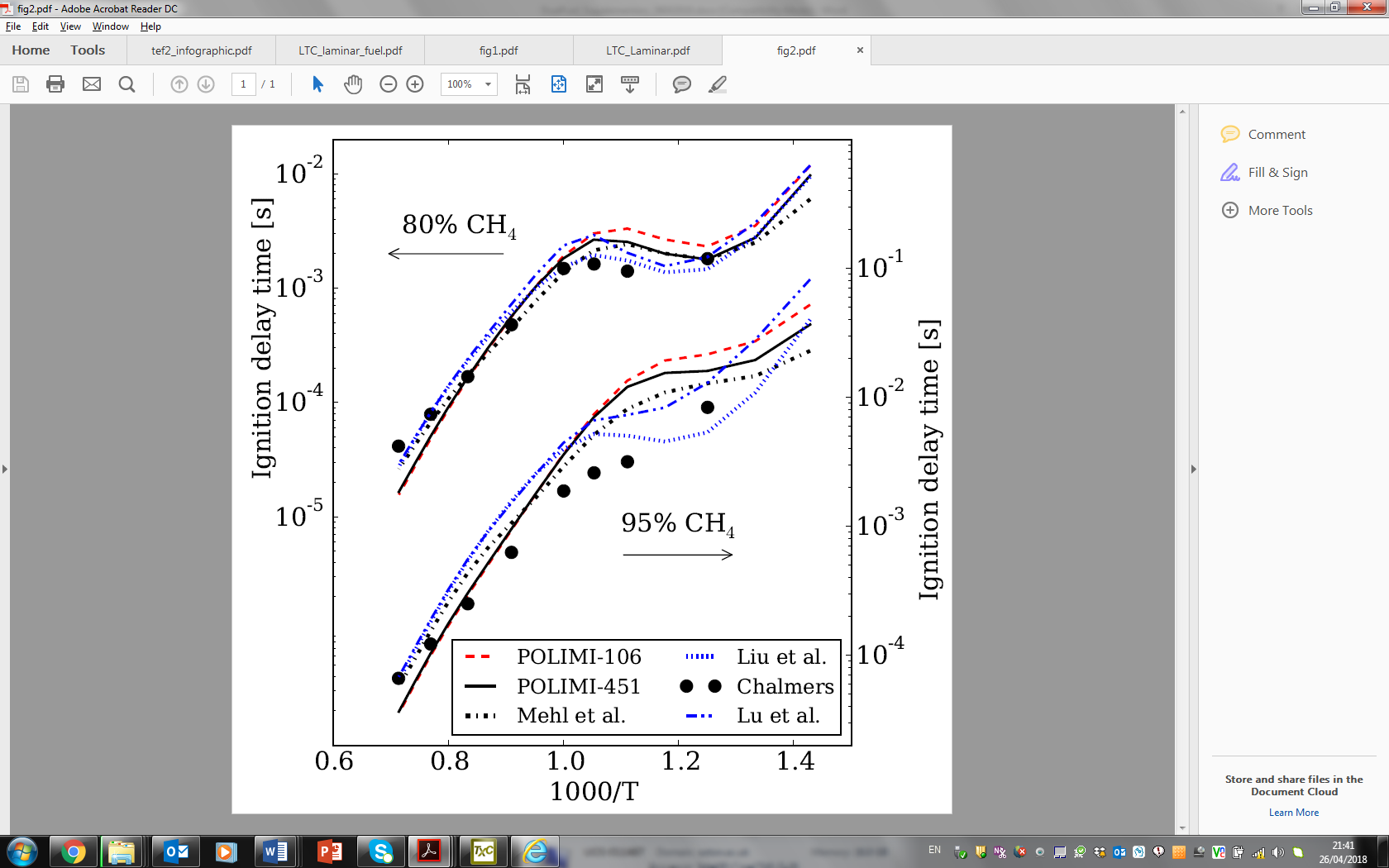


Figure S3. Constant-volume ignition delay times for stoichiometric methane/n-heptane–air mixtures at 30 bar with 80%vol CH4 (left axis) and 95%vol CH4 (right axis) in the fuel blend.

