Research article

An efficient coal pyrolysis model for detailed tar species vaporization

Jianqing Li, Simcha L. Singer*

Dept. of Mechanical Engineering, Marquette University, Milwaukee, WI, United States

ARTICLE INFO

ABSTRACT

An accurate and computationally efficient model for the vaporization of many tar species during coal particle pyrolysis has been developed. Like previous models, the molecular fragments generated by thermal decomposition are partitioned into liquid metaplast, which remains in the particle, and vapor, which escapes as tar, using a vapor-liquid equilibrium (VLE) sub-model. Multicomponent VLE is formulated as a rate-based process, which results in an ordinary differential equation (ODE) for every species. To reduce the computational expense of solving many ODEs, the model treats tar and metaplast species as a continuous distribution of molecular weight. To improve upon the accuracy of previous continuous thermodynamic approaches for pyrolysis, the direct quadrature method of moments (DQMoM) is proposed to solve for the evolving distributions without assuming any functional form. An inexpensive delumping procedure is also utilized to recover the time-dependent mole fractions and fluxes for every discrete species. The model is well-suited for coal-to-chemicals processes, and any application which requires information on a range of tar species. Using a modified CPD model as the basis for implementation of the VLE submodel, agreement between the full discrete model and DQMoM with delumping is excellent, with substantial computational savings.

1. Introduction

Pyrolysis is the thermal decomposition of a solid fuel, such as coal or biomass, which produces gaseous, liquid and solid products. As a coal particle is heated, its macromolecular structure begins to decompose, creating a wide range of molecular fragments and light gases. A portion of the molecular fragments are released from the particle as tar, and together with the light gases, comprise the volatiles. Hundreds of light gas and tar species are produced during coal pyrolysis [1,2]. While pyrolysis (or devolatilization, in the presence of oxygen) occurs as the initial step during coal combustion and gasification, pyrolysis as a stand-alone process can be used for the production of chemicals and fuels from coal [1]. Knowledge of the tar compounds formed during pyrolysis is important for such coal-to-chemicals processes, as well as for predicting soot formation during coal gasification and combustion by pairing with an elementary reaction mechanism [3].

A range of pyrolysis models have been developed. Single-step models are typically valid only under the conditions for which their kinetic constants have been determined. Distributed activation energy models use Arrhenius rates with a distribution of activation energies to represent the numerous chemical pathways for production of volatiles from coal's complex macromolecular network [4]. The most accurate models are the comprehensive models that account for the coal's molecular structure [5]: Chemical Percolation Devolatilization (CPD) [6],

FLASHCHAIN [7] and FG-DVC [8]. These models are based on a realistic description of a coal's structure, a mechanistic description of its disintegration upon heating, the release of light gases, cross-linking of metaplast and the vaporization of molecular fragments as tar. The tar vaporization model in CPD is based on the flash equilibrium analogy originally developed in a precursor to FLASHCHAIN [9], which is more accurate than the vaporization submodel in FG-DVC.

Rather than predicting the production of individual tar species, CPD and FLASHCHAIN predict the production of lumped tar species as a function of molecular weight. In the CPD model, fragment species are lumped into discrete groups, with each lump typically comprising species with a range of roughly 300 kg/kmol [10,11]. This approach is an example of a discrete component model (DCM), employing quasi-components rather than discrete species. FLASHTWO, a precursor to FLASHCHAIN, assumed that the fragment molecular weights followed a continuous gamma distribution and calculated the evolution of the distribution's parameters with time [9], or specified the distribution to fit experimental data [12]. Treating the species as a continuous distribution constitutes a continuous thermodynamic model (CTM) [13]. However, due to the inaccuracy associated with specifying the distribution function a priori throughout pyrolysis, FLASHCHAIN calculates the fragment distribution from population balance equations for each fragment size [7], which can again be considered a quasi-DCM, as in CPD.

