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Chemical kinetic study of the oxidation of toluene and related cyclic compounds

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Abstract

Chemical kinetic models of hydrocarbons found in transportation fuels are needed to simulate combustion in engines and to improve engine performance. The study of the combustion of practical fuels, however, has to deal with their complex compositions, which generally involve hundreds of compounds. To provide a simplified approach for practical fuels, surrogate fuels including few relevant components are used instead of including all components. Among those components, toluene, the simplest of the alkyl benzenes, is one of the most prevalent aromatic compounds in gasoline in the U.S. (up to 30%) and is a promising candidate for formulating gasoline surrogates. Unfortunately, even though the combustion of aromatics been studied for a long time, the oxidation processes relevant to this class of compounds are still matter of discussion.

In this work, the combustion of toluene is systematically approached through the analysis of the kinetics of some important intermediates contained in its kinetic submechanism. After discussing the combustion chemistry of cyclopentadiene, benzene, phenol and, finally, of toluene, the model is validated against literature experimental data over a wide range of operating conditions.

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.

The study of the combustion of gasoline and diesel fuels, however, has to deal with their complex compositions, which generally involve hundreds of compounds whose relative amount depends on the origin of the feedstock, economic and even seasonal factors.

In response to these issues, surrogate fuels are proposed. Surrogate fuels are defined as mixtures of a limited number of hydrocarbons whose relative concentrations is adjusted in order to approximate the chemical and physical properties of a real fuel. To better mimic the combustion behavior and the emissions produced by the combustion in engine conditions of real fuels, a suited formulation of the surrogate is crucial. Reproducing the qualitative composition of the fuel of interest in terms of iso and normal paraffin, aromatic and oxygenated content, for instance, is an effective way to approximate not just the ignition behavior of a real fuel, but also its burning rate and sooting tendency. For a long time primary reference fuels, mixtures of n-heptane and iso-octane, have been the most used surrogates of gasoline and diesel fuel. Nowadays, formulations including more components are investigated to better reproduce the complex behavior of different fuel typologies.

Aromatics account for a significant fraction (up to the the 25%) of gasoline fuel composition. Toluene in particular, the simplest of the alkyl benzenes, is one of the most used aromatics in the formulation of gasoline surrogates. Toluene has drawn recent interest because of its reported ability to increase the effective range of boosted operation for HCCI engines when toluene is added in large quantities to the fuel [1]. These factors provide motivation for better understanding the chemical kinetics of toluene.

Unfortunately, even though the combustion of the aromatic ring has now been studied for a long time, the oxidation processes relevant to this class of compounds still resists a fully successful implementation in most of the kinetic mechanisms available in literature.

More than 20 years ago, Brezinsky [2] proposed the first detailed mechanism of toluene oxidation. Later works carried out in Princeton extended the results of that first work to include new details and different aromatic hydrocarbons [3-5]. These mechanisms still remain a reference for most of the existing schemes even though more details and modified kinetic constants have now been identified and incorporated into more recent models. Together with these models, other studies based on ab initio calculations and experimental investigations, provided a deeper insight in some of the fundamental steps involved in the oxidation of aromatics. A more extensive review of these contributions will be presented later.

This work's aim is to present the model activity carried out in collaboration by two different research groups, comparing the main pathways and results, matching data carried out in different devices both for pure toluene and mixtures. The two mechanisms here presented have been developed during the years adopting different approaches. The model developed at Lawrence Livermore National Lab (LLNL) is intended to be a fully detailed kinetic mechanism of combustion of hydrocarbons. This model is mainly focused on the oxidation processes, with particular regard to the autoignition propensity of hydrocarbons.

The model is constantly updated taking advantage of the latest available information coming from ab initio calculations and experimental data. Because of the high level of detail, the number of species accounted in this mechanism is generally high. As a matter of an example, the sole oxidation mechanism of C1 C4 hydrocarbons includes 230 species. Because of the a priori method, this approach is particularly suited to the fundamental study of combustion kinetics and to the development of kinetic mechanisms for fuels which behavior is still partially unknown. Because of the large number of species required, it is necessary to reduce the size of the model for most of the practical applications.

On the other hand, the kinetic mechanism developed by Milano's group (here referred as PoliMi) is a semi-detailed mechanism. Lumping procedures are used to limit the number of chemical species while maintaining an effective description of the processes involved the oxidation. The historical roots of this model is in the study of pyrolysis of larger hydrocarbons, so a good detail is devoted to the formation of unsaturated species and PAH growth. The size of this mechanism is smaller than the LLNL's one, the same C1-C4 mechanism earlier mentioned accounts for just about 60 species. The total number of reactions, on the other side, is generally comparable (if not greater) to a detailed mechanism because of the generalized approach here adopted for abstraction reactions: all the most relevant radicals can virtually abstract hydrogen atoms from any molecule, depending on the relative energy required by each site. The compactness of this model makes it particularly suited for many practical applications. Among its most recent uses it should be mentioned the application to the post processing of computational fluid-dynamic applications and to the study of the autoignition propensity of gasoline fuels.

Both the mechanisms have been built according hierarchical and modular criteria and, several times in the past, collaborations between the two groups brought improvements to both the models implementing common solutions.

In this work the combustion kinetics of the first aromatic ring will be analyzed on the basis of the current experimental information and rate constant estimations, considering not just the oxidation of toluene, the most investigated fuel in the class of compounds of interest, but also cyclopentadiene and benzene chemistry. These species, and their radicals, are indeed fundamental intermediates along the oxidation pathways of alkyl aromatics.

The chemistry of benzene oxidation is a fundamental reference for the study of heavier aromatics and toluene. When the ring starts to be oxidized, the elimination of CO reduces the size of the ring to 5 carbon atom. The resulting cyclopentadiene is then oxidized trough the formation of its radical (C5H5), a cyclic resonant structure having many aspects in common with other aromatic structure. Because of the strong hierarchical dependence of the reaction mechanisms of these species, is fundamental to develop and validate the kinetic model progressively on all of them.

After analyzing the most critical aspects in the oxidation of C5H6, C6H6 and C7H8, a comprehensive set of comparisons with the available experimental data will be presented. Most of these comparisons refer to the oxidation of toluene at high temperature (>1000K). Nonetheless, gasoline surrogates work in the engine also at lower temperatures, and because of the presence of very reactive alkanes, they may undergo autoignition even at these milder conditions. This issue will be addressed in future works.

The oxidation of cyclopentadiene

Previous investigations on the cyclopentadiene oxidation chemistry

Despite its relevance to the oxidation of aromatic hydrocarbons, cyclopentadiene is not considered as a fuel of interest for practical application. Most of the studies involving cyclopentadiene were aimed to determine the role it plays in PAH formation and its soothing properties. The important role of cyclopentadiene in the combustion of heavier aromatic has been immediately recognized as it was found to be one of the major detectable intermediates in the flow reactor experiments carried out in Princeton [2-3]. Similar evidences were collected in the burner-stabilized low-pressure benzene flame of Bittner and Howard [6] and in the laminar flames of benzene-air and toluene-air mixtures [7-8]. The first specific study on the intermediate produced by its decomposition is maybe due to Wang and Brezinsky [9]. In their work the thermochemistry of the cyclopentadiene derivatives is analyzed together with the thermal degradation kinetics of cyclopentadienone.

Zhong and Bozzelli analyzed the reaction of the cyclopentadienyl radical with oxygen and other relevant radical species on the basis of ab initio calculation, proposing a detailed kinetic model for the oxidation of C5H6 which includes a large number of reactions leading to ring opening [10]. One more kinetic mechanism has been proposed by Burcat and coworkers [16] in 2001, which performed also some shock tube measurements in validation to the model. Their model was obtained combining set of reactions from the GRI [11] and LLNL [12-13] models for the core mechanism, Frenchlach's mechanism [14] for the formation of benzene and, finally, Bittker [15] and Emdee's mechanisms [3] for the C5H6 ring. Some of these rate constants were modified to better fit the experimental data.

In a paper published in 2002 Lindsted and Rizos discussed the formation of aromatics from cyclopendadiene combustion [17] identifying the formation of methylcyclopentadiene as a fundamental step in the formation of the first 6 membered aromatic ring. The decomposition and ring expansion of methylcyclopentadiene under reflected shock waves was experimentally and numerically studied by Lifshitz and coworkers [18] while few years later

Wing Tsang and coworkers analyzed the ring expansion of tert-butylcyclopentadiene [19]. A recent paper by Kislov and Mebel discussed the formation of double ring aromatics from cyclic C5 structures combustion by mean of ab initio calculations focusing on the rearrangement of the C5H5-C5H4 radical [20]. The only flow reactor study on the oxidation of cyclopentadiene was finally published in 2009 by Buttler and Glassman, who carried out some speciation measurements at 1150K both in pyrolytic and oxidative regime [21].

