

IMPLEMENTATION OF A DETAILED REACTION MECHANISM FOR THE MODELING OF DIOXINS' PRECURSORS FORMATION

Elena Daniela Lavric, Alexander A. Konnov and Jacques De Ruyck

Department of Mechanical Engineering, Vrije Universiteit Brussel, Pleinlaan 2, Brussels, 1050, Belgium

Introduction

Modeling of the dioxins' precursors formation in the wood combustion is an important step towards controlling the toxic emissions from dedicated industrial burners. A problem in the use of biomass combustors has emerged from the new EC regulations regarding the classification of biomass and of waste combustion systems. According to these, many biomass residues (e.g. non-dangerous wood residues) will be subject to severe dioxin emission regulations, because a perfect separation of «clean» wood and «non-clean» varieties (from demolition, containing laminates or particleboard) is often impossible at the post-consumer level. This compromises a large part of the potential use of biomass combustors, in particular in the small scale applications.

This report summarizes the progress in the modeling of a wood combustor in the framework of the Flemish IWT project 010027 «Abatement of dioxins, NO_x and dust-emissions from combustion of lightly contaminated wood of small granulometry» in cooperation with Vyncke NV, Belgium. The objective of this project was to improve the design and to establish the adequate operating conditions of 1.7 MW industrial wood combustion system. In a first stage of the project, in parallel with experimental studies, significant efforts are devoted to the modeling of the combustion process in the system with particular attention to the prediction of pollutant (CO, NO_x and dioxins) formation. The aim of the present work in particular was the development and implementation of the detailed reaction mechanism for the modeling of dioxins' precursors formation in the wood combustion.

Approach and Methods

To obtain a reliable knowledge of the physical and chemical phenomena occurring in the combustor, a hybrid approach is being realized. The procedure consists of complementary CFD modeling and reactor network modeling as described elsewhere.¹ The reactor network of plug flow and well-stirred reactors with interconnecting feeds is to be built into a process simulation software. It includes a detailed chemical mechanism for bio-gas combustion and pollutant formation. To define the volume of and flow through plug flow or well-stirred reactors, CFD modeling is to be used. On the other hand, the reactor network modeling gives detailed understanding of the chemical processes occurring in different zones of the combustor, which is necessary in pollutant abatement.

Testing of measures to reduce dioxins is hampered by the high costs of full dioxins measurements. A possible alternative is to measure the concentration of some surrogate chemical, linked in a known fashion to products of incomplete combustion. Research has been performed to identify the suitable surrogate, and statistically good relations were found between PCDD/F and poly-chlorinated benzenes (PCBz).² All the observed chlorobenzenes roughly correlate with I-TEQ. Experimental results infer that on-line measurement techniques of chlorobenzenes' concentration may be used to control and optimize combustors by direct primary measures. Monochlorobenzene in particular is found to be a very sensitive surrogate, which is suited for on-line detection.

FORMATION AND SOURCES

Modeling Details

A detailed C/H/N/O reaction mechanism for the combustion of small hydrocarbons³ was used as a starting point for the model development. This mechanism has been validated with experimental data available for oxidation, ignition, and flame structure of hydrogen, carbon monoxide, formaldehyde, methanol, methane, ethane, propane, and some of their mixtures. The list of reactions and species has been dramatically extended to include hydrocarbons up to C10 and chlorinated hydrocarbons up to C8. More than 1000 technical papers, books and dedicated databases have been analyzed. The reaction mechanism obtained after the elimination of the redundant reactions consists of 3600 independent reactions among 900 species. Thermodynamic data of the chemical species were collected from the dedicated databases. Due to lack of experimental data for many species the thermodynamic data were calculated using Thergas code.⁴ The Chemkin Collection of Codes Release 3.5⁵ is used for the modeling of perfectly stirred reactors.

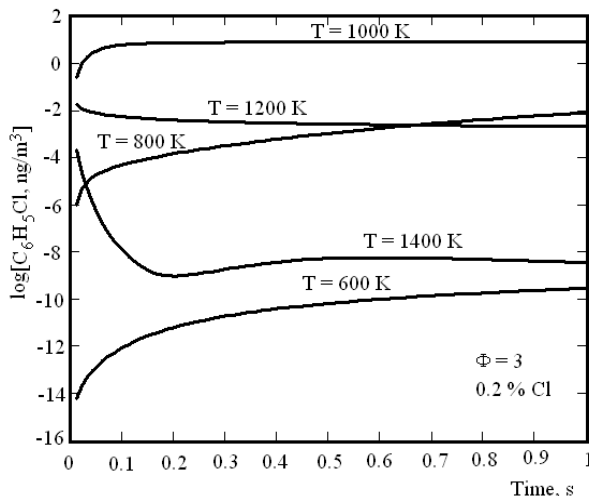


Figure 1. Time variation of mono-chlorobenzene concentration with the temperature as parameter

