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1. INTRODUCTION

Lignin is an under-utilized major component of lignocellulosic biomass, which has the potential to be an important resource for renewable fuels. Due to the nature of lignin, depolymerization produces a large number of phenolic components. [1] In a recent presentation at the 15th international conference on Combustion Technologies for a clean environment [2], Meziane and coworkers presented laminar burning velocity (LBV) measurements for phenol and the cresol isomers together with a newly developed kinetic model called Colibri, which was assembled from validated sub-mechanism from the literature. The prediction underestimated the LBV for all four species, indicating that the current knowledge of the combustion of these phenolic species needs to be improved. Furthermore, the model treat cresol as a lumped species, hence does not provide any reactivity differentiation among the three isomers. On the other hand, the LBV results clearly showed notable differences among these isomers. While an early experimental and modelling study [3] on phenol pyrolysis and oxidation suggested that similar pathways would be operational, a recent theoretical study on phenol by Pratali Maffei et al. [4] indicate that in oxidation the role of aryl radicals formed through H abstraction from the aromatic ring should be more important than previously thought.

The current study has multiple objectives. First, to replace rate expressions for “lumped” cresol in the current version of the Colibri model with cresol isomers specific reactions and rate expressions. Second, additional chemistry relevant to the aryl radicals of phenol and cresol will be added. Finally, the updated kinetic model will be applied to the LBV experiments to test, if the modifications lead to improvements of the predictions in terms of quantitative LBVs and the relative differences seen for the four fuels.

2. MATERIALS AND METHODS

The newly developed rate expressions are calculated with the Gaussian G16 software using the CBS-QB3 and G4 levels of theory. The methodology has been described in various previous studies [5] and are only briefly summarized here. Electronic energies for the lowest energy conformers are converted with the atomization method to enthalpies of formation. Thermal enthalpy contributions, entropies, and heat capacities were calculated with methods from statistical mechanics using the harmonic oscillator-rigid rotor assumption except for internal rotations which are separately evaluated as one-dimensional internal rotors with effective rotational constants. These internal rotor potentials also help to identify the lowest energy structure. Thermodynamic data for reactants, products and transition states are stored as NASA polynomials. Transition state (TST) calculations using these polynomial expressions yield high pressure limited rate expressions. Tunnelling contributions are accounted for using Eckart asymmetric potentials. At this stage, the TST results are directly implemented in the kinetic model to identify if the newly added reactions are important. If so, the pressure-dependence of these reactions will be taken into account in a later stage. O₂ addition reactions to aryl radicals proceed without barrier. For these reactions, a temperature-independent rate coefficient of 2E13 cm³mol⁻¹s⁻¹ was assumed for the forward reaction while that of the reverse reaction was calculated based on the thermodynamic data.

3. RESULTS

H abstraction reactions from the phenolic or benzylic sites are energetically strongly favoured. For OH as abstracting radical, the abstraction of an aryl hydrogen is also exothermic, hence these reactions are potentially important [4]. The formed aryl radicals may be divided into two types: one in which the radical



site is located next to a OH or CH₃ substituted carbon and the second one which contains isolated aryl radicals. Peroxy radicals in vicinity of a HO or CH₃ group may abstract internally an H atom from this group leading to OH elimination and the formation of a quinone methide. On the other hand, aromatic peroxy radical isolated from other substituents proceed to form CO₂ and a substituted cyclopentadiene (later easily releases a H atom and thus keeps the chain propagation alive). Since o-, m- and p-cresol form progressively less isolated aryl radicals and peroxy radicals, this might explain the observed differences in LBVs. The poster will present the modelling results and address the question if this explanation is valid.

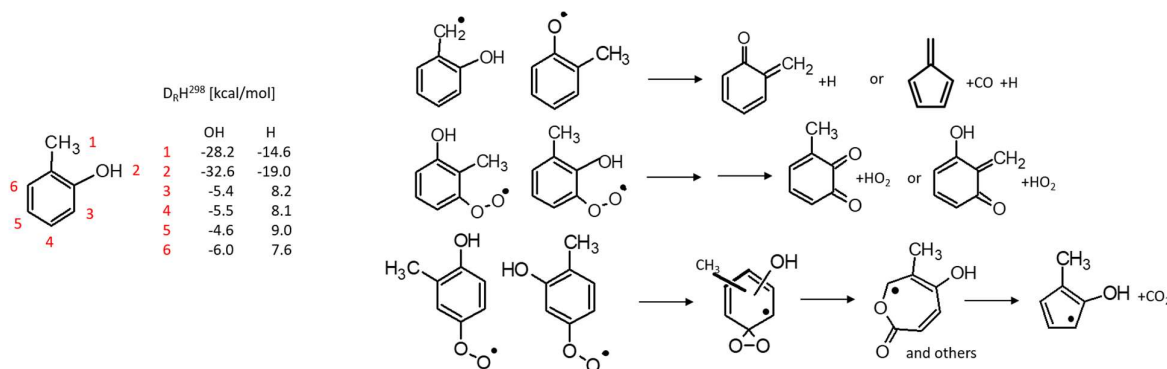


Figure 1: Left: enthalpies of reactions for H abstraction from o-cresol by OH and H. Right: Proposed dominant reaction pathways for the different radical types of o-cresyl radicals.

4. CONCLUSIONS AND RECOMMENDATIONS

Rate expressions for dominant pathways for phenol and the three cresol isomers are presented. It is demonstrated that depending on the radical site, very different reaction products are formed. More details on this and the impact of these reactions on LBV predictions will be presented in the poster.

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REFERENCES

- [1] Battin-Leclerc, F., Delort, N., Meziane, I., Herbinet, O., Sang, Y., & Li, Y. (2023). Possible use as biofuels of monoaromatic oxygenates produced by lignin catalytic conversion: A review. *Catalysis Today*, 408, 150–167.
- [2] Meziane, I., Delort, N., Bourgalais, J., Herbinet, O., Bounaceur, R., Battin-Leclerc, F. (2023). Experimental Study of the combustion of phenol and cresol isomers. *15th International Conference on Combustion Technologies for a Clean Environment* June 25-29, 2023, Lisbon, Portugal
- [3] Brezinsky, K.; Pecullan, M.; Glassman, I. (1998). Pyrolysis and Oxidation of Phenol. *Journal of Physical Chemistry A* 102, 8614 - 8619
- [4] Pratali Maffei, L., Pelucchi, M., Faravelli, T., Cavallotti C. (2020) Theoretical study of sensitive reactions in phenol decomposition. *Reaction Chemistry & Engineering* 5, 452 – 472.
- [5] Tran, L.-S., Carstensen, H.-H., Foo K.K., Lamoureux, N., Gosselin, S., Gasnot, L., El-Bakali, A., Desgroux, P. (2021). Experimental and modeling study of the high-temperature combustion chemistry of tetrahydrofurfuryl alcohol. *Proceedings of the Combustion Institute*, 38, 631 – 640.