### Flame speed

Figure S4 presents stoichiometric methane–air flame speeds at 10 bar for equivalence ratios spanning 0.7 to 1.2 at 360 and 400 K, comparing experimental measurements [‎12] and numerical predictions of methane-air flame speeds for the detailed methane mechanisms and the reduced n-heptane mechanisms. Similar data for ambient pressure are presented in Figure S5.

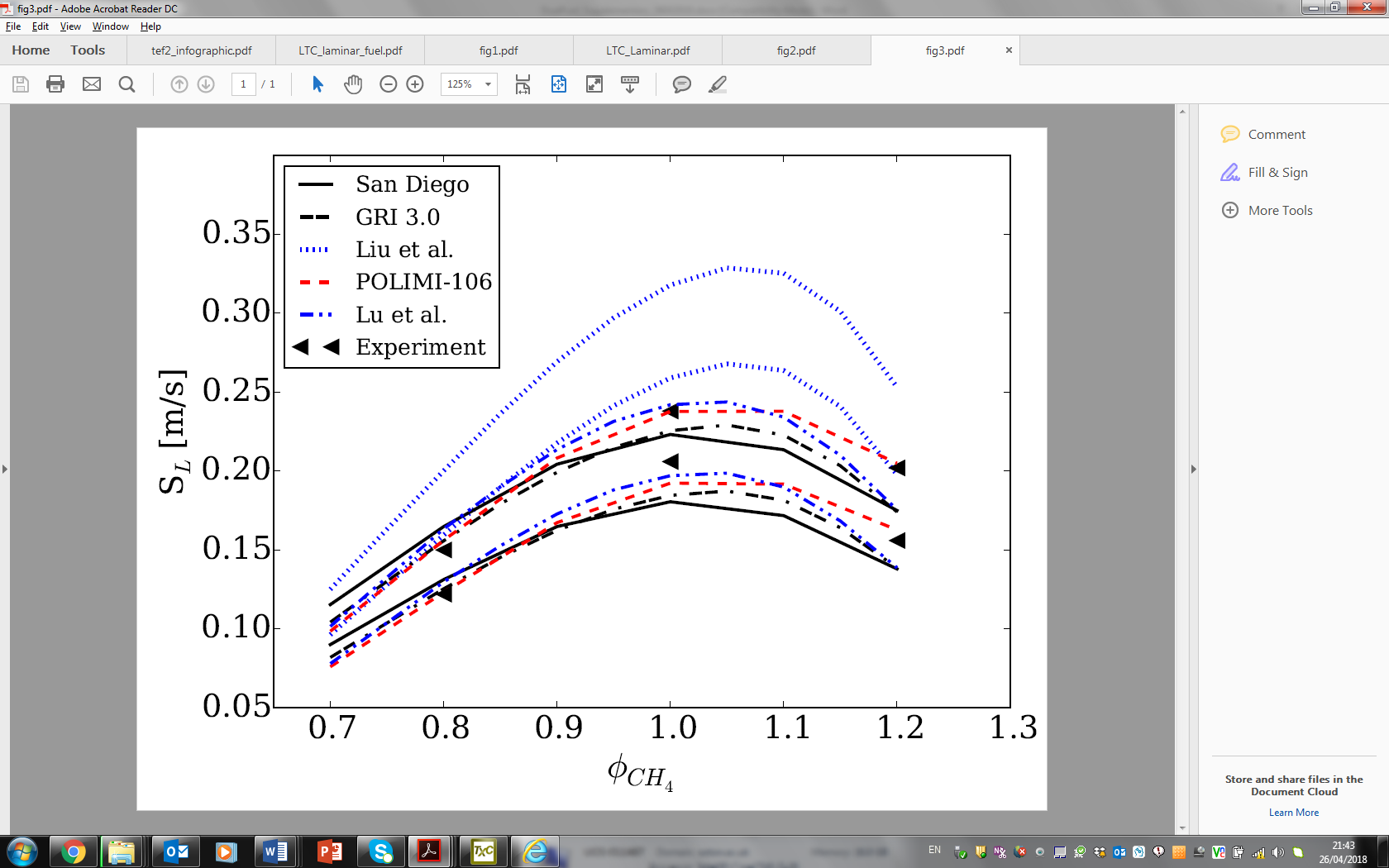


Figure S4. Laminar flame speed of methane–air flames versus equivalence ratio for 360 K (lower speeds) and 400 K (higher speeds) at 10 bar. ◄◄ experimental data [‎12].