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* Corresponding author.
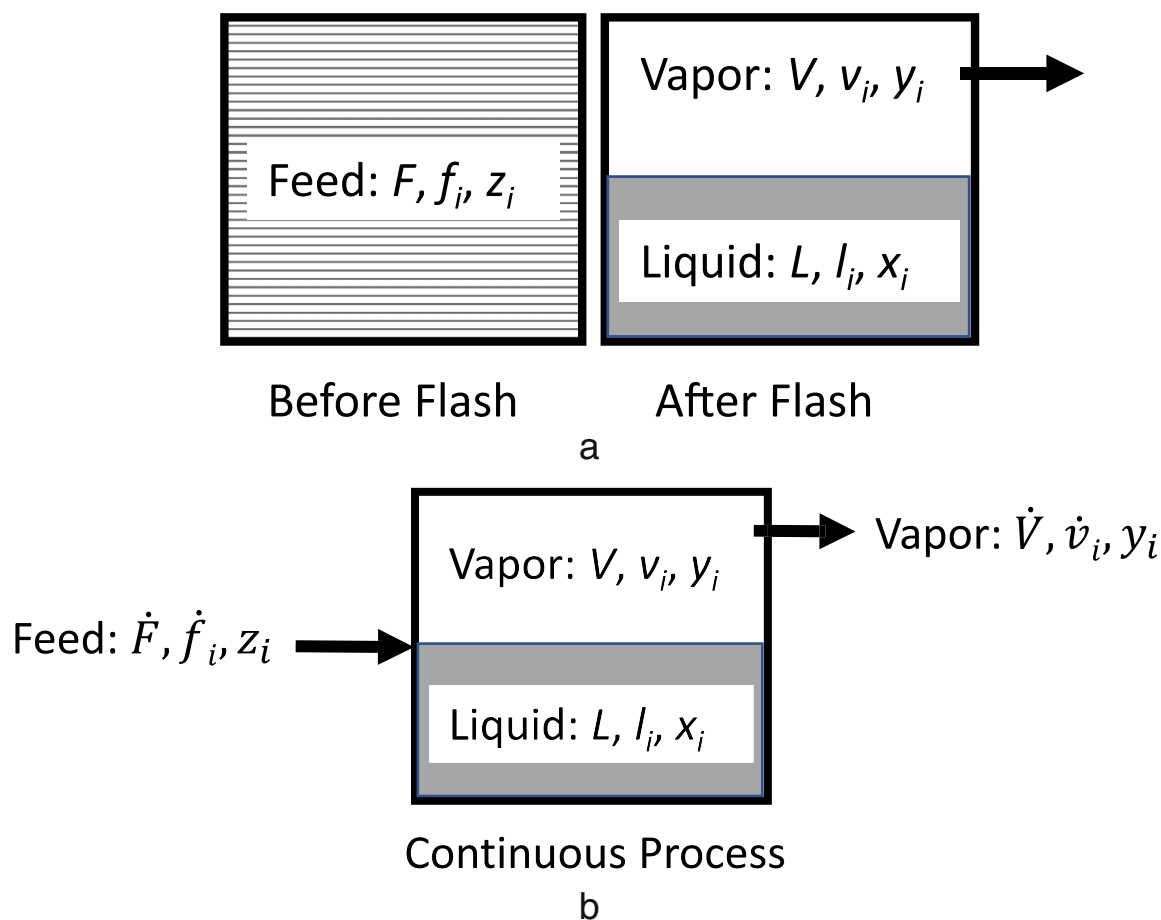*E-mail address:* simcha.singer@marquette.edu (S.L. Singer).

Fig. 1. (a) Vapor-liquid equilibrium as a batch process, and (b) as a continuous process.

In general, for problems governed by differential equations, DCM approaches yield information on every discrete (or quasi-discrete) species but can become computationally intensive when the number of species becomes large. CTM approaches are computationally efficient, but can be less accurate due to the assumption of the form of the distribution function, and only provide information on the distribution, rather than on individual species.

This paper presents an accurate and efficient CTM for tar vaporization during coal pyrolysis, as well as a delumping step which combines the advantages of DCMs and CTMs. To remove the computational time-step dependence [11] in the CPD VLE model, the vaporization process is treated as a rate-based process [14], as in FLASHCHAIN [7]. However, rather than solving an ordinary differential equation for every discrete or quasi-discrete species, a CTM is employed, as in FLASHTWO [9]. The first novelty of the model presented is that rather than using a continuous distribution function that is specified a priori [9], the Direct Quadrature Method of Moments (DQMoM) is used to efficiently and accurately solve for the evolution of the distribution of tar and metaplast species without assuming any functional form. The second novelty is an accurate and inexpensive delumping procedure that is used to recover the time-dependent mole fractions and fluxes for every discrete tar and metaplast species, providing the same information as a DCM at a significantly reduced computational cost.

The tar vaporization model described in this paper is well-suited to kinetic models which produce many tar species. Molecular dynamics simulations have recently been applied to coal pyrolysis to predict individual reaction products for a variety of coals [15–17], represented by large-scale coal models [18,19]. However, these simulations have not yet included models to partition the molecular fragments generated into tar (vapor) and metaplast (liquid) and simulate very short periods of

time. Recently, an extension of the CPD model has been developed that can predict the formation of specific tar compounds [3]. Future models might combine the advantages of these two simulation approaches, parametrizing kinetic schemes based on functional groups [8,20] with detailed species information obtained from molecular dynamics simulations. DQMoM for tar vaporization is applicable to any kinetic scheme for macromolecular decomposition, while application of the delumping procedure is restricted to models without reactions between individual metaplast species, such as the biomolecular recombination reactions in FLASHCHAIN [7].

The rate-based tar vaporization model is presented in discrete form in Section 2.1. The discrete version of the model is computationally expensive if applied to many species. Section 2.2 describes the DQMoM approach for coal tar vaporization and the delumping procedure is outlined in Section 2.3. The test case for the model is based on a modified version of the CPD model and is described in Section 3. Results and discussion comparing the DQMoM and delumping models to the DCM are presented in Section 4, with conclusions in Section 5.

2. Tar vaporization model

2.1. Discrete component model

2.1.1. Vapor-liquid equilibrium in CPD

The vapor-liquid equilibrium (VLE) submodel in the CPD model applies Raoult's Law to relate the liquid (x_i) and vapor (y_i) mole fractions of a quasi-discrete fragment species, i,

$$y_i = K_i x_i \tag{1}$$

and the nonlinear Rachford-Rice equation to calculate the phase of