Modelling the Super-Equilibrium of Sodium, Potassium, Sulphur and Chlorine in the Recovery Boiler Fume

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ABSTRACT

The combustion of black liquor in a recovery boiler has been modelled based on the constrained multiphase thermodynamic model. The presented model provides a quantitative description of the observed super-equilibrium of excess sodium, potassium, sulphur and chlorine in the fume of the recovery boiler. In addition the respective effects of super-equilibrium on the condensed phases in the flue gas have been described. The model is based on the Constrained Free Energy (CFE) technique, which is an extension of the conventional Gibbs free energy minimisation method and as a rule applied to estimate kinetically controlled and local equilibria of multiphase chemical systems. This works extends the system of Na-K-S-Cl-C-O-H-N used for ash chemistry studies by introducing additional constraints for the volatility of Na, K, S and Cl. In addition, black liquor is introduced as an additional phase of the thermochemical system enabling energy balance studies of combustion process.

Parameters such as elementary composition and heat of combustion of black liquor, volatility of sodium and sulphur, enrichment factors of potassium and chlorine, air content in combustion as well as the combustion temperature are used as model parameters. With a two-stage reactor model the composition of fume, smelt and condensed phases can be estimated. The reaction enthalpy is also calculated simultaneously. The results indicate that the constraint model can be used to predict the lowered sticky temperatures of the condensed phases from fume.

The proposed method can be utilised for larger process simulations as well as for ash chemistry studies. It provides a simple and thermodynamically based practice to describe the known super-equilibrium of recovery boiler chemistry. The presented methodology enables simultaneous estimation of chemical reactions and heat of combustion in the recovery boiler.

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[1] *Kangas P, Koukkari P, Lindberg D, Hupa M*. **Modelling black liquor combustion with the constrained Gibbs energy method**. 8th International Black Liquor Colloquium, Belo Horizonte, Brazil: 2013.

[2] *Kangas P, Koukkari P, Lindberg D, Hupa M.* **Modelling black liquor combustion with the constrained Gibbs energy method** (submitted). The Journal of Science and Technology for Forest Products and Processes: 2013.