Taking advantage of these previous works, the two mechanisms developed by LLNL and Milano's groups have been updated and validated on the basis of the available experimental information. The mechanism has been then used to investigate the main reaction pathways and the most sensitive steps determining the combustion behavior of cyclopentadiene.

The kinetic mechanism of cyclopentadiene

A crucial aspect in the oxidation process of C5H6 is the high concentration level of the cyclopentadienyl radical, whose formation is favored because of its resonantly stabilized structure. Cyclopentadienyl is formed by the omolitic cleavage of the C-H bond (R1) and by abstraction reactions, which are highly selective on the secondary hydrogen site (R2-5):

Because of the abundance of the C5H5, when oxygen is not present, the main reaction pathways involve the radical recombination reactions. The reaction of C5H5+fuel plays a very important role in the formation of the first polycyclic species such as naphthalene (via dihydronaphtalene), indene, azulene and fulvalene [22].

	A	n	Ea [cal/mol]	
C5H6 = C5H5+H	1.00E+15	0.0	78000.0	R1
C5H6+H = C5H5+H2	1.60E+06	2.4	4471	R2
C5H6+O = C5H5+OH	6.03E+10	0.7	7633	R3
C5H6+OH = C5H5+H2O	4.12E+06	2	-298	R4
C5H6+HO2 = C5H5+H2O2	4.00E+12	0	15900	R5
C5H5+C5H5 = C10H10	1.00E+12	0	10000	R6
C5H6+C5H5 = INDENE+CH3	2.00E+12	0	20000	R7

The formation of benzene occurs mainly via ring enlargement through the addition of the methyl radical, dehydrogenation to fulvene and fast isomerization to the 6 membered ring configuration, as described in [19]. The HACA mechanism contributes to the formation and growth heavier species to form heavier soot precursors.

During the pyrolysis of cyclopentadiene the formation of linear species is observed too. Direct ring opening reactions are generally difficult (77000 kcal of activation energy) but small linear compounds can be formed via radical addition on the fuel molecule followed by the decomposition of the adduct. Methyl radicals are mainly formed by C5H5+fuel reactions followed by ring rearrangement and decomposition to indene and CH3 (R7).

When oxygen is present the degradation of the ring is still relatively slow and requires the rearrangement of the molecular structure to get the opening of the ring. The delocalization of the radical makes indeed the structure refractory to decomposition reactions. For this reason the concentration of cyclopentadienyl radical builds up into the reacting system making the growth of aromatic species, typical of pyrolytic conditions, competitive with the usual oxidation reactions.

The degradation of the ring structure generates linear unstable radicals that rapidly decompose and oxidize leading to the formation of H radicals that contribute to the chain branching.

The main reaction pathways of cyclopentadiene are shown in figure 1.

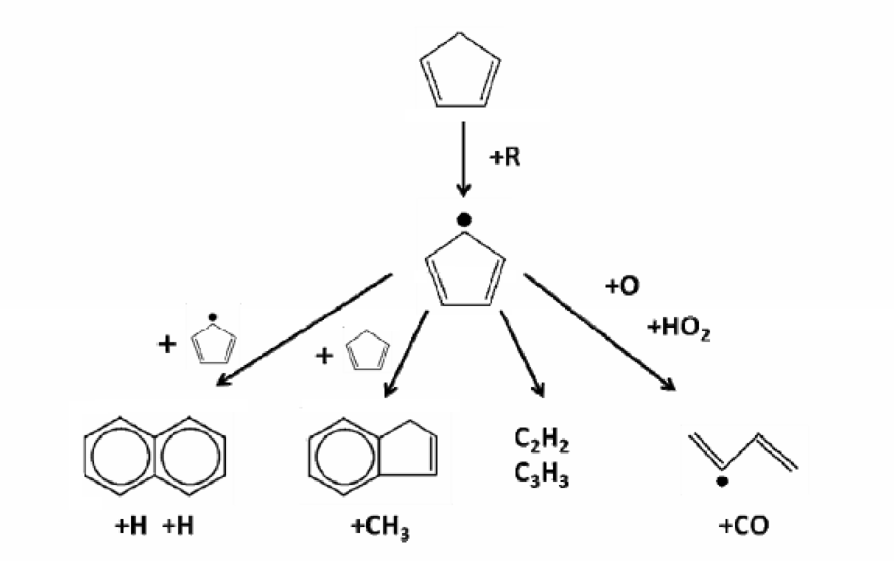

Fig. 1 - Cyclopentadiene main reaction pathways

The validation of the cyclopentadiene mechanism

The two models have been validated against different sets of experimental data. The most extensive experimental investigations were from Butler and Burcat, who provided respectively speciation data in the flow reactor and ignition delay times in the shock tube.

Butler tested the degradation of cyclopentadiene both in pyrolytic and oxidative conditions, measuring the main products and determining the main reaction routes.

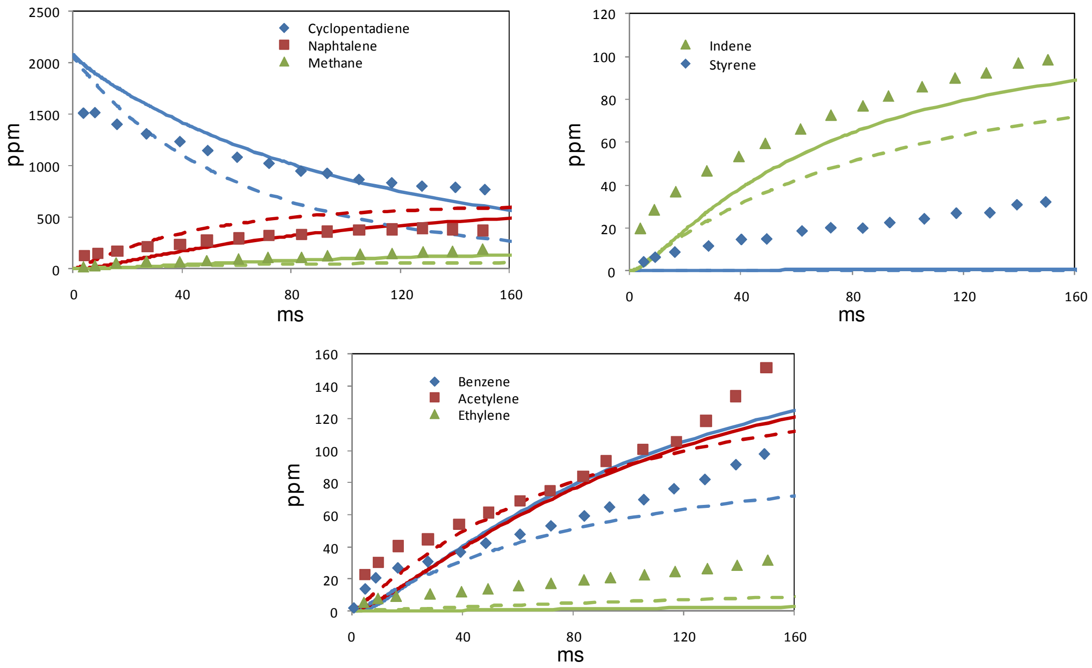

Fig. 2 – Pyrolysis of cyclopentadiene in a flow reactor at 1200K [21]: Symbols: data, Solid line: LLNL Mechanism, Dashed lines: PoliMi Mechanism.

Figure 2 shows models predictions against the experimental dat. Pyrolysis data suggest naphthalene to be the major product followed by methane, acetylene, benzene and indene.
As already mentioned, the recombination of cyclopentadienyl radicals is the main reaction pathway leading to the formation of naphthalene while indene and methane are mostly produced by the attack of the cyclopentadienyl radical on the fuel. Both the models do a fairly good job in reproducing all the main species even though Milano's mechanism tends to overestimate the conversion of the fuel.

