

CONTINUOUS KINETIC LUMPING FOR LIGNITE LIQUEFACTION

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INTRODUCTION

The need for an alternative energy source to counteract both short-term petroleum supply interruptions and the eventual depletion of petroleum reserves has resulted in an increased interest in the utilization of domestic coal. While coal can be utilized directly for energy applications such as electrical power generation, much of the petroleum demand is based in the liquid fuel and liquid feedstock areas. This potential demand for liquid fuel and feedstock has caused a renewed interest in coal liquefaction technology. However, the development of coal liquefaction technology to an industrially applicable level has been hindered by the lack of a suitable kinetic model. Current kinetic models are based upon simplified analytical techniques in which components are lumped into several solubility or volatility classes. These models must be used cautiously since compounds within the same solubility or volatility class do not necessarily undergo similar reactions. In addition, each kinetic model applies only to the particular coal studied. A critical need exists for a kinetic model based upon the actual chemical reactions occurring and which is applicable to a variety of coals. The development of such a kinetic model is the goal of the coal liquefaction studies at Texas A&M University.

The development of a kinetic model capable of describing a complex, many-component reaction, such as coal liquefaction, requires the investigation of several supporting areas: experimental reactions, analytical method, component lumping, reactor modeling, and parameter estimation. All of these areas depend on each other; hence, the resulting kinetic model is dependent on, and limited by, each area. Any attempt to improve the kinetic model must therefore effect an improvement in one or more of the supporting areas. The coal liquefaction research at Texas A&M University has resulted in significant advances in the areas of analytical technique, component lumping, and reactor modeling, thus providing the foundations for the development of a powerful new kinetic model.

The sections below describe the results which have been achieved and the course of the research now being followed in each of the supportive areas: experimental reactions, analytical method, component lumping, reactor modeling, and parameter estimation. In particular, several of the more significant developments are described and compared to the methods currently being used. These new developments include an improved analytical technique, the SEC-GC-MS method, based upon a combination of size-exclusion chromatography (SEC), gas-chromatography (GC), and mass spectroscopy (MS); an optimum component lumping technique developed by embedding the classical kinetic and equilibrium equations into the vector space of generalized functions; and a reactor model which incorporates an equation-of-state equilibrium calculation to predict the compositions of the reactants in both the liquid and vapor phases.

EXPERIMENTAL REACTIONS

The commonly used types of coal liquefaction laboratory reactors have been discussed in detail by Shah (1). Continuous-flow reactors were not considered for this study due to the possibility of different residence times existing for each phase, a condition difficult to model, and due also to the difficulty in establishing a steady-state condition for the solid phase. The batch reactors commonly used in laboratory studies thus far are the batch autoclave, the rapid-injection autoclave, and the tubing-bomb microreactor. Of these three, the tubing-bomb microreactor was chosen for this kinetic study due to the reactor's low thermal inertia, good heat and mass transfer characteristics, and the small amount of reactor feed required (2).

The tubing-bomb reactors used at Texas A&M typically consist of a 6 inch long 3/4 inch o.d. stainless steel tube capped on each end. A thermocouple extends into the reactor via a 1/4 inch o.d. thermowell assembly. A 1/8 inch o.d. line to the reactor serves for gas charge and evacuation in addition to providing for pressure measurement during an experimental run. Various tubing-bomb reactors used at Texas A&M and the corresponding experimental procedures are described by Helton (3), Haley (4), Shumbera (5), and Koker (6).

ANALYTICAL METHOD

The purpose of an analytical method, as applied to kinetic model development, is to provide a measure of the change which has occurred during the experimental reaction. This "measure of change" provided by the analytical method must 1) relate to the kinetic properties of the reaction mixture, so that the fundamental equations governing the chemical reactions may be easily applied, and 2) the properties relating to the uses of the reaction product, so that the resulting kinetic model may be used to optimize product yield and composition. When the reaction mixture is simple, consisting of relatively few components, the analytical technique provides an exact analysis; thus, both Criteria 1 and 2 above are readily satisfied. However, when the reaction mixture is complex, consisting of many components, an exact analysis is often impossible. An approximate analytical technique must then be used, and this approximate technique must attempt to satisfy the above criteria. Therein lies the failing of the approximate analytical techniques commonly used for coal liquefaction studies: solubility analysis and distillation analysis.

