

Experimental and modeling study of the oxidation of benzaldehyde

S. Namysl¹, M. Pelucchi², O. Herbinet¹, A. Stagni², T. Faravelli², F. Battin-Leclerc¹

1. *Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, ENSIC, Nancy Cedex, France*

2. *CRECK Modeling Lab - Dipartimento di Chimica, Materiali e Ing. Chimica "G. Natta" – Politecnico di Milano – Milano, Italy*

Introduction

Benzaldehyde is the lightest aromatic aldehyde and it is one of the major intermediates in the combustion and atmospheric oxidation of toluene. For this reason, its formation and consumption are accounted for in detailed kinetic models for the combustion of toluene and heavier aromatic compounds. Furthermore it is also an interesting surrogate to represent the reactivity of some compounds present in bio-oil coming from lignin. However, its oxidation has never been previously investigated experimentally, and no product formation profiles were reported in the few studies performed under pyrolysis conditions. Benzaldehyde pyrolysis had already been studied in batch reactors by Hurd and Bennet [1] and by Solly and Benson [2] covering a temperature range from 573K to 963K at atmospheric pressure. Experiments on this reaction have also been carried out in flow reactors by Grela et al. [3] at high temperatures (1005-1270K) and low-pressure ($P=0.001\text{atm}$), by Bruinsma et al. [4] at atmospheric pressure and over a temperature range from 773K to 1173K and by Vasiliou et al. [5] between 1200K and 1800K and between 0.1 and 0.2 kPa. These studies showed that benzaldehyde decomposes to phenyl radical plus H atoms and CO:



contrary to the typical decomposition of aliphatic aldehydes where the alkyl bond vicinal to the aldehydic moiety is the weakest (R-CHO). However none of these studies provided mole fraction profiles for the fuel or the decomposition products for benzaldehyde pyrolysis. Also, to the best of our knowledge, no oxidation study was performed.

Experimental set-up

In this work, the gas-phase oxidation of benzaldehyde has been investigated in a jet-stirred reactor at 107 kPa, temperatures between 500 and 1100 K, with a fixed residence time of 2 s and at three equivalence ratios (0.5, 1 and 2).

The jet-stirred reactor (e.g. Figure 1) in Nancy consists of a fused silica sphere (volume 92 cm³) equipped with four injection nozzles positioned in cross at the center of the sphere. This injection method ensures high turbulences in the reactor and leads to homogeneity in both temperature and product concentration of the gas phase.

The outlet gas leaving the reactor was then transported by a heated line to GCs, where the quantification and identification of the products is performed. Due to our analytical set-up, the quantification of hydrogen and water is not possible. The maximum relative error in mole fractions is estimated to be $\pm 5\%$ for the species calibrated with standards and $\pm 10\%$ for species calibrated using the effective carbon number method.



Figure 1. Jet-stirred reactor. The inlet-cross is placed in the center of the sphere

Experimental results

In the present study, 54 species were analyzed using gas chromatographs coupled with flame ionization detectors and a thermal conductivity detector.

The products can be sorted in three different categories:

- Linear compounds: carbon monoxide, carbon dioxide, methane, acetylene, ethylene, ethane, propene, allene, propyne, acetaldehyde, acrolein, acetone, butenyne, butadiene
- Cyclic oxygenated compounds: cyclopentenone, anisole, benzoquinone, phenol, benzofuran, benzodioxol, hydroxybenzaldehyde, cresol, acetophenone, benzodioxol-2-one, methylbenzofuran, ethylphenol, cinnamaldehyde, diphenylether, dibenzofuran, indanone
- Cyclic hydrocarbonated compounds: cyclopentadiene, benzene, toluene, ethylbenzene, xylene, phenylacetylene, styrene, cumene, methylstyrene, indene, methylindene, dihydronaphthalene, naphthalene, biphenyl, acenaphthylene

The main products are carbon monoxide and dioxide, phenol, acrolein, acetaldehyde and ethylene as presented in Figure 2. The mole fraction profiles of fuel and several main species are plotted in Figure 3.

