

Chemical Kinetics of Ignition of *n*-Hexane by a Moving Hot Sphere

Rémy Mével, Josué Melguizo-Gavilanes, Stephanie Coronel and Joseph Shepherd
California Institute of Technology, Pasadena, USA

1 Introduction

The risk of accidental ignition of flammable mixtures by a hot surface is of particular importance for the commercial aviation industry. In order to increase their fuel efficiency, the next generation of aircraft will incorporate large amounts of composite materials. In the case of a lightning strike on the aircraft structure, hot particles might be ejected from the composite material surface and could potentially ignite the flammable vapor space of a fuel tank. Quantifying the risk of ignition of aviation fuels by hot particles is thus a key issue for both engineering design and safety analyses. A very limited number of studies have been performed on ignition by hot particles. Silver [1] and Beyer et al. [2] investigated the ignition of a variety of fuels including hydrogen and pentane. Silver employed moving particles whereas Beyer used stationary spheres. More recently, Coronel et al. [3] studied the ignition of *n*-hexane-air mixtures by a moving hot sphere. These previous studies enabled quantifying the minimum surface temperature required for ignition to occur and demonstrating the effects of particle size and velocity.

The purpose of the present paper is to investigate in detail the chemical kinetics of the ignition of *n*-hexane, selected as the kerosene surrogate, by a moving hot sphere. In particular, we seek to clarify the importance of the chemical processes that occur below 1000 K. Non-reactive two-dimensional simulations of the transient viscous flow around a moving heated sphere were performed to obtain the temperature conditions the mixture experiences in the thermal boundary layer. The resulting temperature profiles were imposed to a non-adiabatic constant pressure reactor to enable a thorough study of the kinetics of the ignition process using a variety of detailed reaction models.

2 Experimental results

The ignition experiments were performed in a closed, cylindrical, stainless steel combustion vessel with a volume of approximately 22 L. Two parallel flanges are used to mount windows for visualization. Above the 22 L vessel sits a cylindrical, aluminum chamber with a volume of approximately 0.1 L. The aluminum chamber is used to heat small metal spheres. The chamber has two parallel flanges that are used to mount tungsten electrodes which can be actuated linearly using pneumatic actuators. To heat a sphere, the tungsten electrodes which are connected to a 12 V Bosch car battery (CCA 850 Amps) make contact with the sphere on opposite sides. High current passes through the sphere thereby heating it. The tip of each electrode is contoured to maximize contact with the sphere to ensure minimal contact resistance and uniform heating. Once the desired sphere temperature is reached, one of the electrodes retracts allowing the sphere to fall. The sphere exits into the combustion vessel, containing the flammable gas mixture. A two-color pyrometer is used to measure the sphere surface temperature during heating. The temperature recorded during an ignition event and a no ignition event is the sphere surface temperature prior to being released.

Ignition tests were performed for *n*-hexane-air mixtures at an initial temperature and initial pressure of 298

K and 100 kPa, respectively. The mixture equivalence ratio, Φ , was fixed at 0.9 and titanium (Ti-6Al-4V) spheres 4 mm in diameter were used as the ignition source. Examples of an ignition and a no ignition case are shown in Figure 1 (Left) in the form of schlieren images. Figure 1 (Right) shows the ignition results. A narrow overlap region of 1150-1170 K exists between the ignition and no ignition results; this overlap can be attributed primarily to uncertainty in the temperature measurements, and variability in the speed of the sphere and trajectory of the sphere.