Solubility analysis consists of the separation of coal liquefaction products into portions which are soluble in a series of extraction solvents. A commonly used series of solvents consists of hexane, toluene, and tetrahydrofuran. Hexane solubles are designated as "oil," toluene solubles are designated as "asphaltenes," and tetrahydrofuran solubles are designated as "preasphaltenes." All of the material insoluble in tetrahydrofuran is considered to be unreacted coal, char, and ash. The solubility analysis method provides a rough picture of the changes occurring in the reaction mixture, and kinetic models have been developed using the component classes: oil, asphaltenes, preasphaltenes, and unreacted coal. However, the solubility analysis method fails to satisfactorily meet Criteria 1 and 2 mentioned above.

First, each component class, or lump, consists of a broad range of component types. The kinetic behavior of the component lump will, in general, depend in a complicated manner upon the components contained within the lump. Therefore, any information relating to actual molecular mechanism of coal liquefaction, which is formulated in terms of individual molecular types, will be difficult to incorporate into the overall kinetic model, which is formulated in terms of the lumped component classes. Furthermore, coal liquefaction is a multiphase process; the individual components within the reaction mixture are dispersed throughout the solid, liquid, and vapor phases. Since each phase may be expected to exhibit different reaction behavior, the distribution of each component in each phase may significantly affect the kinetic behavior of the reaction mixture. Hence, properties which describe the affinity of each component to a particular phase, such as volatility, should be included in the kinetic model. The solubility analysis method fails to provide such information, since each solubility lump may contain components with a broad range in volatility.

The solubility analysis also fails to satisfy the product criterion; the solubility lumps — oil, asphaltenes, and preasphaltenes — are difficult to relate to the end uses of the product. When the liquefaction products are to be used as chemical feedstock, the engineer is primarily interested in a particular component or group of components. The solubility lumps which contain the desirable group of components may also contain undesirable components. Hence, the liquefaction process cannot be easily optimized for the desired products. When the liquefaction products are to be used as fuel or fuel feedstock, volatility properties of the product become important; however, solubility lumps fail to incorporate such volatility information.

Distillation analysis also fails to satisfy the reaction and product criteria. Distillation

analysis separates the mixture into several volatility classes. However, these volatility classes contain several types of chemical components, with each component type exhibiting different kinetic behavior in the reaction mixture; hence, the volatility lumps, like the solubility lumps, are unable to provide a precise description of the reaction. Furthermore, a product description in terms of volatility lumps fails to provide chemical information about the product, which is often needed when the product is to be used as a chemical feedstock.

The failings of the traditional solubility and distillation analyses led to the development of the SEC-GC-MS analytical method at Texas A&M. In the SEC-GC-MS method, the tetrahydrofuran soluble portion of the liquefaction products is first separated into several fractions (usually 9) using size-exclusion chromatography (SEC) with tetrahydrofuran (THF) as the mobile phase. As shown by Anthony et al. (7), size-exclusion chromatography effects a separation of the mixture based upon molecular size and functionality, with alkanes eluting first, followed by phenols, and then aromatics. Each of the fractions obtained using size-exclusion chromatography is then analyzed using gas chromatography (GC), which effects a separation based upon volatility. A mass spectroscopic (MS) detector can be used with the GC to aid in peak identification. Details of the SEC-GC-MS method have been provided by Anthony et al. (8).

The SEC-GC-MS analytical method provides a distribution of the coal liquid sample with respect to the SEC retention index, which provides a measure of component functionality, and with respect to the GC retention index, which provides a measure of component volatility. This bivariate distribution (Figure 1) provided by the SEC-GC-MS method exhibits several advantages over the univariate distributions provided by the solubility and distillation methods. First, since the SEC-GC-MS method provides a separation of the mixture based on both volatility and component functionality, the bivariate distribution is easily related to both the kinetic properties of the reaction mixture and to the properties relevant to the desired uses of the product. Second, since all components eluting within a particular SEC-GC retention region can be expected to have similar chemical and volatility properties, lumping of neighboring components (components which elute with similar SEC and GC retention times) may be justified. Such lumping may be required when the chromatograms are poorly resolved, or lumping may be desirable to reduce the number of parameters within a kinetic model. Furthermore, all coals can be expected to yield the same types of components upon liquefaction, and these types of components should consistently elute with the same SEC and GC retention time, independent of the coal type being liquefied. This separation of the kinetic model from coal type was not possible with solubility analysis, since solubility lumps derived from different coals do not always contain the same amount of each component, or even the same components.