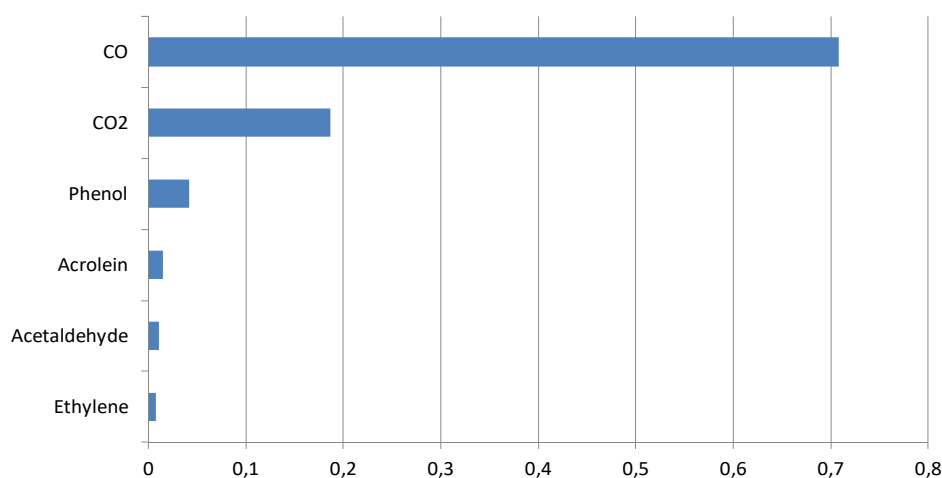


Figure 2. Selectivity analysis at 850K and for stoichiometric conditions

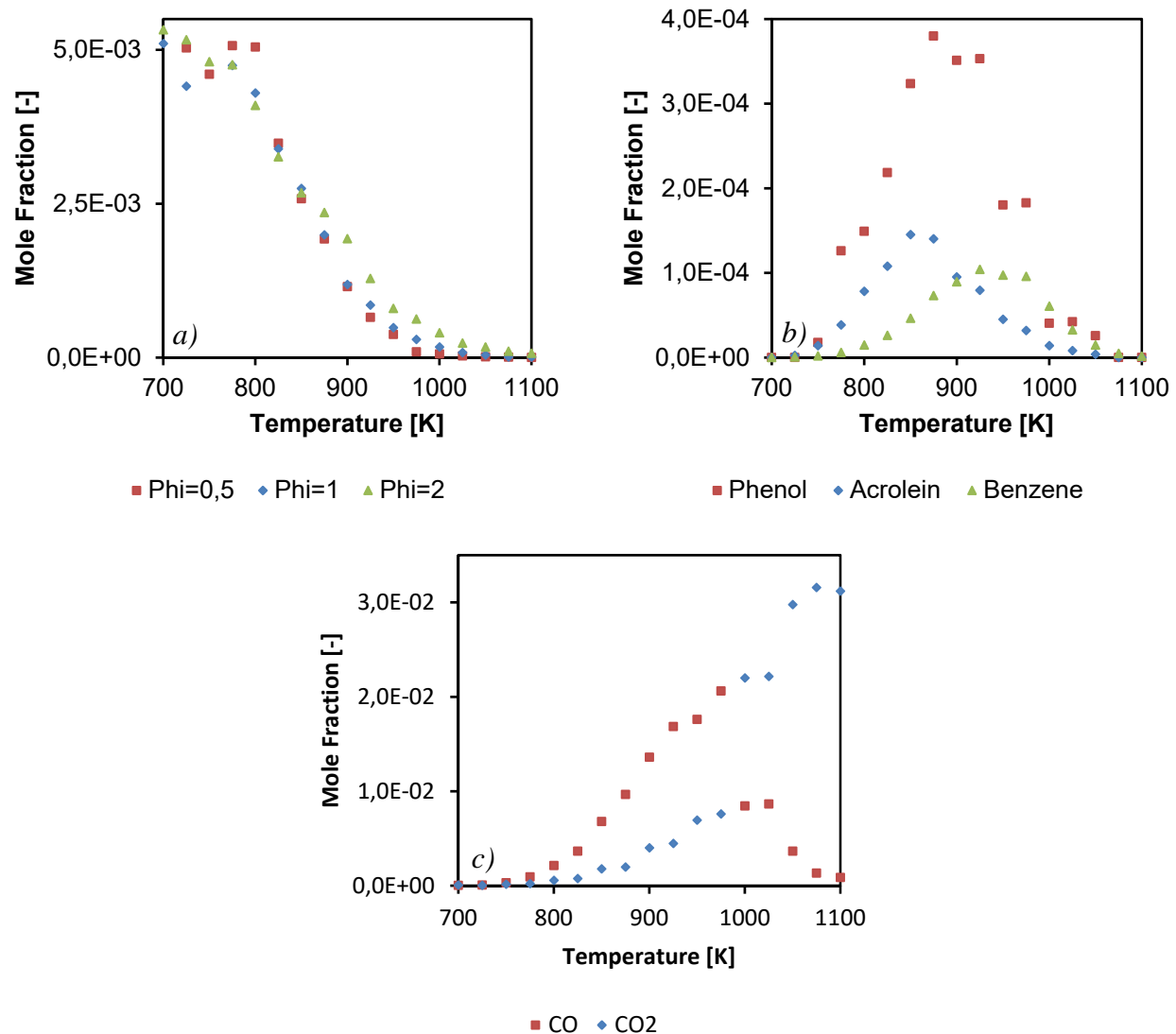


Figure 3. a) Fuel conversion for each equivalence ratio b) Mole fraction profile of three of the main products in stoichiometric conditions c) Mole fraction profile of carbon monoxide and dioxide in stoichiometric conditions

To model the oxidation of benzaldehyde, a subset of species and reactions has been added to the existing CRECK mechanism. Simulations have been performed using the OpenSMOKE++ software. The model for benzaldehyde has been based on the work of Bounaceur et al. [6] on toluene and on the model proposed by Pelucchi et al. [7] also on toluene.

Conclusion

The aim of this study is to propose a first set of data for the oxidation of benzaldehyde in a jet-stirred reactor (JSR) coupled with gas chromatographs (GC) and to interpret them by means of an updated kinetic model. Using different type of detectors mole fractions profiles were obtained for benzaldehyde and 48 of its products.

Acknowledgment

This work has received funding from the European Union H2020 (H2020-SPIRE-04-2016) under grant agreement n°723706 and from the COST Action CM1404 “Chemistry of smart energy carriers and technologies”.

References

