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Kinetic Modeling of Toluene Oxidation for Surrogate Fuel Applications

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1. Introduction

New environmental issues, like the effect of combustion-generated greenhouse gases, provide motivation to better characterize oxidation of hydrocarbons. Transportation, in particular, significantly contributes to energy consumption and CO₂ emissions. Kinetic studies about the combustion of fuels under conditions typical of internal combustion engines provides important support to improve mechanism formulation and to eventually provide better computational tools that can be used to increase the engine performance.

It is foreseeable that at least in the next 30 years the main transportation fuels will be either gasoline or diesel. Unfortunately, these fuels are very complex mixtures of many components. Moreover, their specifications and performance requirements significantly change the composition of these fuels: gasoline and diesel mixtures are different if coming from different refineries or they are different from winter to summer. At the same time a fuel with a well defined and reproducible composition is needed for both experimental and modeling work. In response to these issues, surrogate fuels are proposed. Surrogate fuels are defined as mixtures of a small number of hydrocarbons whose relative concentrations is adjusted in order to approximate the chemical and physical properties of a real fuel. Surrogate fuels are then very useful both for the design of reproducible experimental tests and also for the development of reliable kinetic models. The primary reference fuels (PRF) are a typical and old example of surrogate fuel: n-heptane and iso-octane mixtures are used to reproduce antiknock propensity of complex mixtures contained in a gasoline. PRFs are not able to surrogate gasoline in operating conditions different from standard ones and new surrogates have been recently proposed. Toluene is included in all of them as a species able to represent the behavior of aromatic compounds.

On the other side, the toluene oxidation chemistry is not so well established and uncertainties still remain in the mechanism. This is especially true in the low temperature regime (< 850K). In these conditions, the toluene reactivity is too low to be conveniently investigated. Nonetheless, gasoline surrogates work in the engine at low temperatures, because of the presence of very reactive alkanes. The effect of these component interactions have to be taken into account.

This work's aim is to present the model activity carried out by two different research groups, comparing the main pathways and results, matching data carried out in different devices both for pure toluene and mixtures. This is the starting point for a further activity to improve the two kinetic schemes.

2. Mechanism

Brezinsky [1] proposed more than 20 years ago a mechanism of toluene oxidation. Primary reactions are mainly H-abstractions on toluene forming the resonantly stabilized benzyl

radical. The ipso-addition reaction of H producing benzene and methyl competes with the H-abstractions. The O addition on the ring followed by H depletion gives rise to cresoxy radical, whose stability makes its amount significant and favors termination reactions especially with H forming cresols. The long life of radicals induced by resonance is one of the main characteristics of the radicals involved in this system and of the benzyl in particular. Benzyl then reaches quite high concentration and acts as a radical scavenger through termination reactions. Interactions with OH, CH₃ and another benzyl respectively form benzyl alcohol, ethylbenzene and bibenzyl. Another intermediate is benzaldehyde which comes from benzyl reaction either directly with O (and H depletion) or with HO₂ and the successive OH and H release. The pyrolysis mechanism has been recently upgraded [2]

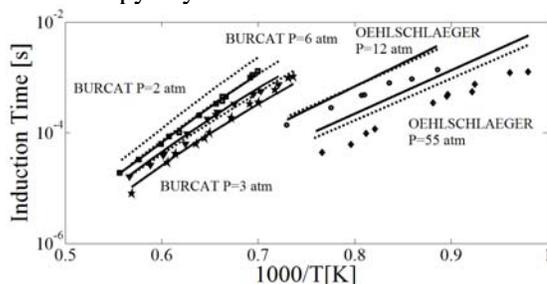


Figure 1. Comparison between predicted (solid lines POLIMI; dotted lines LLNL) and experimental [7-8] induction delays at $\Phi=1$.

Burcat [6]: 0.497%mol. toluene in Ar at 2, 6 atm;

1.497%mol. toluene in Ar at 3 atm;

Oehlschlaeger [7]: 2.281%mol. Toluene in N₂.

This mechanism still remains a reference for both the schemes here discussed, even though larger details and modified kinetic constants are adopted. The relative importance of the pathways and the competition among them will be discussed in the following paragraph.