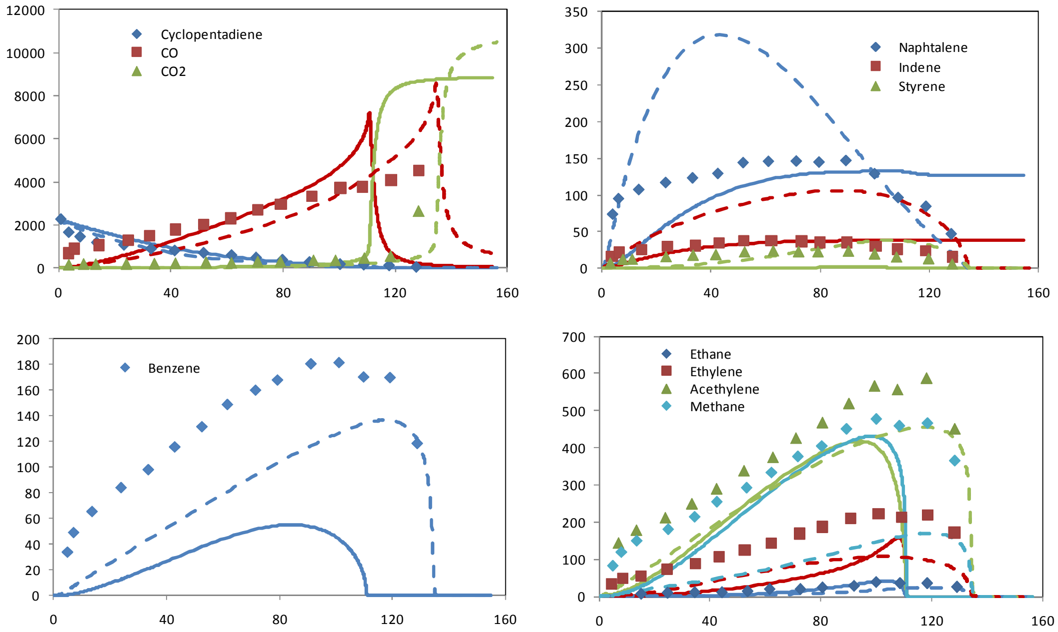

Fig. 3 – Oxidation of cyclopentadiene in a flow reactor at 1200K [21]: Symbols: data, Solid line: LLNL Mechanism, Dashed lines: PoliMi Mechanism.

The stoichiometric oxidation experiments showed in Figure 3 confirm the general validity of the models. In this case the reactivity is slightly overpredicted by the LLNL model that anticipates the ignition by about 10%. Acetylene, methane, ethylene, naphthalene and benzene are the main products. The mechanism by LLNL doesn't show the consumption of the heaviest species since it doesn't incorporate a full PAH chemistry. The absolute amount though is correctly reproduced. The predicted amount of benzene is lower than the experiments while all the other major species concentration profiles are correctly reproduced. PoliMi's predictions are more consistent with the data when it comes to benzene prediction and PAH profiles (the position of the peaks is correctly reproduced), but overestimates their absolute amount.
The model has been also validated against the ignition delay times collected by Burcat et al. [16] at different stoichiometries and fuel concentrations (figure 4). Both the models correctly reproduce the magnitude of the ignition delay times at about 1300K but, in the case of PoliMi's mechanism, the activation energy is overestimated. The LLNL mechanism consistently predicts the ignition delay times over the entire temperature window. Moreover both the models The effect of the air fuel ratio is correctly reproduced by both the model as well as the influence of the fuel concentration.

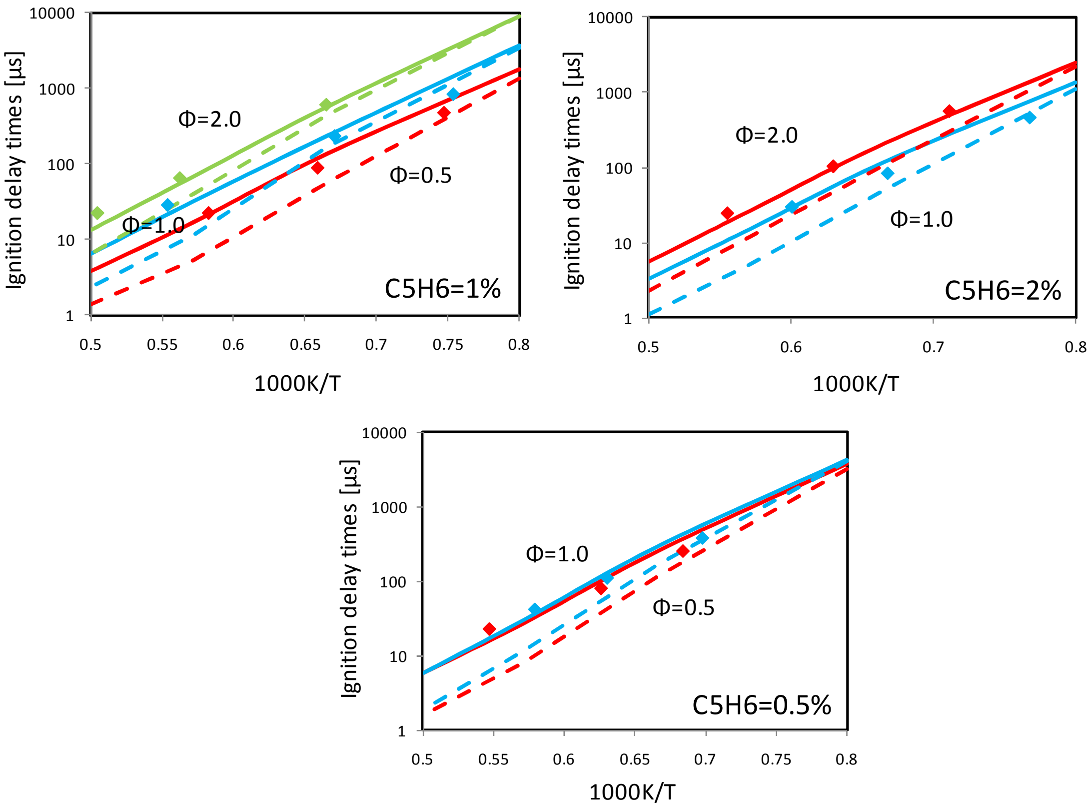

Fig. 4 – Ignition delay times of cyclopentadiene in a shock tube [16]: Symbols: experimental data, Solid line: LLNL Mechanism, Dashed lines: PoliMi Mechanism.

The combustion of benzene and phenol

Previous investigations on benzene and phenol oxidation

The first detailed studies specifically devoted to the combustion behavior of benzene are dated in the beginning of the 1980's when the structure of a near-soothing premixed benzene flame was investigated by Bittner and Howard [6]. About fifty species were identified and measured and a reaction mechanism was proposed to explain the formation of some of the major intermediates. In this early study the formation of the phenoxy radical followed by the elimination of CO to form cyclopentadienyl was identified as a fundamental step in the oxidation of the aromatic ring, consistently with previous works carried out in the 1970s [23-28]

In 1982, a high temperature investigation in a flow reactor of benzene, toluene and ethyl benzene was published by Venkat et al. [29], confirming the importance of the described steps. In a later work, Brezinsky [30] further developed the thesis expressed by Venkat et al. including several pathways leading to the formation of the phenoxy radical.

The first detailed mechanisms of the oxidation of C6H6 were developed by Bittker [15] and Emdee [3] who discussed the oxidation of benzene in the context of a detailed mechanism of toluene. Both the models are based on the previous qualitative mechanism by Brezinsky.

Other literature models are from Lindstedt and Skevis [32] and Zhang and McKinnon [33], Shandross et al. [34] and Richter et al. [35].

All these modeling attempts were mostly focused on the high temperature reactivity of the aromatics with particular regard to the issue of soot formation in flames. Meanwhile

Brezinsky et al. [36], aware of the importance of the oxidation of the phenoxy radical, investigated the pyrolysis and oxidation of phenol in a flow reactor over a wide range of air-fuel ratios. This work provided fundamental information necessary to better assess the oxidation kinetics of aromatic compounds.

In the last decade, few modeling attempts are attested shifting the interest from the high temperature window to milder conditions in continuous reactors. Alzueta [37] and Schöbel-Ostertag [38] performed both experimental and numerical investigations using flow reactors, while Ristori [39] and Da Costa [40] adopted a stirred reactor configuration.

A final consideration involves the more recent fundamental investigations by ab initio calculations. Starting from the year 2000, several studies attempted to identify some of the most relevant reaction pathways to aromatic oxidation and to provide more precise reference values. Among these works figure those on the C6H6+O system [41-42], C6H5+O2 [43-44]

The oxidation mechanism of benzene and phenol

The oxidation of benzene is strictly connected with the degradation and oxidation processes of phenol. For this reason, the oxidation of benzene will be analyzed starting from the pyrolysis of C6H5OH followed by phenol oxidation and, finally, by benzene combustion.

The first steps in the pyrolysis of phenol are the initiation reactions leading to the formation of phenoxy and H radicals. The formation of phenoxy radical is favored by its aromatic resonance and its concentration is thermodynamically controlled. The decomposition of the phenoxy radicals lead, as mentioned before, to the formation of CO and cyclopentadienyl. The ring opening of the C5 cyclic structure is the main source of acetylene end other aliphatic products. The decomposition to linear fragments is an important branching step leading to H radical formation. Those H radicals are partially consumed by abstraction reactions on the easily attackable phenoxyl H and by termination with the resonant stabilized radicals. The phenoxy radical strongly reduces the reactivity of the aromatic ring.