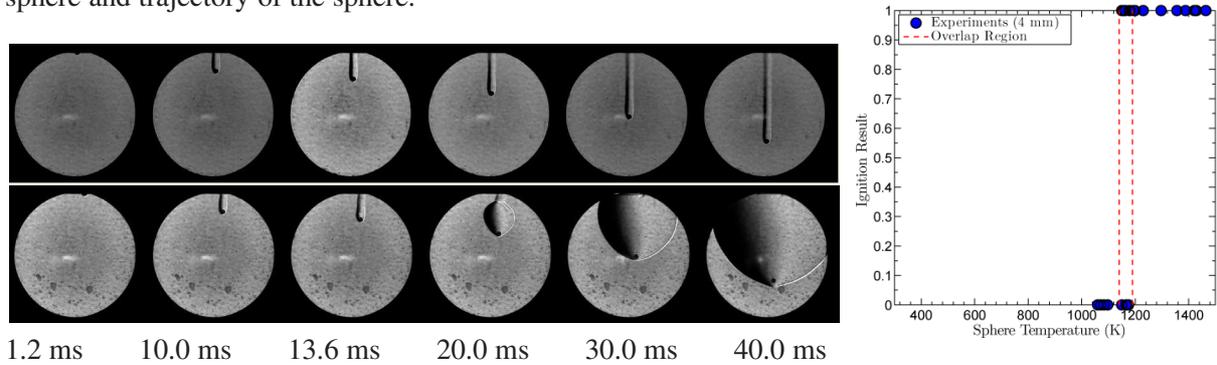


Figure 1: Left) Schlieren images of a no ignition case (top) and an ignition case (bottom). Right) ignition results for 4 mm diameter sphere with a speed of 2.4 m/s. Conditions: $n\text{-C}_6\text{H}_{14}\text{-air}$ at $\Phi=0.9$; $P_1=100$ kPa; $T_1=300$ K.

3 Quantification of the residence time

To quantify the condition of temperature the fluid experiences as it is heated by a moving hot sphere, non-reactive two-dimensional simulations have been employed. The computations have been performed using the Open source Field Operation And Manipulation (OpenFOAM) toolbox. The problem is described using the compressible Navier-Stokes equations with temperature dependent transport properties. The Sutherland Law, the Eucken Relation and the JANAF polynomials are used to account for

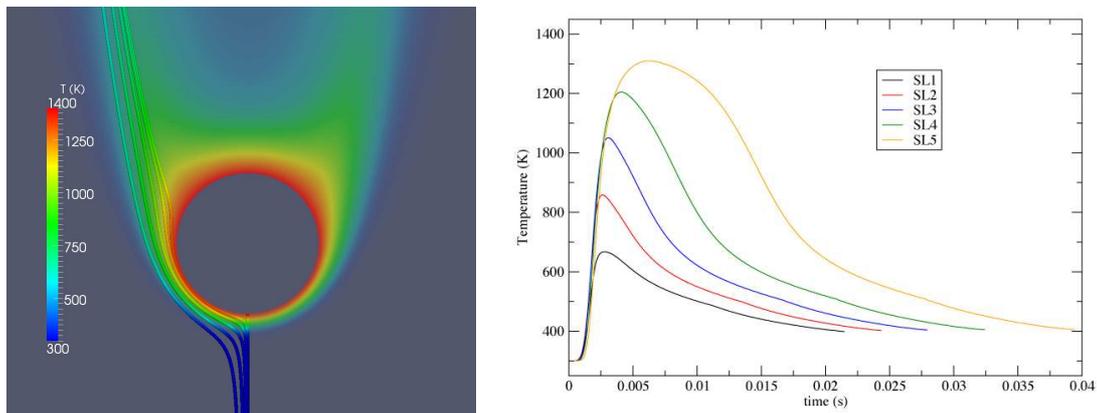


Figure 2: Results from 2D non-reactive simulation of a hot sphere falling in N_2 . Left): temperature field and streamlines positions. Right): temperature histories of some fluid parcels travelling along the streamlines. Conditions: $X_{\text{N}_2}=1$; $P_1=100$ kPa; $T_1=300$ K; $T_{\text{sphere}}=1400$ K; $U_1=0$ m/s.

the functional dependence of mixture viscosity, thermal conductivity and specific heat at constant pressure, respectively. The Lewis number is assumed to be unity. The computational domain consists of a square of side $20d$, with a sphere (cylinder in 2D) of diameter $d=4$ mm located in the center. A resolution of approximately 300k cells is used, compressed near the sphere, with a minimum cell size of $60 \mu\text{m}$ to ensure that the thermal and hydrodynamic boundary layers are properly resolved. Initial conditions are

$P_1=100$ kPa, $T_1=300$ K, $U_1=0$ m/s and $X_{N_2}=1$, with a constant sphere surface temperature, T_{sphere} , ranging from 1200K to 1600K. The frame of reference is attached to the sphere, hence, a time dependent inflow boundary condition is prescribed at the bottom of the computational domain to properly simulate the fall of the heated particle, as its velocity increases at a rate of 9.81 m/s². At the top, a non-reflective/pressure transmissive boundary condition is used to simulate an outflow. The simulation is run for 0.25 s (experimental fall time), after which time, five streamlines (SL) within the thermal boundary layer are selected, and the respective properties (temperature, velocity and position) are extracted along them (see Figure 2 Left)). Subsequently, the particle paths are computed, and the temperature histories plotted as shown in Figure 2 Right), which displays the temperature that a massless parcel of gas experiences as it approaches, enters and exits the thermal boundary layer.