Results and Discussion

The influence of the temperature ($T \hat{=} 600 \div 1400\text{K}$), the reaction time, the air factor and the chlorine biomass concentration on the monochlorobenzene formation was tested. The composition of the reactor input mixture was assumed equal to that obtained from the wood pyrolysis at 900°C .¹ Taking into account the relatively high reaction rates, a reaction time of one second was chosen for the discontinuous perfectly stirred reactor. At the beginning of the chemical process, the formation rate is important, decreasing as the reaction time increases. As expected, complex precursors, like C_6H_4ClOH have much smaller concentrations than simpler ones, like C_6H_5Cl , due to the simpler reaction chain implied by C_6H_5Cl formation, thus larger probability for it to happen. At a higher temperature, all the reaction rates increase, so the concentrations of all precursors increase too (fig. 1). Being the intermediate species, the precursors are consumed immediately after formation in process having greater reaction rates than the formation ones. As their concentrations decrease, the consumption rates

FORMATION AND SOURCES

decrease too, permitting the formation process to balance the consumption. Comparing the time patterns of the C_6H_5Cl concentration, with temperature as parameter (fig.1), the dominant process is better clarified. At low temperatures, the formation process dominates, while above 1000 K

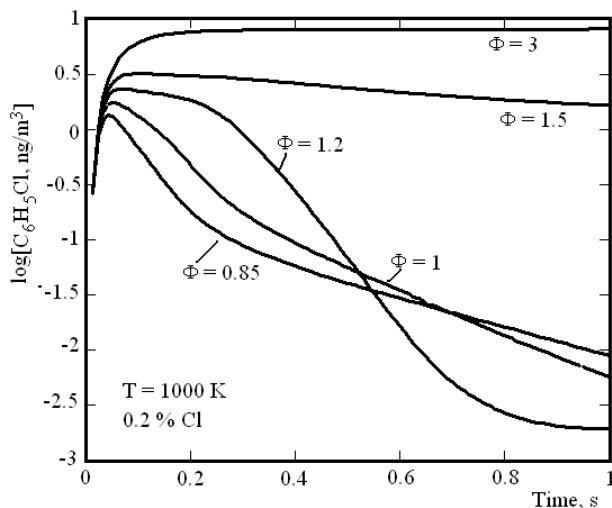


Figure 2. Time dependency of mono-chlorobenzene's concentration with the air factor as parameter

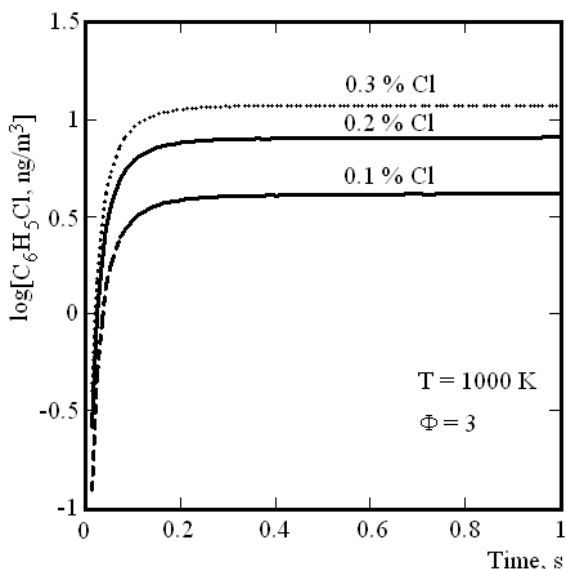


Figure 3. Time dependency of chlorobenzene's concentration with chlorine content of biomass as parameter

FORMATION AND SOURCES

consumption process dominates. At 1000 K there is a maximum value for mono-chlorobenzene's concentration.

Fig. 2 presents the influence of the air factor (considered at 1000 K, since there the maximum values were observed) on the chlorobenzene's concentration. The effect of decreasing the air factor is that the plateau of the concentration is shorter and become a maximum. After this maximum value (which is moving toward shorter reaction time) the precursor degrades rapidly. As expected, a higher level of chlorine yields higher concentrations of precursors (fig. 3).

Acknowledgements

The Government of Brussels is acknowledged for the financial support of E.D. Lavric through the "Research in Brussels" grant. Part of this work has been performed in the framework of the IWT project 010027 / Vyncke NV: "Abatement of dioxins, NO and dust-emissions from combustion of lightly contaminated wood of small granulometry."

References

1. Konnov A.A., El Asri R., De Ruyck J., Courquet J., Simonin O., and Allard G. (2000) Proceedings of the 1st World Conference "Biomass for Energy and Industry", Sevilla, vol. 2, 1797
2. Lavric E.D., Konnov A.A. and De Ruyck J. (2002) Indicator parameters for dioxins in incineration - a survey. Submitted.
3. Konnov, A.A. (2000) Detailed reaction mechanism for small hydrocarbons combustion, Release 0.5, WWW <http://homepages.vub.ac.be/~akonnov/>.
4. Muller C., Michel V., Scacchi G. and Côme G.M., (1995) *J. Chim. Phys.* 92, 1154
5. Kee, R.J., Rupley, F.M., Miller, J.A., Coltrin, M.E., Grcar, J.F., Meeks, E., Moffat, H.K., Lutz, A.E., Dixon-Lewis, G., Smooke, M.D., Warnatz, J., Evans, G.H., Larson, R.S., Mitchell, R.E., Petzold, L.R., Reynolds, W.C. Caracotsios, M., Stewart, W.E., and Glarborg, P. (1999) Chemkin Collection, Release 3.5, Reaction Design, Inc., San Diego, CA.