#### Figures/fig3_NTP.pdf

Figure S5. Laminar flame of methane-air flames versus equivalence ratio at 300K, 1.01bar. Refer to Figure S4 for legend.

## Flame speed data used in order to fit the flame speed models

Flame speeds (cm.s-1) and adiabatic flame temperatures (K) for equivalence ratio , unburnt temperature , pressure bar for (a) pure methane fuel; (b) pure n-heptane fuel; (c) a methane/n-heptane blend with ; and (d) additional diluted flames with burned product mass fraction of at , K and bar. The burned products are assumed to consist of CO2, H2O and N2 only.

(a)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| CH4 | Tu [K] | = 0.8 | | = 1.0 | | = 1.2 |  |
| 20bar |  | ***SL*** | ***Tb*** | ***SL*** | ***Tb*** | ***SL*** | ***Tb*** |
| 700 | 44.7 | 2295.6 | 60.7 | 2515.7 | 56.8 | 2435.0 |
| 775 | 60.6 | 2350.9 | 79.9 | 2559.6 | 76.0 | 2491.1 |
| 850 | 80.9 | 2405.9 | 103.8 | 2603.0 | 100.2 | 2547.1 |
| 925 | 106.6 | 2460.2 | 133.2 | 2645.9 | 130.3 | 2602.5 |
| 1000 | 138.7 | 2513.7 | 169.5 | 2688.3 | 167.4 | 2656.8 |
| 40bar | 700 | 32.5 | 2300.3 | 45. 6 | 2532.6 | 43.1 | 2438.3 |
| 775 | 44.5 | 2356.9 | 60.4 | 2578.5 | 57.8 | 2495.9 |
| 850 | 60.0 | 2413.4 | 79.0 | 2624.2 | 76.5 | 2553.6 |
| 925 | 79.7 | 2469.6 | 102.2 | 2669.4 | 100.0 | 2611.2 |
| 1000 | 104.3 | 2525.0 | 130.8 | 2714.1 | 129.3 | 2668.2 |
| 60bar | 700 | 27.6 | 2302.6 | 39.2 | 2541.5 | 37.7 | 2439.9 |
| 775 | 37.9 | 2359.8 | 52.1 | 2588.6 | 50.5 | 2498.0 |
| 850 | 51.2 | 2417.1 | 68.3 | 2635.5 | 66.7 | 2556.5 |
| 925 | 68.1 | 2474.1 | 88.6 | 2682.0 | 87.3 | 2615.1 |
| 1000 | 89.5 | 2530.7 | 113.6 | 2728.0 | 113.0 | 2673.5 |

(b)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| C7H16 | Tu [K] | = 0.8 | | = 1.0 | | = 1.2 | |
| 20bar |  | ***SL*** | ***Tb*** | ***SL*** | ***Tb*** | ***SL*** | ***Tb*** |
| 700 | 70.9 | 2359.7 | 88.8 | 2576.3 | 85.1 | 2518.2 |
| 775 | 92.8 | 2413.6 | 113.9 | 2618.3 | 110.4 | 2574.2 |
| 850 | 121.2 | 2470.9 | 144.8 | 2660.3 | 141.6 | 2629.1 |
| 925 | 155.5 | 2524.0 | 182.5 | 2702.3 | 179.6 | 2682.2 |
| 1000 | 197.2 | 2575.4 | 228.2 | 2743.8 | 225.6 | 2734.0 |
| 40bar | 700 | 56.6 | 2366.7 | 72.9 | 2596.8 | 69.3 | 2523.4 |
| 775 | 74.5 | 2421.7 | 93.9 | 2641.2 | 90.5 | 2581.8 |
| 850 | 103.9 | 2479.3 | 121.5 | 2685.0 | 119.4 | 2640.2 |
| 925 | 128.0 | 2535.9 | 153.6 | 2730.0 | 151.4 | 2695.4 |
| 1000 | 161.0 | 2590.0 | 189.9 | 2773.0 | 187.7 | 2750.5 |
| 60bar | 700 | 49.5 | 2369.4 | 65.1 | 2607.5 | 62.0 | 2526.1 |
| 775 | 65.5 | 2425.1 | 84.0 | 2653.5 | 81.0 | 2584.4 |
| 850 | 86.1 | 2690.0 | 107.6 | 2690.0 | 104.8 | 2690.0 |
| 925 | 117.6 | 2541.3 | 143.9 | 2744.7 | 142.5 | 2701.1 |
| 1000 | 143.4 | 2597.4 | 171.2 | 2788.9 | 169.5 | 2758.5 |