When oxygen is present, the bimolecular initiation by O_2 (abstraction on the hydroxyl H) gets more important.

The resonance in the phenoxy radical allows the radical site to move on the ring and to react with atomic oxygen and HO2 to form 1,4-benzoquinone plus H. The attack of reactive radicals on this oxygenated species represents an alternative way to break the aromatic ring.

The initiation reaction of benzene leads to the formation of the phenyl radical. The decomposition of this aromatic structure is inhibited by the presence of double bonds in the ring. As mentioned in the beginning of the paragraph when oxygen and oxygenated radicals are present, they easily recombine with the phenyl radical generating phenoxy radicals (R8-9). Another important source of phenoxy radicals is the O addition on the ring followed by H depletion (R10).

	A	n	Ea [cal/mol]	
C6H5+O2= C6H5O+O	8.21E+41	-7.74	27770	R8
C6H5+HO2= C6H5O+OH	3.00E+13	0	0	R9
C6H6+O=C6H5O+H	2.48E+14	-0.34	4674	R10

Once the addition of O atom the ring happens, the main reaction pathways are analogous to phenol’s ones.

Figure 5 summarizes some of the most relevant reaction pathways to the oxidation of benzene.

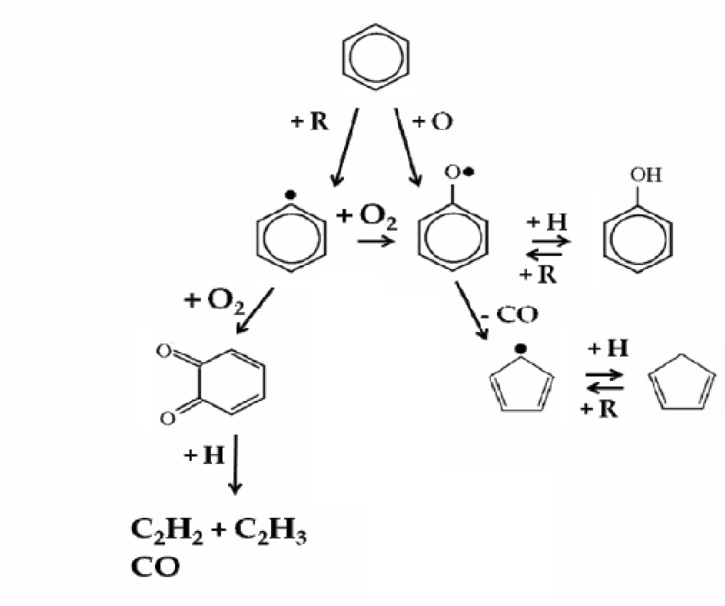

Fig 5. – Main reaction pathways involved in benzene oxidation

The validation of the C6 ring oxidation mechanism

As well as cyclopentadiene submechanism, the pyrolysis and oxidation mechanism of benzene and phenol was validated in a wide range of experimental conditions.

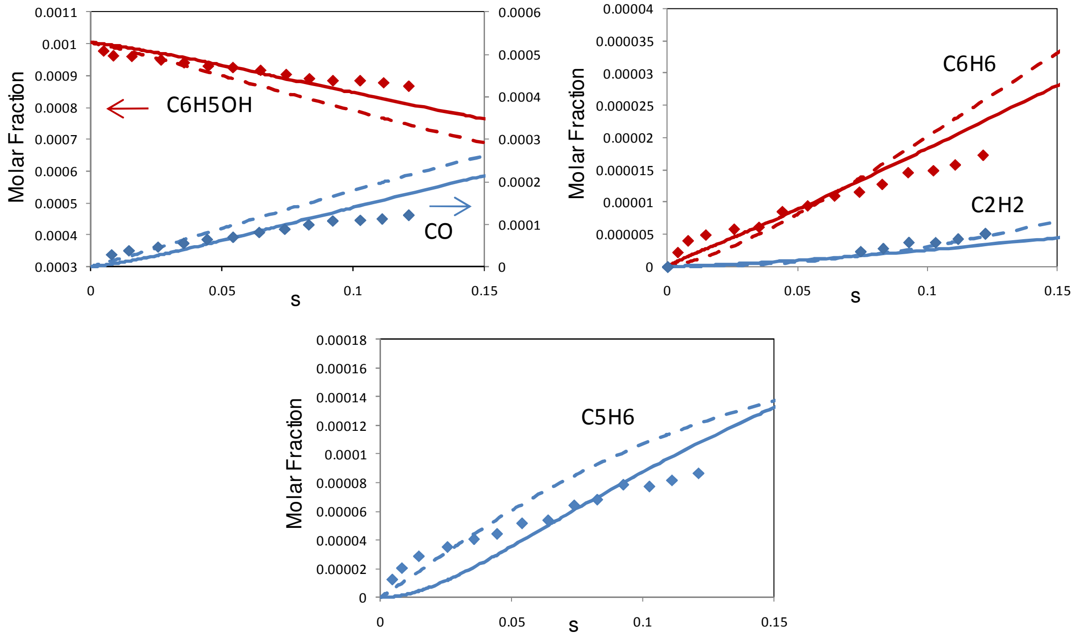

Fig. 6 – Pyrolysis of phenol in a plug flow reactor at 1173K, 1 atm

Figure 6 reports the pyrolysis of phenol in the Princeton atmospheric flow reactor. Both the LLNL and the PoliMi mechanisms correctly reproduce the consumption of C6H5OH, even though PoliMi's mechanism tends to overpredict the decay of the fuel. The main products, CO, C6H6 C2H2 ad cyclopentadiene are correctly reproduced.

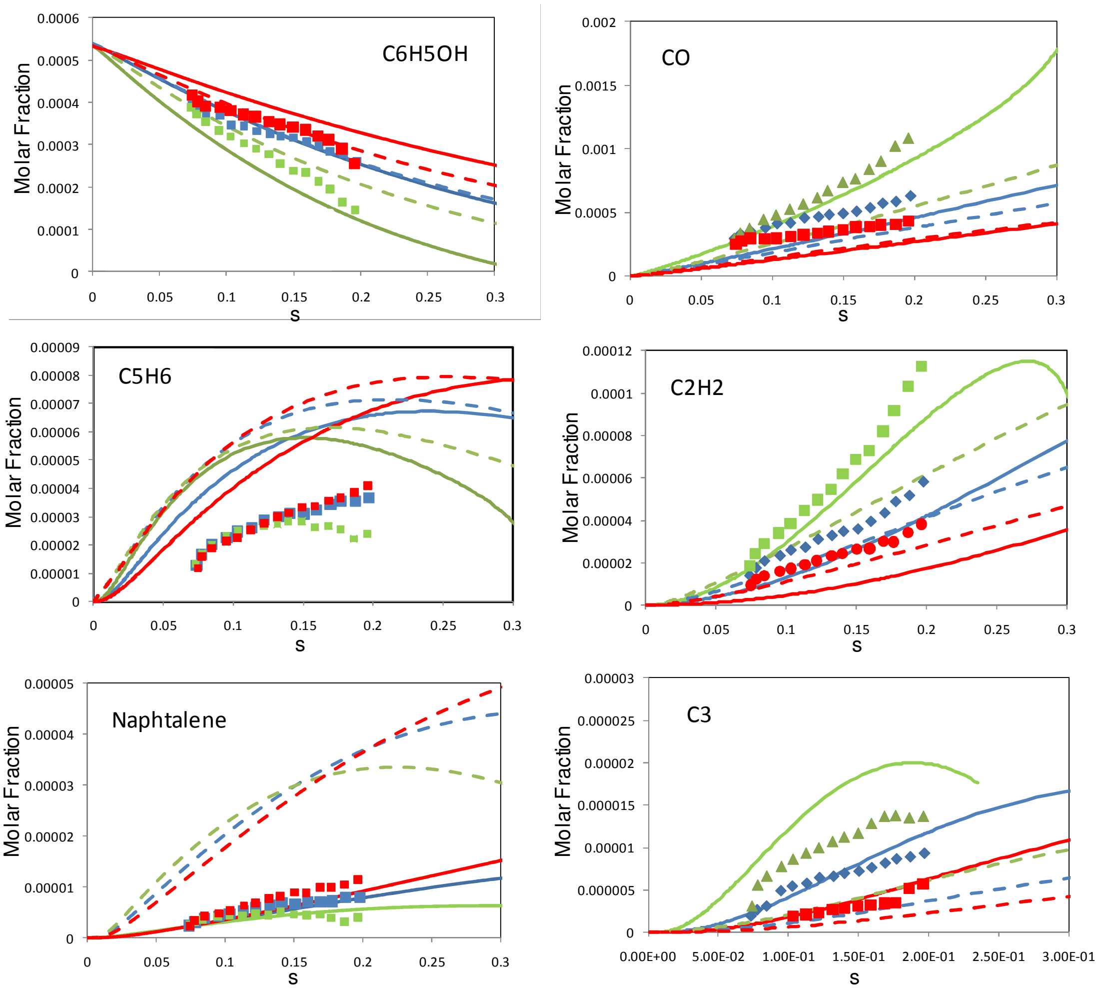

Fig. 7 – Oxidation of phenol at 1170K, 1 atm and different stoichiometries. Blue $\Phi=1$; Red $\Phi=1.73$, Green $\Phi=0.64$. Solid lines refer to the LLNL mechanism, dashed ones to the PoliMi mechanism

The comparisons shown in figure 7 refer to the oxidation of phenol at different stoichiometries. Once again both the models successfully predict the main oxidation intermediates. The cyclopentadiene concentration is overpredicted by almost a factor two. That suggests the existence of an alternative pathway to the degradation of the C6H5O radical to cyclopentadienyl plus CO. The LLNL mechanism better reproduces the amount of naphthalene consistently, as was also shown in figure 3 for the cyclopentadiene oxidation experiments.