4 Quantification of the chemical scales

4.1 Reaction models

A number of detailed reaction models include the kinetics of *n*-hexane and can potentially be employed to model the ignition of *n*-C₆H₁₄-air mixtures by a moving hot sphere: the models of (i) Ramirez et al. [4], 1789 reactions and 401 species, (ii) Dagaut [5], 2628 reactions and 531 species; (iii) Blanquart [6], 1119 reactions and 172 species; (iv) Livermore [8], 2827 reactions and 654 species; and (v) the JetSurf [7], 2163 reactions and 348 species. Figure 3 Left) compares the predictions of the five reaction models considering ignition at constant pressure of a lean, $\Phi=0.9$, *n*-hexane-air mixture. The models can be divided into two groups, based on the shape of the ignition delay time plots: on the one hand those that have an essentially constant slope, JetSurf and Blanquart's models; and on the other hand Ramirez's, Dagaut's and Livermore's models which exhibit a more complex evolution. The difference in shape between

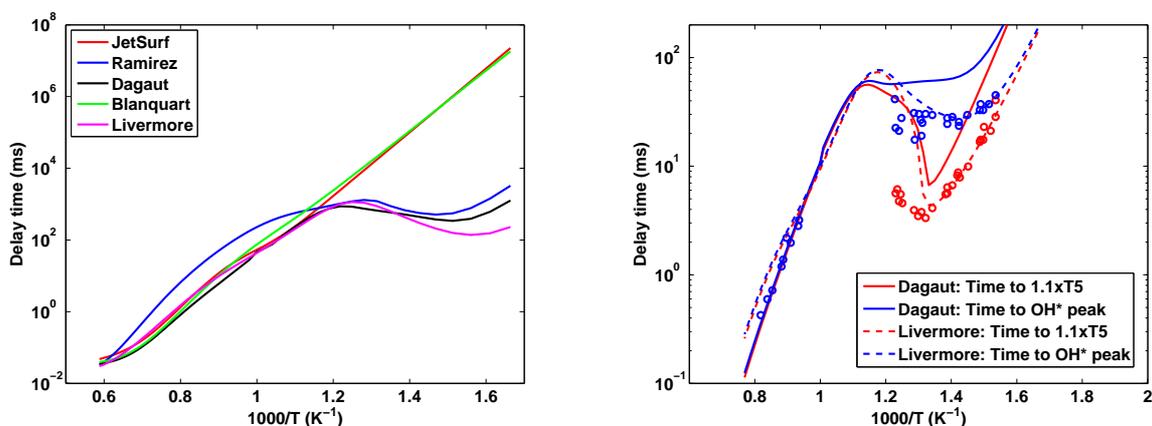


Figure 3: Left) Comparison between the predicted ignition delay-time of a *n*-hexane-air mixture by several detailed reaction models [4–8]. Conditions: $\Phi=0.9$; $P_1=100$ kPa. Right) Comparison between the experimental ignition delay-time for *n*-heptane [9] and the prediction for *n*-hexane of the detailed reaction models from Dagaut [5] and from Livermore [8]. Experimental conditions: $X_{NC_7H_{16}}=0.0102$; $X_{O_2}=0.1500$; $X_{CO_2}=0.0500$; $X_{Ar}=0.7898$. In simulations, *n*-hexane is used instead of *n*-heptane.

the two groups is due to the lack of low-temperature chemistry for *n*-hexane in JetSurf and Blanquart's models. This results in non-physical ignition delay-times in the range of 600-800 K. On the contrary, Ramirez's, Dagaut's, and Livermore's models include the low-temperature chemistry for *n*-hexane. At high-temperature, the prediction of the five models are close except for the model from Ramirez which exhibits significantly longer delay-times. In Figure 3 Right), the predictions of the models of Dagaut and of Livermore for *n*-hexane-based mixtures are compared with the experimental results of Campbell et al. [9] obtained with *n*-heptane. Campbell's results have been used because of the lack of data for *n*-hexane and the similarity of the two fuels. Dagaut's model predicts faster ignition at high-temperature but does

not reproduce very well the first-stage ignition in the low-temperature range, in contrast with Livermore's model predictions.