(c)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Tu [K] | = 0.8 | | = 1.0 | | = 1.2 | |
| 20bar |  | ***SL*** | ***Tb*** | ***SL*** | ***Tb*** | ***SL*** | ***Tb*** |
| 700 | 59.2 | 2328.8 | 76.6 | 2546.4 | 72.3 | 2477.8 |
| 775 | 78.6 | 2383.7 | 99.2 | 2589.5 | 95.1 | 2533.9 |
| 850 | 102.9 | 2437.8 | 127.0 | 2632.2 | 123.3 | 2589.5 |
| 925 | 133.1 | 2491.2 | 161.2 | 2674.4 | 157.9 | 2643.9 |
| 1000 | 170.6 | 2543.7 | 202.7 | 2716.0 | 199.6 | 2696.5 |
| 40bar | 700 | 45.3 | 2334.7 | 60.0 | 2564.7 | 56.6 | 2482.1 |
| 775 | 60.7 | 2391.0 | 78.6 | 2610.5 | 75.1 | 2539.1 |
| 850 | 80.1 | 2446.7 | 101.1 | 2655.1 | 97.7 | 2596.6 |
| 925 | 104.3 | 2502.1 | 129.2 | 2700.0 | 126.2 | 2653.9 |
| 1000 | 134.6 | 2556.9 | 163.2 | 2743.8 | 160.8 | 2710.2 |
| 60bar | 700 | 38.6 | 2335.2 | 52.7 | 2574.5 | 50.0 | 2483.7 |
| 775 | 52.5 | 2394.4 | 68.8 | 2620.7 | 66.1 | 2542.1 |
| 850 | 69.6 | 2449.7 | 89.6 | 2667.6 | 86.7 | 2600.3 |
| 925 | 91.0 | 2507.5 | 114.1 | 2713.5 | 111.8 | 2658.3 |
| 1000 | 117.7 | 2563.5 | 144.5 | 2759.1 | 142.6 | 2716.1 |