Both mechanisms (LLNL [3-4] and POLIMI [5-6]) are the results of a long activity since many years, with continuous proper tunings and validations. The schemes include the kinetics of toluene and other aromatics, like benzene, and aliphatics, with specific attentions to typical gasoline

compounds (n-heptane and iso-octane) and additives. As mentioned, this joint activity aims to further improve both the models by the comparison of the results and of the characterization of main pathways involved, with their rate constants.

3. Results

3.1 Pure Toluene

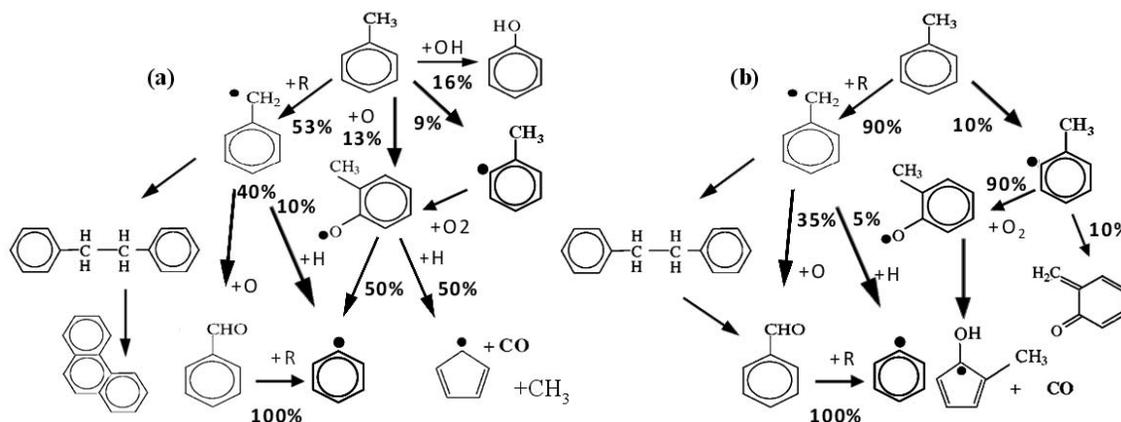


Figure 2. Comparison between the main reaction paths occurring in the shock tube experiment [8]

a) POLIMI; b) LLNL.

Figure 1 shows the comparisons between models and experimental data of ignition delay times measured in shock tube experiments [7-8]. Despite the quite wide range of pressures investigated both the models reveal able to catch the main trends. The activation energy of the

global process is correctly reproduced, even though some overestimations of the induction period are present, especially at lower temperatures and higher pressures. A comparison of the main reaction paths in these conditions (fig. 2) highlights that reactions involving the ring play a more important role in the POLIMI mechanism.

O addition to form cresoxy radical, OH ipso addition toward phenol with methyl depletion and H abstractions to form methyl-phenyl radicals account up to about 40% of toluene disappearance. This mechanism increases its importance with temperature. Cresoxy radical formation can reach up to 40% of the initial reactions at temperatures of about 1300K. On the contrary, in LLNL mechanism 90% of toluene is transformed in benzyl radical by metathesis reactions. Successive benzyl reactions give rise to phenyl through the benzaldehyde intermediate.

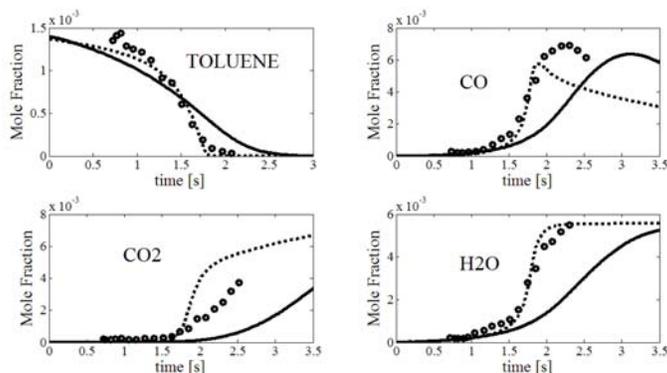


Figure 3. Comparison between predicted (solid lines POLIMI; dotted lines LLNL) and experimental [9] concentrations (PFR $P=12.5[atm]$; $T=920[K]$; $2.1\%mol. O_2$ and $0.14\%mol. Toluene$).