A similar set of experiments was used in the validation of benzene mechanism. The results are qualitatively similar to the one of phenol, but in this case the amount of C5H6 is better reproduced by both the mechanisms.

Other sets of data collected in continuous stirred reactors have been considered, but the results are omitted here by reason of space. The results are consistent with what shown for the flow reactor configuration.

A last set of data here considered refers to benzene ignition delays measured in a shock tube at different stoichiometries.

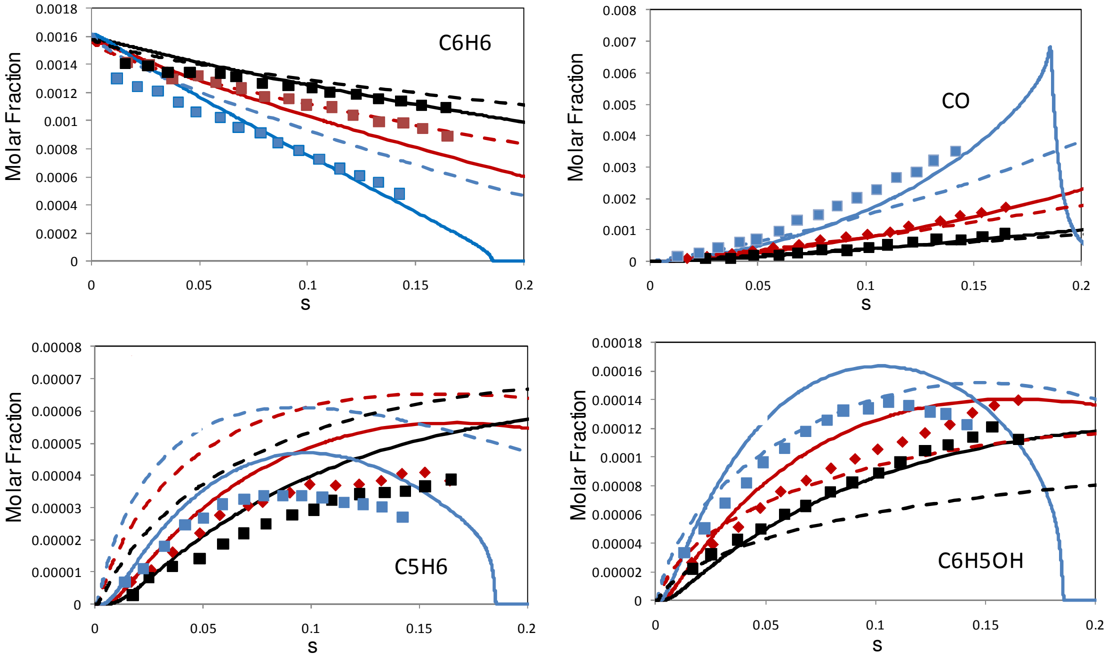

Fig. 8 - Benzene oxidation in a plug flow reactor at 1100K, 1 atm [31] at different stoichiometries. Red: Φ=1, Black: Φ=1.36, Blue: Φ=0.76. Solid lines correspond to the LLNL mechanism, dashed lines to the PoliMi mechanism

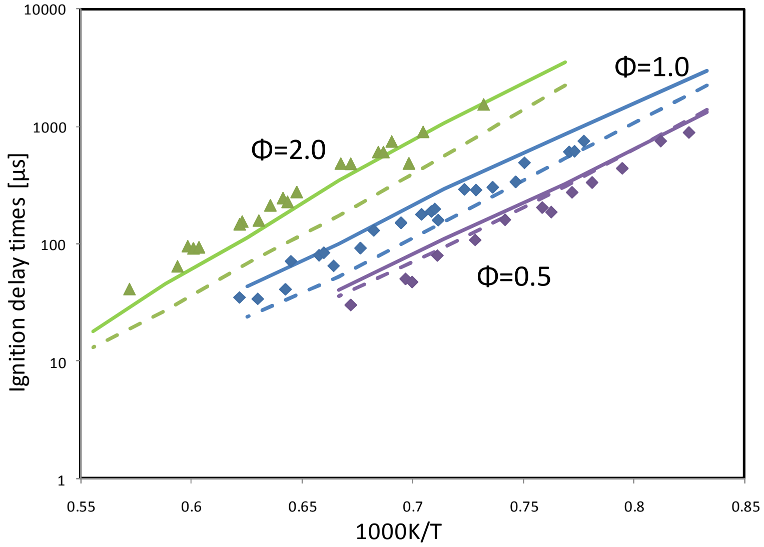

Fig. 9 – Experimental and calculated ignition delay times of benzene in Ar at different stoichiometry at 2 atm [45]. Solid lines: LLNL, Dashed lines: PoliMi

Figure 7 reports the ignition delay times of benzene at lean, stoichiometric and rich conditions in a temperature window spanning from 1200K and 1800K .
Both the models perform satisfactorily with the PoliMi mechanism showing a bit prompter reactivity.

The combustion of toluene

Previous works on the combustion of toluene

The first two detailed mechanism of the oxidation of toluene were developed in the ’90 by Emdee et al [3] and Lindsteadt et al.[32]. Both the models were validated at high temperature only. A great interest was devoted to toluene in the past decade and these first attempts were followed by several improvements by Brezinsky himself and other authors that based their mechanism on his original work. In 2000 a work by Robaud et al. [46] analyzed the ignition behavior of several substituted aromatic species in a rapid compression machine. Toluene was among them. Similarly in 2001Cadman [47] studied the ignition of toluene sprays in as shock tube. One year later a new mechanism by Dagaut et al. [48] was published together with some new experimental data collected in an atmospheric jet stirred reactor. In 2003 Ellis et al. [49] investigated the slow oxidation of toluene in the low temperature region in a batch reactor mixing the fuel with hydrogen and oxygen. This approach allowed to better identify the role of some specific reactions such as the abstraction on the benzyl site by H radicals. A later modeling study by Bounaceur et al. [50] provided also new data new data in a stirred reactor in a temperature spanning from 872K to 923K with contact times of several seconds.

In the same period several shock tube data were also published. Sivararnakrishnan et al. [5] studied the oxidation of toluene at very high pressure (>500bar) while the Stanford group performed various experiments investigating the ignition delay times of toluene at in a wide range of pressures and the concentration profiles of some species of interest such as benzyl and OH [51-54]. The capability of measuring species concentration allowed the authors to use shock tube data to investigate specific reactions in order to identify more precise reaction rates. In 2007 a new semidetailed mechanism was produced by Andrae et al. [55]. That model was mainly aimed to the prediction of autoignition of alkanes and toluene mixture in engine like conditions.

The oxidation mechanism of toluene

Toluene reactivity is characterized by the formation of the benzyl radical. The omolitic cleavage of the C-H benzylic bond requires less than 90 kcal/mol and abstraction reaction are highly selective on the methyl H, especially at relatively low temperatures (R12-17). The bimolecular initiation reaction with oxygen is extremely important at low temperature (R13).

Because of the high concentration reached by the C6H5CH2 radical, termination reactions play also an important role in reducing the reactivity of the systems rich in fuel. The most relevant are C6H5CH2+ C6H5CH2 and C6H5CH2+CH3 (R18-19).

The oxidation of the side chain occurs mostly through the interaction of the benzyl radical with HO2 and O radicals producing of benzaldehyde and active radicals such as OH and H. Benzalehyde easily undergoes abstraction reactions because of the weak acylic H and decomposes to CO and phenyl radicals (R20), whose oxidation processes were already discussed.