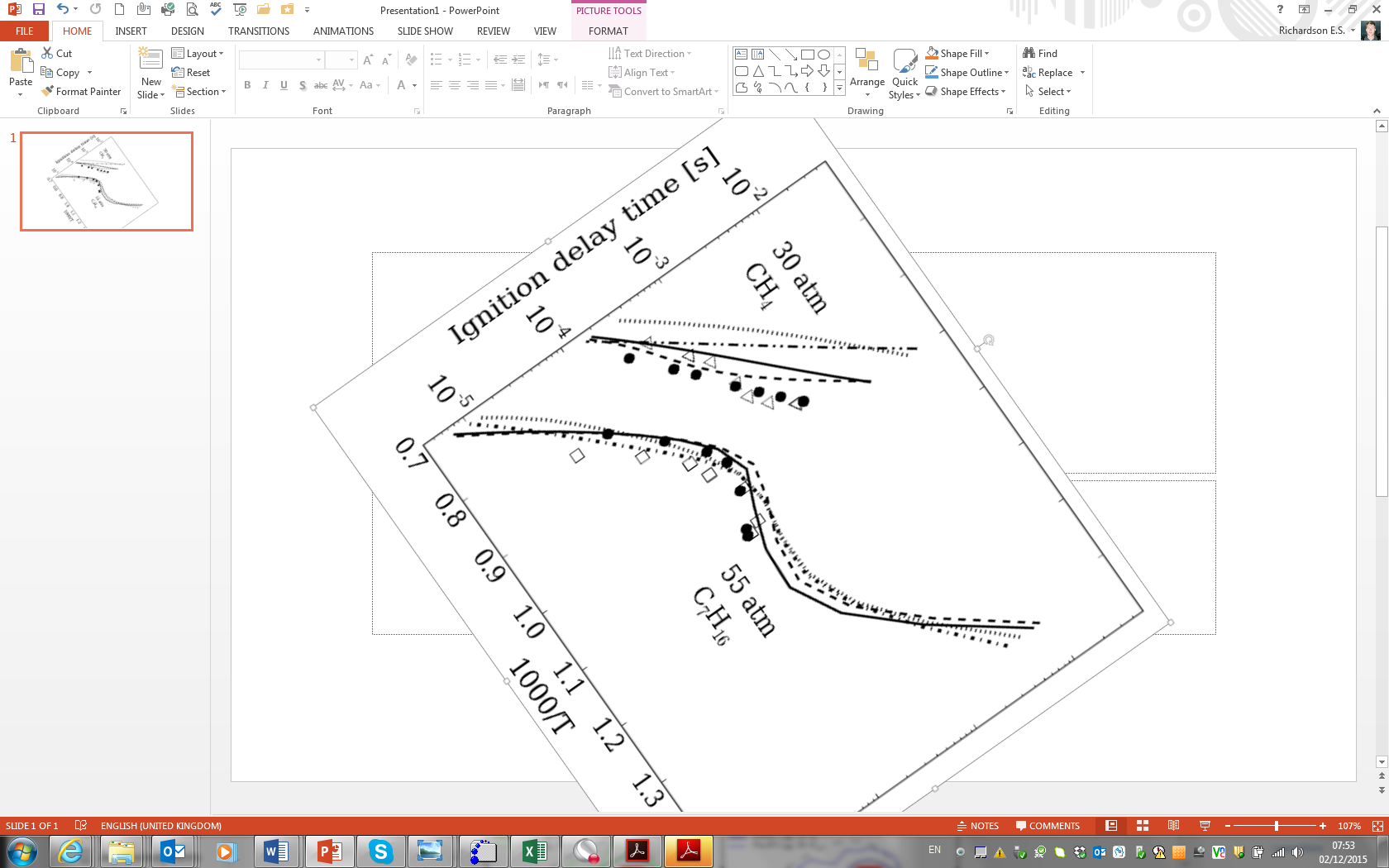
d)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | C7H16 | | CH4 | |  | |
|  | ***SL*** | ***Tb*** | ***SL*** | ***Tb*** | ***SL*** | ***Tb*** |
| 0.05 | 103.7 | 2620.2 | 64.8 | 2557.8 | 86.0 | 2289.3 |
| 0.1 | 89.0 | 2549.9 | 52.7 | 2488.6 | 72.2 | 2520.2 |
| 0.15 | 75.4 | 2475.2 | 42.0 | 2415.8 | 59.7 | 2447.3 |

## Additional data comparing alternative mixing-rules.

Figure S6 presents the performance of the linear [‎13] and Hirasawa *et al.* [‎14] flame speed mixing rules for the case of = 0.8, showing that both models are satisfactory also for this condition. The burned temperature mixing rule given by Hirasawa *et al.* [‎14] is evaluated in Figure S7, again showing that this model is satisfactory for modelling the burnt temperatures of methane/n-heptane mixtures.

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Figure S6. Variation of flame speed with equivalence ratio for methane/n-heptane fuel blends at 850K and 40bar: Polimi-106 simulations for = 0 (●), 0.8 (♦) and 1.0 (★ ); Fitted flame speeds from Eq. 5 (C:\Users\Bruno\Desktop\44species.png); and linear [‎13] (C:\Users\Bruno\Desktop\ranzi skeletal.png) and Hirasawa *et al.* [‎14] ()mixing-rules.

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Figure S7. Variation of flame temperature with equivalence ratio for methane/n-heptane fuel blends at 850K and 40bar: Hirasawa *et al.* [‎14] mixing-rule (C:\Users\Bruno\Desktop\ranzi skeletal.png) for = 0.5 (left) and 0.8 (right); Polimi-106 simulations for = 0 (●), 0.5 or 0.8 (★ ), and 1.0 (♦).

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