Chaos et al. [9] investigated 0.14% toluene lean oxidation ($\Phi=0.6$) in pressurized flow reactor (PFR) at lower temperatures (920 K) and relative high pressures (12.5 atm). In these conditions the POLIMI mechanism starts reacting in advance (fig. 3), but the reactivity is lower than the experimental profiles. LLNL is more in line with the measurements. Once again the difference between the two

models lies in the importance of the pathways which involve the aromatic ring and the methyl group. Again in this case, LLNL mechanism explains toluene depletion mainly via benzyl formation, whilst POLIMI mechanism includes a significant role of the cresoxy radical.

At even lower temperatures, continuously stirred reactor (CSTR) data from Bounaceur et al. [10] can be a further interesting test for both the kinetic schemes.

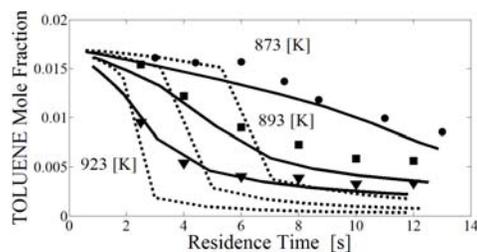


Figure 4. Comparison between predicted (solid lines POLIMI; dotted lines LLNL) and experimental [10] toluene concentration at different temperatures (isothermal CSTR $P=1 [atm]$; stoichiometric $1.7 \%mol. Toluene$ in He).

Figure 4 shows the comparison between the two models with the oxidation of a toluene/oxygen/helium mixture (toluene $1.7\%mol$ and $\Phi = 0.9$) at atmospheric pressure and temperatures in the 873-923 range. In this case POLIMI model better reproduces the experimental evidence of a slow reactivity with residence time, whilst LLNL mechanism behaves as before in the PFR, with an initial induction time followed by sharp increase in reactivity with temperature.

Measurements carried out in Orleans [11] allow testing of the selectivities of the two mechanisms towards main and minor intermediate products. These data from an isothermal jet stirred reactor at atmospheric pressure refer to a mixture of toluene/oxygen/nitrogen ($0.15\% mol$) at Φ 0.5 and 1.5 with a temperature range between 1000 and 1300 K. Figures 5 shows a sample of comparisons of model predictions and measurements.

Also in this case, POLIMI reacts in advance and toluene disappearance is smoother, especially at lower Φ , when compared with LLNL. The experimental data are more in line

with the LLNL predictions. The difference in the reactivity does not allow an easy comparison of the products at different temperatures. For this reason, figure 5 shows the mole fractions of a few species vs. toluene conversion. Despite the uncertainties in the characterization of toluene profile, POLIMI predicts the species selectivity quite well. Both the peaks and trends of the major and minor species are correctly estimated.

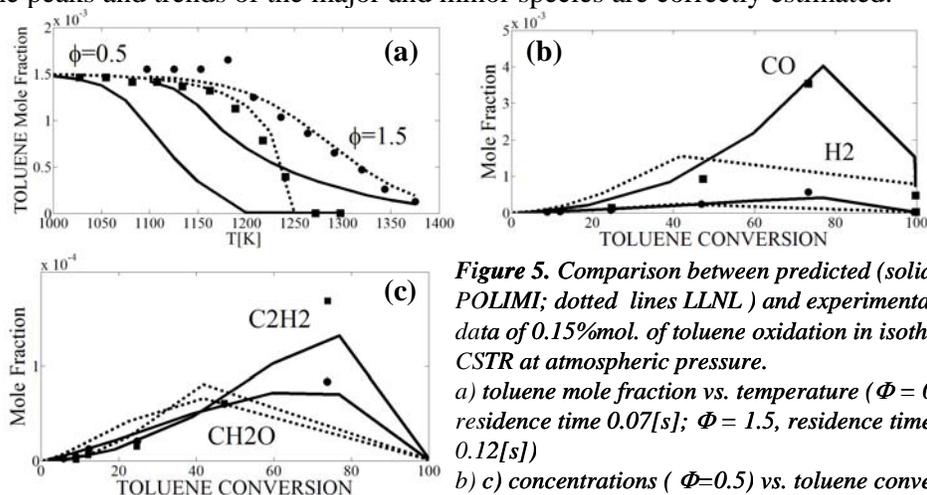


Figure 5. Comparison between predicted (solid lines POLIMI; dotted lines LLNL) and experimental [11] data of 0.15% mol. of toluene oxidation in isothermal CSTR at atmospheric pressure.

a) toluene mole fraction vs. temperature ($\Phi = 0.5$, residence time 0.07[s]; $\Phi = 1.5$, residence time 0.12[s])

b) c) concentrations ($\Phi = 0.5$) vs. toluene conversion

3.2 Mixtures

Toluene, as most aromatics, is an effective octane enhancer, because of its low reactivity. The aromatic ring is very stable and its activation requires high activation energy. The peculiarity of toluene is its blending anti-knock performance. As mentioned, the main pathway of toluene decomposition, in particular at low temperatures, is the H-abstraction forming benzyl radical.