4.2 Chemical kinetics along streamlines

To estimate the chemical activity under conditions representative of those encountered during heating of a *n*-hexane-air mixture by a moving hot sphere, we performed constant pressure simulations in a non-adiabatic 0-D reactor with a time-dependent heat transfer coefficient. During the heating period, the reactor receives energy from a hot surface maintained at a fixed temperature with $T_{sphere}=1200-1600$ K. During the cooling period, the reactor loses energy to a surface with a temperature that progressively drops to 300 K. The temperature profile used was that of the streamline closest to the sphere. Figure 4

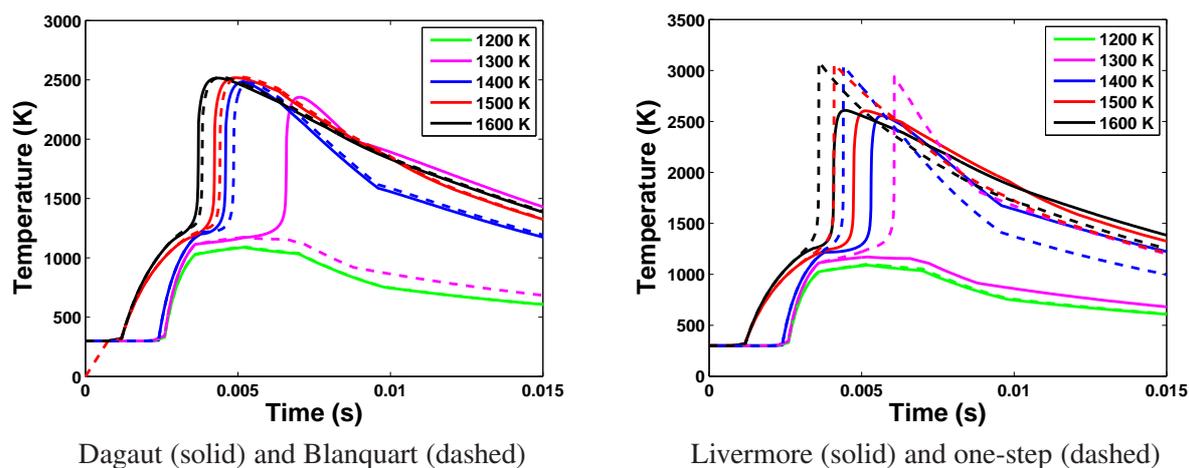


Figure 4: Comparison between the temperature profiles along the streamline closest to the sphere for different surface temperatures obtained with several reaction models. Conditions: *n*-C₆H₁₄ at $\Phi=0.9$; $P_1=100$ kPa; $T_{sphere}=1200-1600$ K.

shows the evolution of the temperature along the closest streamline predicted by several reaction models for different surface temperatures. The model of Dagaut predicts ignition for T_{sphere} as low as 1300 K whereas the models of Blanquart and of Livermore do not predict ignition below 1400 K. In addition, a one-step reaction model has been developed from Dagaut's model. This simple model is described by: Reactant \rightarrow Product; chemical energy: $q_{chem}=2.461 \times 10^6$ J/kg; and reaction rate: $k=0.1618 \times T^3 \times \exp(-158280/RT)$. As seen in Figure 4 Right), the one-step model predictions are consistent with those of Dagaut's model with ignition occurring with $T_{sphere}=1300$ K. This suggests that the low-temperature chemistry does not play a significant role during the ignition of *n*-hexane under the present conditions.

This aspect is also illustrated in Figure 5, which shows the temperature and species profiles, and Figure 6 which shows the most important reaction pathways. Figures 5 and 6 have been obtained with Dagaut's model at $T_{sphere}=1200$ and 1300 K. For the no-ignition case, $T_{sphere}=1200$ K, very little consumption of the reactants is observed. Formation and accumulation of C₂H₄, H₂, CO, H₂O₂, H₂O and CO₂ are observed. As seen in Figure 6, no significant pathways are available to consume C₂H₄. A small amount of OH radical is produced but [OH] drops down as the temperature decreases. This is due to the low extent of the chain branching process which is taking place at this temperature with only 6% of oxygen consumed by H atoms. Both H and OH essentially react with *n*-hexane to form hexyl radicals and H₂ and H₂O, respectively. This indicates that pyrolysis and partial oxidation are favored in the range of temperature the mixture undergoes for $T_{sphere}=1200$ K. In the ignition case, $T_{sphere}=1300$ K, a large fraction of the initial fuel is converted to C₂H₄ and H₂ before ignition occurs. At the same time, the concentrations of CO, CO₂ and OH increase progressively and then very rapidly as ignition occurs. Rapid formation of OH radical is sustained by branching process with 45% of O₂ consumed by H. In addition, the formation of CO₂ is mostly due to CO+OH=CO₂+H which sustains the regeneration of H atoms along with significant

heat release. For both cases, $T_{sphere}=1200$ and 1300 K, very weak chemical activity is observed during the heating period which is too short for reactions to proceed. The mixture is rapidly heated to a relatively constant temperature. The time spent at this quasi-constant high-temperature determines if ignition occurs.