An alternative oxidation pathway involves the attack on the ring. A highly reactive OH radical can abstract a phenyl H and form a methylphenyl radicals. Analogously to phenyl radicals these species can react with oxygen or oxygenated species and radicals to form a methyl phenoxy radical. Another important route for the formation of methyl phenoxy radicals is the O addition on the ring followed by H depletion (R21).

	A	n	Ea [cal/mol]

C6H5CH3=C6H5CH2+H	2.09E+15	0	87463.4	R12
C6H5CH3+O2=C6H5CH2+HO2	2.18E+07	2.5	46045	R13
C6H5CH3+H=C6H5CH2+H2	6.47E+00	3.98	3384	R14
C6H5CH3+O=C6H5CH2+OH	6.00E+10	0.7	7632	R15
C6H5CH3+OH=C6H5CH2+H2O	1.77E+05	2.394	-601.8	R16
C6H5CH3+HO2=C6H5CH2+H2O2	7.00E+02	3	12000	R17
C6H5CH2J+CH3=C6H5C2H5	1.20E+13	0	200	R18
C6H5CH2J+C6H5CH2J=C14H14	5.00E+12	0	454	R19
C6H5CJO=C6H5+CO	1.37E+21	-2.179	39400	R20
C6H5CH3+O=OC6H4CH3+H	2.48E+14	-0.34	4674	R21
C6H5CH3+H=C6H6+CH3	1.30E+06	2	943	R22
C6H5CH3+OH=C6H5OH+CH3	7.83E+02	2.884	3219.3	R23

The formation of the cresoxy radical ends up in the elimination of CO, the formation of smaller cyclic radicals and finally ring opening with the formation of aliphatic species.

The abstraction reactions forming the benzyl radical deactivate the system because of the low reactivity of the resonantly stabilized radical, the attacks on the ring, on the contrary are important branching sources since they lead to the formation of H and O radicals that drive the reactivity.

Other relevant pathways involve the substitution of the methyl function by H and OH radicals, resulting in benzene and phenol (R22-23).

The main reaction pathways are summarized in figure 10.

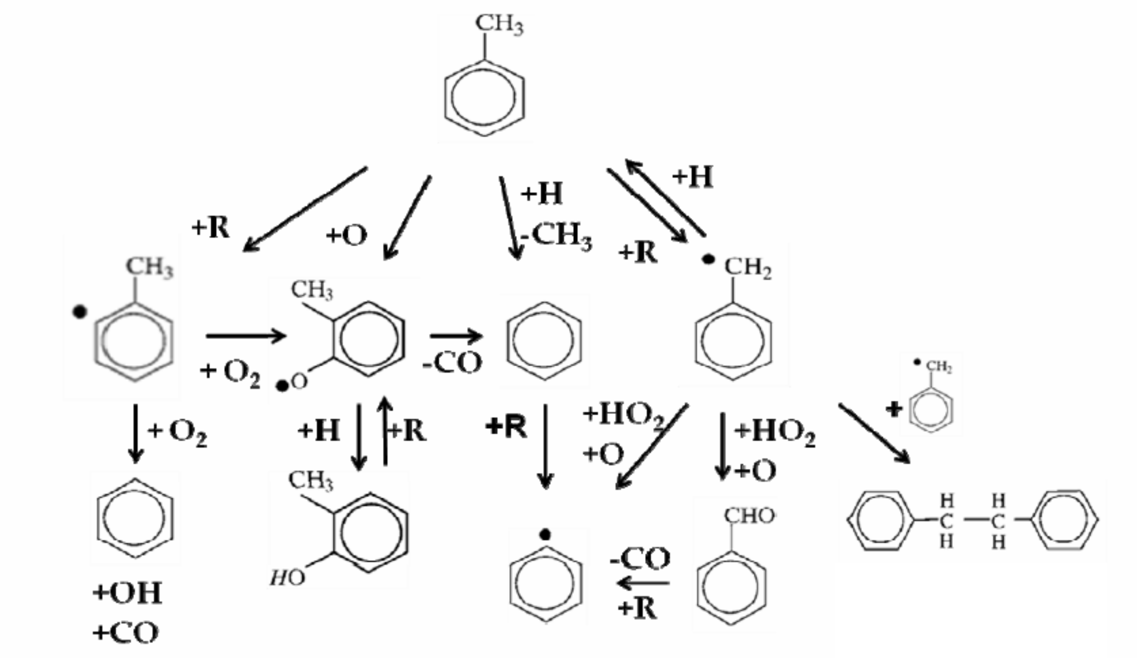

Fig. 10 - Toluene main reaction pathways

The validation of the toluene mechanism

The mechanism of toluene has been validated on a wide range of data including pyrolysis condition, flow reactor data, jet stirred reactor data and shock tube data.

The first set of comparisons here presented refers to the pyrolysis of toluene in a shock tube at different temperatures [56] (Figure 11).

Both the mechanisms show good agreement with the experimental fuel consumption. The main species are correctly reproduced as well even though the LLNL mechanism tends to underpredict the amount of methane and to overpredict the C6H6 concentration. The PoliMi mechanism performs generally better in determining the decomposition products of the fuel even if the reactivity is the same for the two mechanisms

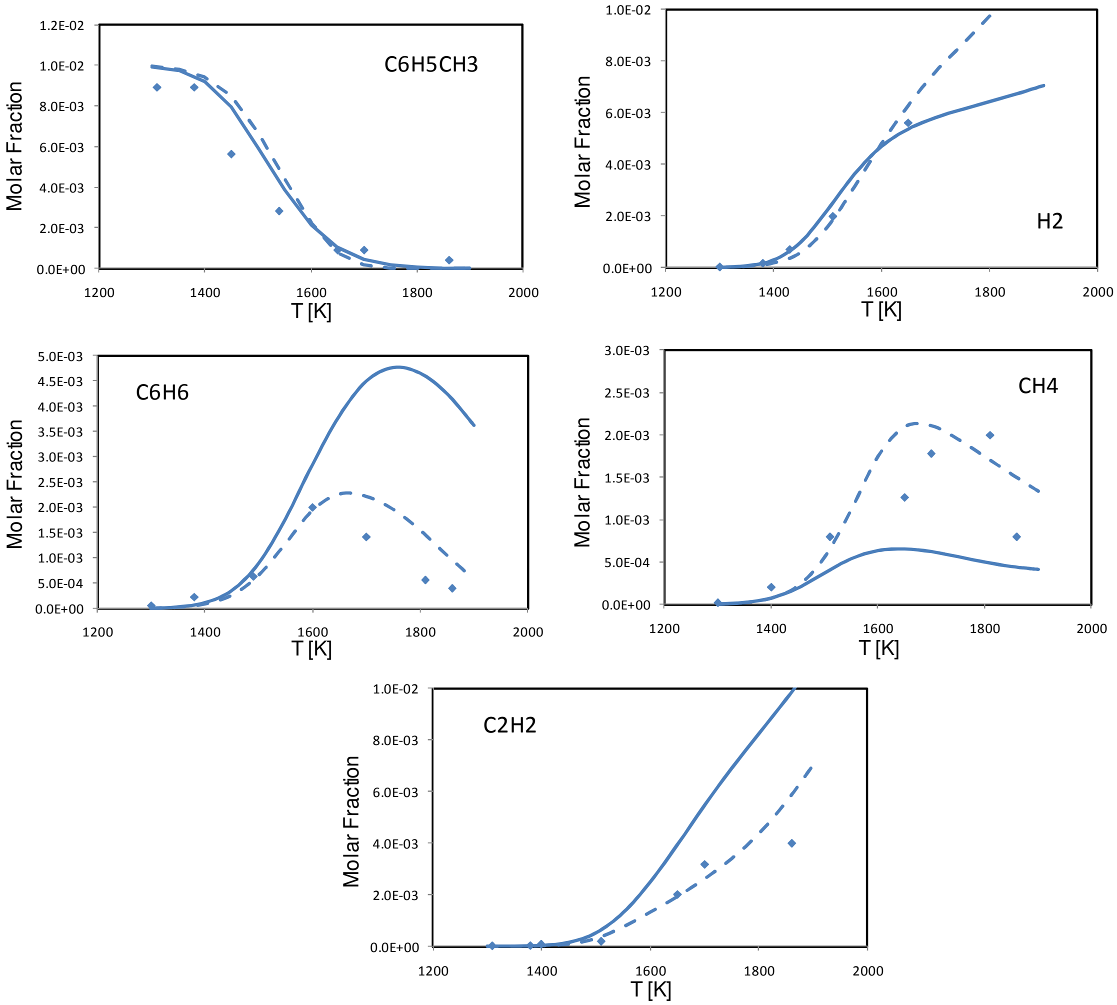

Fig. 11 – Concentration profiles obtained in a shock tube at 10 atm. toluene(1% mol.)-argon(99%mol. [56]) Solid line: LLNL, Dashed line: PoliMi

A second set of comparisons refers to the formation of the benzyl radicals (Figure 12). Also in this case the data were collected in a shock tube and the effect of the temperature and the fuel concentration are considered.The LLNL mechanism correctly reproduces the radical concentration profiles in most of the cases, especially at lower temperatures and lower fuel concentration. The PoliMi mechanism tends to under predict the concentration of C6H5CH2 but correctly reproduces the experimental trends. It's interesting to note the discrepancy at the highest temperature an highest fuel concentration, where both the model predict a flat profile for the longest contact time where the experiments show a steady increase.