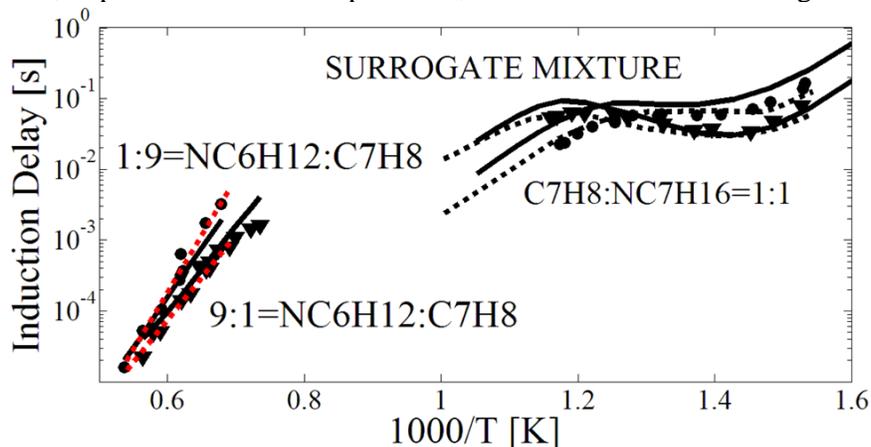


Figure 6. Comparison between predicted (solid lines POLIMI; dotted lines LLNL) and experimental induction delays of different stoichiometric mixtures oxidation.

At higher temperatures effect of different toluene-1hexene ratios in shock tube experiments [13].

At lower temperatures, data from RCM of toluene/n-heptane (NC7) 1/1 and of a mixture of isooctane/toluene/1-hexene 47/35/18 (mol) [14].

This means that very reactive small radicals, like H, OH or HO₂, are converted into the stable and then much less reactive benzyl radical. Moreover, the very high stability of this long-lived resonantly radical permits its accumulation and consequently benzyl acts as a radical scavenger drastically reducing the overall reactivity of the other gasoline components. This is not the case of benzene, for example, whose role in gasoline is just to reduce knock

propensity through its high stability, but without important blending effects: phenyl is a very reactive radical and thus has a low synergistic mixture effect [3, 12].

This toluene property highlights the important aspect of the cross interactions between species. Radicals formed from H-abstraction on a fuel component have to interact with the surrounding environment (abstracting hydrogens, adding on double bonds or recombining with other radicals), especially if this radical is very stable like benzyl or if it does not easily decompose like phenyl. On the contrary, radicals with possible and favorable β -scissions can mainly decompose (or isomerize and then decompose) as in the case of peroxy radicals formed during the low temperature oxidation of either large alkanes or alkenes.

Figure 6 shows a first set of comparisons between experimental data [13-14] and model predictions. The measurements are carried out in shock tube at 2 bar and quite high temperatures for two different mixtures of hexene/toluene. In these conditions, no low temperature mechanism phenomena can be observed and the chemistry of hydrocarbons is very similar. As a matter of fact, toluene is not very effective at reducing the overall reactivity. Even increasing its concentration by 9 times, does not significantly affect the ignition delay time. The theoretical results are in line with the experimental evidence.