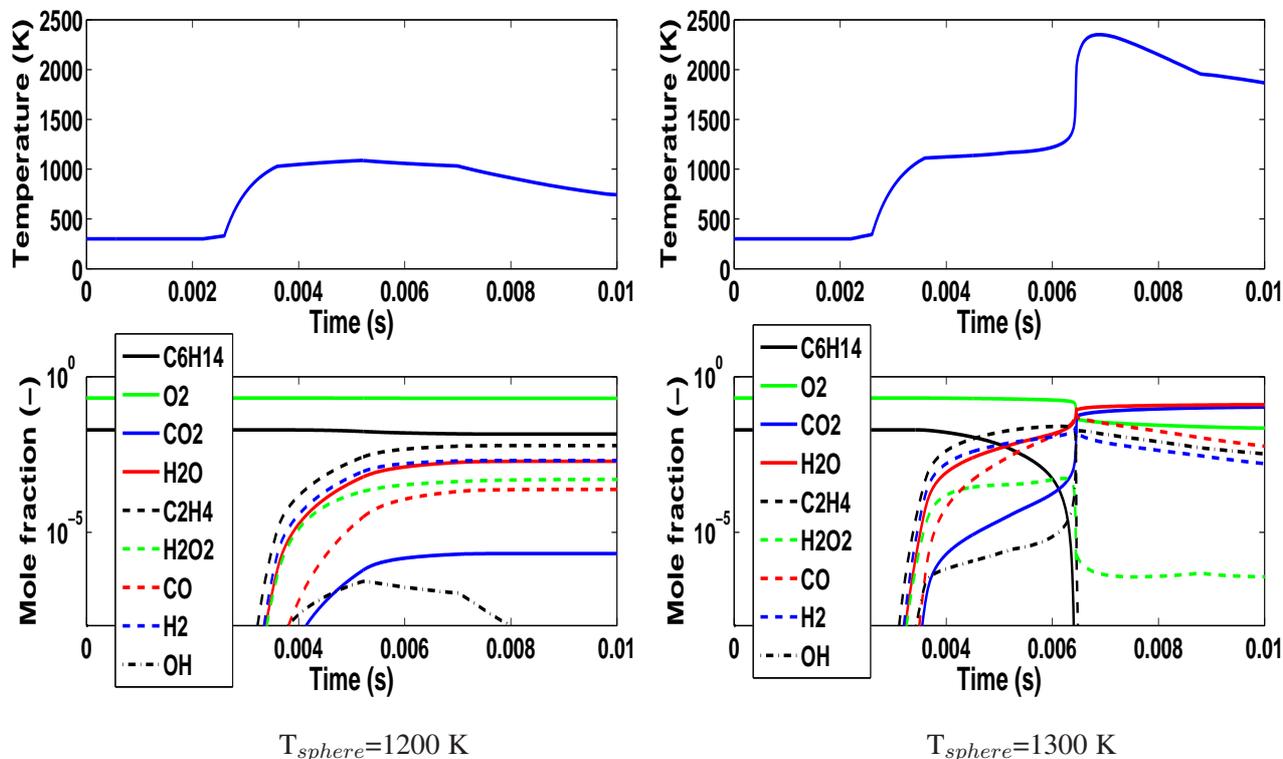


Figure 5: Calculated temperature and species profiles along the streamline closest to the sphere for different surface temperatures obtained with Dagaut's model. Conditions: *n*-C₆H₁₄ at $\Phi=0.9$; $P_1=100$ kPa.

5 Conclusion

In the present study, the kinetics of the ignition of *n*-hexane by a moving hot sphere has been analyzed. Non-reactive two-dimensional simulations have been performed to quantify the condition of temperature that the fluid experiences as it is heated by the hot sphere. Using these temperature profiles, the chemical activity predicted by several detailed reaction mechanisms as well as a one-step model has been studied. The results suggest that under the conditions presently considered, the low-temperature chemistry does not play a significant role in the ignition process due to the very short period spent by the mixture below 1000 K. Below the ignition threshold, the chemical activity is very low and the mixture essentially undergoes pyrolysis and partial oxidation. Future work will focus on reactive two-dimensional simulations using the one-step reaction model presently obtained. A parametric study will be performed in order to determine the effects of transport properties as well as of the overall reaction rate.