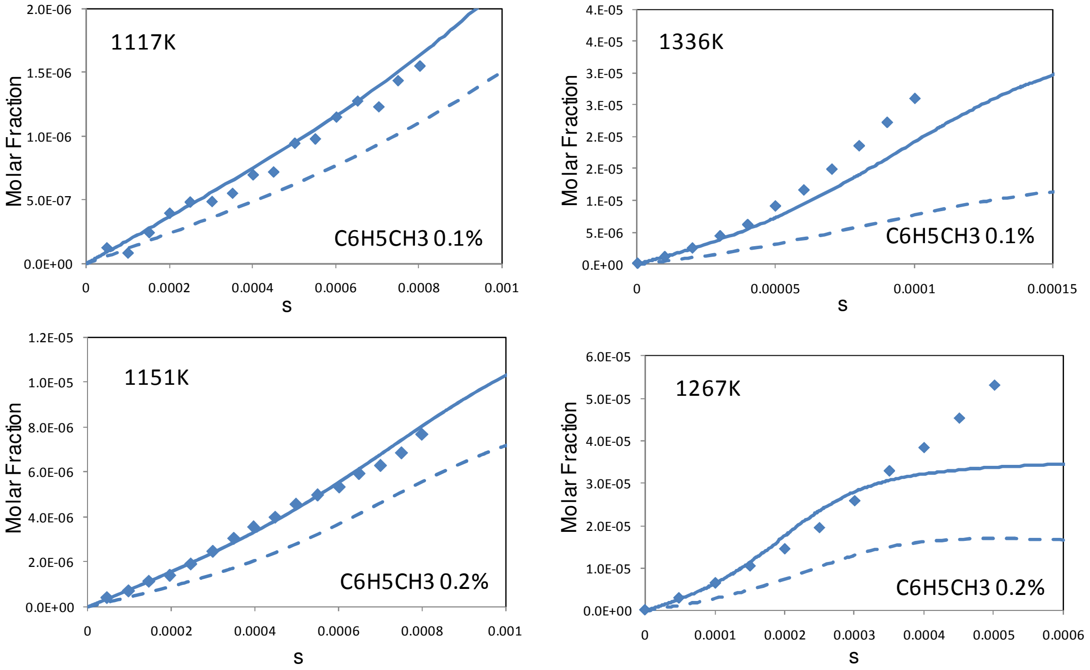

Fig. 12 - Benzyl concentration profiles in a shock tube: toluene in O2/Ar, 1.8 atm [53]

The concentration profiles of the main product intermediates have been also validated in comparison with flow reactor data. Figure 13 shows the species profiles measured in the Princeton flow reactor at different stoichiometries.

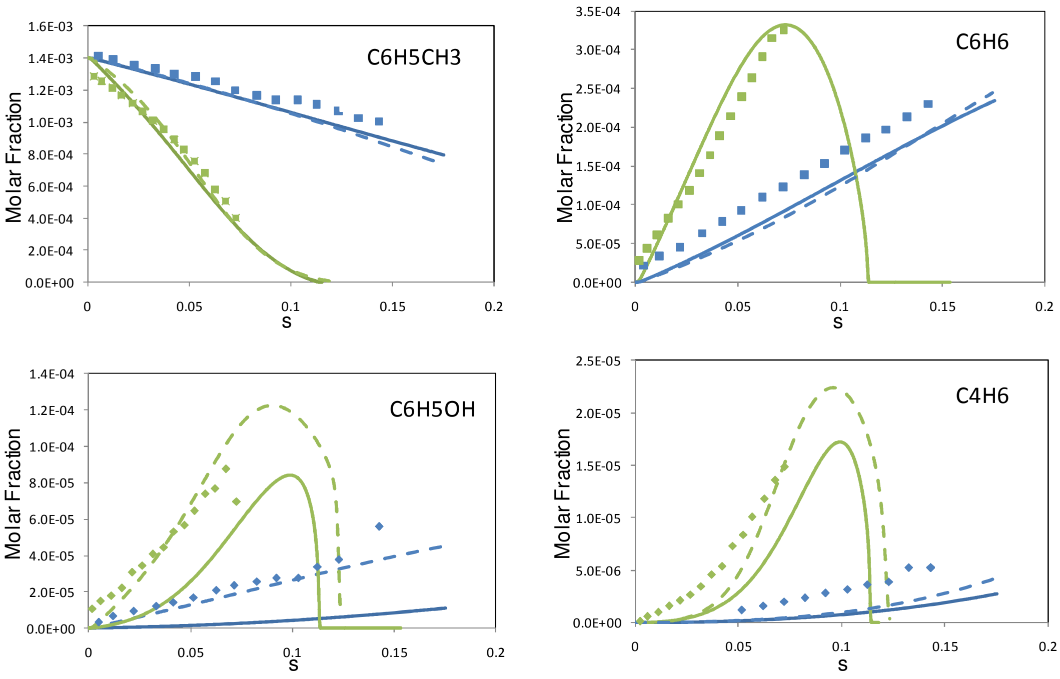

Fig. 13- Toluene oxidation in an atmospheric flow reactor at 1180K and different stoichiometries Blue: Φ=1, Green Φ=0.63. Solid lines: LLNL, Dashed lines: PoliMi

The two model are in good agreement with the experimental data. The PoliMi mechanism performs slightly better than the LLNL one. The fuel conversion profiles are almost coincident but the PoliMi mechanism shows a prompter formation of some of the secondary products (e.g. C_4H_6). This might be related to the different level of detail included in the mechanism. The same global reaction pathways involve a greater number of steps in the LLNL mechanism, therefore a too slow step in the reaction chain is likely to act as a rate determining step for the chain reaction propagation. The qualitative agreement is anyway quite satisfactory.

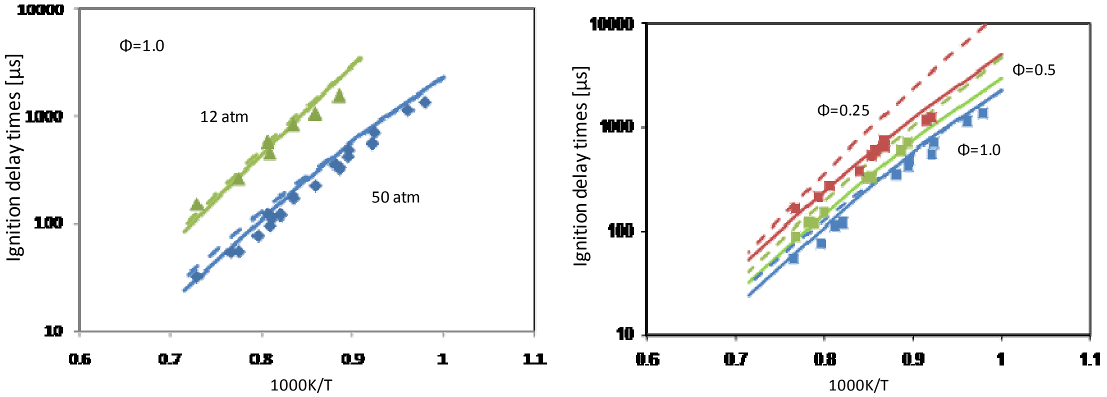

Fig. 14 – Ignition delay times of toluene in air at different pressure and different stoichiometry [57]. Solid lines: LLNL, Dashed lines: PoliMi

A last set of data here presented refers to the ignition delay times of toluene at different pressures and stoichiometries in a shock tube (Fig 14) [57]. The pressure conditions here considered are representative of the typical engine conditions (12-50 atm). The models correctly predict the ignition delay times at phi=1 with a good accuracy. The effect of the stoichiometry is well reproduced too, in particular by the LLNL mechanism..