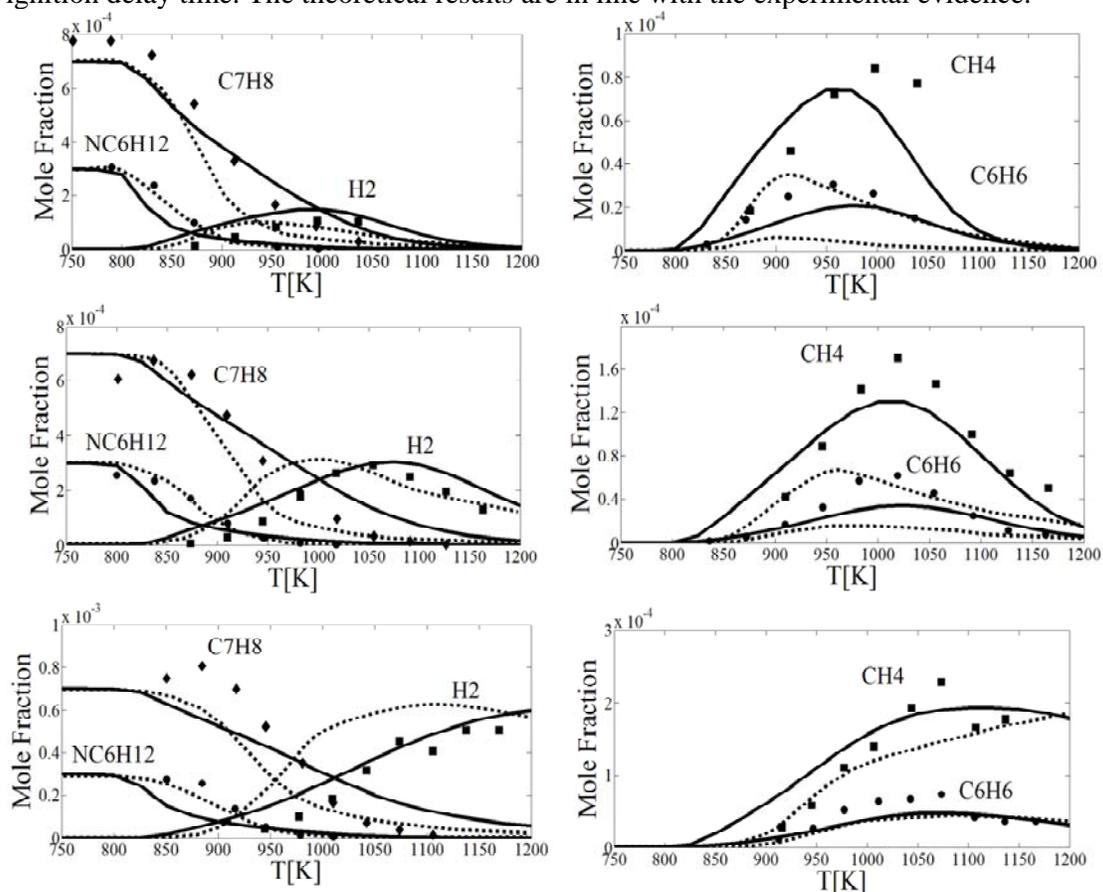


Figure 7. Comparison between predicted (solid lines POLIMI) and experimental [13] concentrations of major and minor species from toluene/hexene (70/30) oxidation in JSR at different stoichiometries (from top $\Phi = 0.5, 1, 1.5$)

In the lower temperature range, data of mixtures of toluene with both n-heptane and n-heptane/isooctane are available. Under these conditions, the negative temperature coefficient (NTC) behavior is quite evident and the models well catch this ‘pathology’ of hydrocarbon oxidation. In particular, the mechanisms well reproduce the crossing of the two mixtures: at

lower temperatures isooctane is less reactive than n-heptane and the ignition times of surrogate mixtures are higher. When the temperature increases, this effect disappears.

A final set of data refers to a mixture of n-hexene/toluene oxidized in JSR at different temperatures and different equivalence ratios [12]. Figure 7 shows the comparisons between measures and predictions. These tests mainly focus on the reliability of the model to reproduce the formation of products. As it can be observed, the agreement is quite good and the effect of stoichiometry is correctly taken into account. Moving toward richer conditions, hydrogen mole fraction notably increases and at $\Phi=1.5$ the maximum is not present. Methane peak is higher when less oxygen is fed, whilst benzene is less sensitive to the equivalence ratio of the mixture.

4. Conclusion

Two mechanisms of toluene oxidation have been analyzed and main differences highlighted. In LLNL model, the H-abstraction reactions to form benzyl are the dominant act of toluene depletion in all the conditions investigated. On the contrary, POLIMI kinetic scheme includes a significant role played by reactions on the aromatic ring and in particular the oxygen atom addition to form cresoxy radical. Despite these differences both the mechanisms are able to catch the main characteristics of toluene oxidation kinetics with a quite good comparison with several experimental data. This work is a starting point of a future synthesis of the models toward a deeper understanding of the real mechanism and a better description of the whole process.

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