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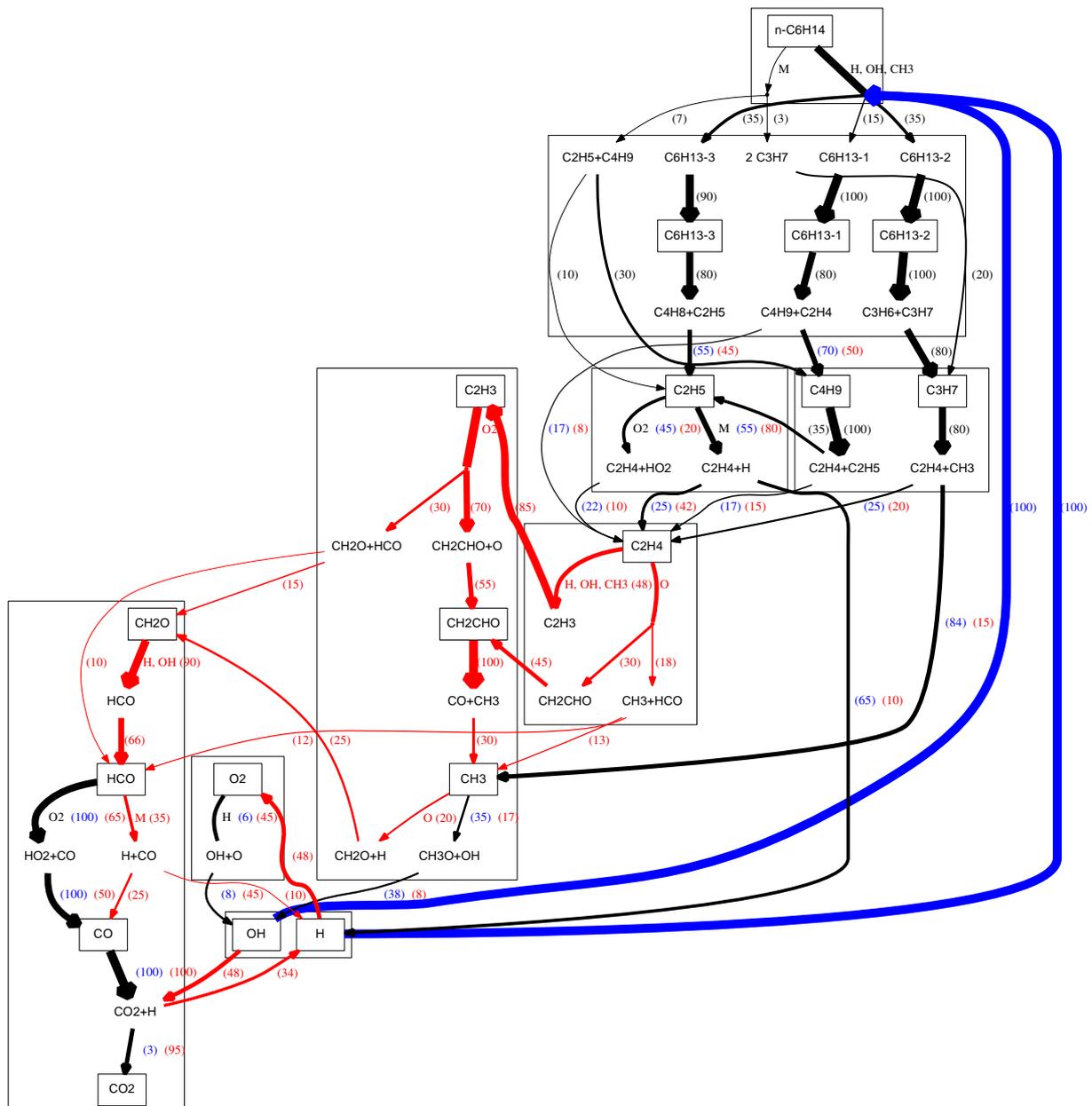


Figure 6: Reaction pathways along the streamline closest to the sphere for different surface temperatures obtained with Dagaut's model. Conditions: $n\text{-C}_6\text{H}_{14}$ at $\Phi=0.9$; $P_1=100$ kPa. Common paths: black. Specific paths: blue for $T_{\text{sphere}}=1200$ K and red for $T_{\text{sphere}}=1300$ K.