Conclusions

In this work, the combustion pathways of toluene are discussed focusing on the main intermediates formed during its oxidation. Two different kinetic models have been developed trough a joined effort: a detailed one (LLNL) and a semidetailed one (PoliMi). Both the models are capable of reproducing the main features of the combustion of the fuels of interests, both in terms of general reactivity and in terms of species profiles. Though the main interest of the mechanism relies in toluene combustion behaviour, the extensive validations on the cyclopentadiene, benzene and phenol chemistry represented a fundamental step in building a more reliable subset of reactions for toluene. This work clearly showed how the hierarchical approach to the development of kinetic scheme is necessary prerequisite for the development of general reaction mechanisms. The present results, though generally satisfactory, still require further investigation to improve the predictivity of the toluene mechanism. The LLNL mechanism in particular needs some more improvement in the area of the pyrolysis of toluene. One more critical aspect is the correct balance between the benzyl site reaction and the ring attacks leading to chain branching. Recent fundamental works are providing a deeper insight into some of the primary reaction governing these steps.

During this work significant steps forward have been done, future work will refine the presented results.

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References

[1] G. Shibata and T. Urushihara, Society of Automotive Engineers, SAE 2008-01-0007 (2008).
[2] K. Brezinsky, T. A. Litzinger, I. Glassman, International Journal Of Chemical Kinetics, 16, 9 (1984)1053–1074
[3] J.L. Emdee, K. Brezinsky, I. Glassman, J. Phys. Chem. 96 (1992) 2151–2161.
[4] S.D. Klotz, K. Brezinsky, I. Glassman, Proc. Combust. Inst. 27 (1998) 337–344.
[5] Sivararnakrishnan, R; Tranter, RS; Brezinsky, K, Comb. & Flame, 139, 4 (2004) 340-350
[6] Bittner, J. D.; Howard, J. B. Eighteenth Symposium (International) On Combustion; (1980); 1105.
[7] Davis, S. G.; Wang, H.; Brezinsky, I.; Law, C. K. Twenty-Sixth Symposium International) On Combustion;.
[8] Lindstedt, R. P.; Maurice, L. Q. Combust. Sci. Technol. 120 (1996) 119.
[9] H. Wang, K. Brezinski, J. Phys. Chem. A 102 (1998) 1530-1541
[10] Zhong, X; Bozzelli, JW, Journal Of Physical Chemistry A, 10, 20 (1998) 3537-3555
[11] Serkauskas, R.V.; Frenklach, M.; Wang, H.; Bowman, C. T.; Smith, G. P.; Golden, D. M.; Gardiner, W. C.; Lissianski, V. An Optimized Detailed Chemical Mechanism For Methane Combustion; Gas Research Institute Topical Report, 1994. Gri Mech 1.1 Available By Ftp From Crvax.Sri.Com Or From Lioness.Cm.Utexas.Edu/Pub/Grl.
[12] Pitz, W. J.; Westbrook, C. K.; Proscia, W. M.; Dryer, F. L. Twentieth Symposium (International) On Combustion (1984) 831–843.
[13] Westbrook, C. K.; Pitz, W. J.; Thornton, M. M. Malte Combust Flame 72 (1988)45–62.
[14] Frenklach, M.; Clary, D. W.; Yuan, T.; Gardiner, W. C.; Stein, S. E. Combust Sci Techn, 50 (1986) 79–115.
[15] Bittker, D. A. Combust Sci Techn 79 (1991) 49–72.
[16] Burcat A., Dvinyaninov M., int J. Chem. Kinet., 29 (1997) 505-514
[17] Lindstedt, Rp; Rizos, Ka, Proceedings Of The Combustion Institute, 29,(2002) 2291-2298
[18] Lifshitz, A.; Tamburu, C.; Suslensky, A., Et Al., Proceedings Of The Combustion Institute 30 (2004) 1039-47
[19] W. Sean Mcgivern, Jeffrey A. Manion, And Wing Tsang, J. Phys. Chem. A 110, 47 (2006) 12822–12831
[20] Kislov, Vv; Mebel, Am, Journal Of Physical Chemistry A, 111(2007) 9532-9543
[21] Butler, Rg; Glassman, I, Proceedings Of The Combustion Institute, 32 (2009) 395-402
[22] V. V. Kislov and A. M. Mebel, , J. Phys. Chem. A, 112, 4 (2008,) 700–716
[23] Slemr, F. And Warneck, P.: Ber. Bunsenge. Phys. Chem. 79 (1975) 152
[24] Kanofsky, J. R., Lucas, D., Pbuss, F. And Gutman, D.: J. Phys. Chem. 78 (1974) 311
[25] Wagner, H. Gg. And Zellner, R.: Ber. Bunsenges. Phys. Chem. 76(1972) 518
[26] Homann, K. H., Schwanebeck, W. And Warnatz, J.: Ber. Bunsenges. Phys. Chem. 79 (1975) 536
[27] Niki, H. And Weinstoek, B.: J. Chem. Phys. 45 (1966). 3468
[28] Homann, K. H., Warnatz, J. And Wellman, C.: Sixteenth Symposium (International) On Combustion (1977) 853

[29] Venkat, C., Brezinsky, K., And Glassman, I., Nineteenth Symposium (International) On Combustion (1982) 143.
[30] Brezinsky, K. Prog. Energy Combust. Sci. 17(1986) 1.
[31] A.B. Lovell, K. Brezinsky And I. Glassman, Proc Combust Inst 22 (1988)1063–1074
[32] R.P. Lindstedt And G. Skevis, Detailed, Combust Flame 99 (1994) 551–561
[33] Zhang, Hy; Mckinnon, Jt, Combustion Science And Technology, 107, 4-6 (1995) 261-300
[34] R.A. Shandross, J.P. Logwell And J.B. Howard, Proc Combust Inst 26 (1996) 711–719.
[35] H. Richter, T.G. Benish, O.A. Mazyar, W.H. Green And J.B. Howard, Proc Combust Inst 28 (2000) 2609–2618.
[36] Brezinsky, K; Pecullan, M; Glassman, I, Journal Of Physical Chemistry A, 102, 44 (1998) 8614-8619
[37] Alzueta, Mu; Glarborg, P; Dam-Johansen, K, International Journal Of Chemical Kinetics, 32, 8 (2000) 498-522
[38] Schobel-Ostertag A, Braun-Unkhoff M, Wahl C, Krebs L, Combustion And Flame, 140, 4 (2005) 359-370
[39] Ristori, A; Dagaut, P; El Bakali, A, Et Al., Combustion Science And Technology, 167 (2001) 223-256
[40] Da Costa I, Fournet R, Billaud F, Battin-Leclerc F, International Journal Of Chemical Kinetics, 35, 10 (2003) 503-524
[41] Devin Hodgson, Hai-Yue Zhang, Mark R. Nimlos, And J. Thomas McKinnon, Journal Of Physical Chemistry A, 105, 17 (2001) 4316-4327
[42] Lam Nguyen, T.; Peeters, J.; Vereecken, L. Journal Of Physical Chemistry A, (2007) 3836-49
[43] Sebbar, N; Bockhorn, H; Bozzelli, J,International Journal Of Chemical Kinetics, 40, 9 (2008) 583-604
[44] Merle John K. ; Hadad Christopher M. The Journal Of Physical Chemistry. A, 108, 40 (2004) 8419-8433
[45] Burcat A., Snyder C., Brabbs T., "Ignition Delay Times of Benzene and Toluene with Oxygen in Argon Mixtures", NASA Technical Memorandum 87312, (1986)
[46] Roubaud, R. Minetti and L. R. Sochet, Combustion and Flame, 121, 3 (2000) 535-541
[47] Cadman, P, Physical Chemistry Chemical Physics, 3, 19 (2001) 4301-4309
[48] Dagaut, P; Pengloan, G; Ristori, A, Physical Chemistry Chemical Physics 4, 10 (2002) 1846-1854
[49] Ellis, C; Scott, MS; Walker, RW, Combustion And Flame, 132, 3(2003) 291-304.
[50] R. Bounaceur, I. Da Costa, R. Fournet, F. Billaud, F. Battin-Leclerc, International Journal Of Chemical Kinetics, 37, 1 (2005) 25-49
[51] Vasudevan, V; Davidson, DF; Hanson, RK, Conference Information: 30th International Symposium on Combustion, Proceedings Of The Combustion Institute, (2005) 1155-1163
[52] Oehlschlaeger, MA; Davidson, DF; Hanson, RK Source: Journal Of Physical Chemistry A, 110, 32 (2006) 9867-9873
[53] Oehlschlaeger, MA; Davidson, DF; Hanson, RK, Combustion And Flame, 147, 3 (2006) 195-208
[54] Oehlschlaeger, MA; Davidson, DF; Hanson, RK, Proceedings Of The Combustion Institute, 31 (2007) 211-219

[55] Andrae, JCG; Bjornbom, P; Cracknell, RF, Kalghatgi GT, Combustion And Flame, 149, 1-2 (2007) 2-24
[56] Colket M.B., Seery D.J., Twenty-Fifth Symposium (international) on Combustion, (1994) 883-891

[57] Shen H.P.S., Vanderover J., Oehlschlaeger M.A., Proceedings of the Combustion Institute (2009)