- [1]C.D. Hurd, C.W. Bennett, THE PYROLYSIS OF BENZALDEHYDE AND OF BENZYL BENZOATE, *J. Am. Chem. Soc.*, 51 (1929) 1197–1201.
- [2]R. Solly, S. Benson, Kinetics of Gas-Phase Unimolecular Decomposition of Benzoyl Radical, *J. Am. Chem. Soc.*, 93 (1971) 2127-.
- [3]M. Grela, A. Colussi, Kinetics and Mechanism of the Thermal-Decomposition of Unsaturated Aldehydes - Benzaldehyde, 2-Butenal, and 2-Furaldehyde, *J. Phys. Chem.*, 90 (1986) 434–437.
- [4]O.S.L. Bruinsma, R.S. Geertsma, P. Bank, J.A. Moulijn, Gas phase pyrolysis of coal-related aromatic compounds in a coiled tube flow reactor: 1 Benzene and derivatives, *Fuel*, 67 (1988) 327–333.
- [5]A.K. Vasiliou, J.H. Kim, T.K. Ormond, K.M. Piech, K.N. Urness, A.M. Scheer, D.J. Robichaud, C. Mukarakate, M.R. Nimlos, J.W. Daily, Q. Guan, H.-H. Carstensen, G.B. Ellison, Biomass pyrolysis: Thermal decomposition mechanisms of furfural and benzaldehyde, *J. Chem. Phys.*, 139 (2013) 104310.
- [6]R. Bounaceur, I. Da Costa, R. Fournet, F. Billaud, F. Battin-Leclerc, Experimental and modeling study of the oxidation of toluene, *Int. J. Chem. Kinet.*, 37 (2005) 25–49.
- [7]M. Pelucchi, C. Cavallotti, T. Faravelli, S.J. Klippenstein, H-Abstraction reactions by OH, HO₂, O, O₂ and benzyl radical addition to O₂ and their implications for kinetic modelling of toluene oxidation, *Phys. Chem. Chem. Phys.*, 20 (2018) 10607–10627.