CONTINUOUS LUMPING

The SEC-GC-MS analytical method yields an overwhelming amount of information. The method provides not only a good overall description of the mixture compositions, but also often provides detailed concentration information about individual components. However, such detail is often not necessary or desirable. The optimum kinetic model should provide the best possible mixture description using the fewest possible parameters. A kinetic model incorporating a large number of parameters is difficult to use; first, the presence of a large number of parameters makes parameter estimation difficult, and second, the large model becomes difficult to apply in subsequent design situations. Hence, a method was needed whereby the detailed SEC-GC-MS analysis could be parameterized using the fewest possible terms while retaining the bulk of the useful information from the SEC-GC-MS analysis. This parameterization procedure is referred to as "component lumping," or simply as "lumping."

The traditional form of lumping is pseudocomponent lumping, where groups of components are treated as individual components. However, we have developed (9) an alternate method, "continuous-lumping," which is particularly well-suited for calculations involving chromatographic data. Continuous-lumping can be considered a generalization, or reinterpretation, of

the theory of continuous mixtures, as described by Cotterman et al. (10) for thermodynamics and by Aris and Gavalas (11) for reaction kinetics. However, our developments have shown (9) that the continuous mixture hypothesis is not required for the method to be valid.

For continuous-lumping, the individual component properties — concentration, volatility, and reactivity — are considered to be functions of some suitable component index, such as molecular-weight or boiling-point. These component indices, in turn, can then be related to chromatographic retention-times. The classical description of the mixture composition (mole fractions) is then converted to a distribution function (similar to a chromatogram) written in terms of the component index. The classical relationships between the component properties (i.e., equilibrium relations, reaction-rate equations, etc.) are then converted to the functional form. The final step in the continuous-lumped method is the expansion of the functional equations in terms of generalized Fourier series to obtain an approximate set of algebraic equations — the continuous-lumped equations.

The bivariate distribution provided by the SEC-GC-MS analytical method is particularly well suited to the continuous lumping method, since the kinetic and volatility properties of the components vary gradually with the SEC and GC retention indices. In fact, the fundamental parameters of a kinetic model may be considered to be functions of the component indices instead of the usual interpretation, where the kinetic parameters are associated with the set of pseudo-components. Thus, the problem of kinetic model development becomes the determination of a kinetic parameter surface over the SEC-GC component index plane. This approach frees the model from the dependence on a particular choice of a pseudo-component lumping scheme, thus enabling comparison of data from two separate investigations in which different lumping schemes happened to be used. Furthermore, all of the components in a small neighborhood of a particular SEC-GC index pair can be expected to be chemically similar; therefore, a particular component from the neighborhood may be selected for a kinetic study. Such a "model compound" study possesses an advantage over a kinetic study of the complete coal liquid, since a particular kinetic parameter may often be determined with greater precision when the effects of the other kinetic parameters have been removed.

The detailed theory behind the continuous lumping method, as applied to vapor-liquid equilibrium calculations, has been developed by Anthony and Moore (9). The theory is presently being extended and fully developed to include reaction kinetics. The continuous lumping method will be incorporated in a reactor model (described in the next section) which will predict conversion and product distributions for the tubing-bomb reactor.

REACTOR MODELING AND PARAMETER ESTIMATION

After the products of the experimental liquefaction reactions have been characterized using the SEC-GC-MS analytical method and the continuous lumping method, the resulting parameterized data, which describes the changes that occur during reaction, must be related to the fundamental kinetic model (in general unknown), which governs the changes that occur during reaction. When the assumed form of the kinetic model is simple, the kinetic and reactor model equations may be solved directly to obtain an analytical equation describing the reaction. The fundamental parameters within the kinetic model may then be estimated by fitting the analytical solution to the lumped data using a regression method. However, the assumed kinetic model and the reactor modeling equations often form a complex system, making an exact analytical solution difficult or impossible to obtain. The combined kinetic and reactor model equations, together with an assumed set of parameters, must then be solved using a numerical method to obtain predictions of reaction behavior. The combined kinetic and reactor model can then be incorporated into a parameter estimation routine, such as the Modified Marquart Method used by Targ (12), in order to obtain optimum estimates of the kinetic parameters. This second approach, the reactor model — parameter estimation method, has been chosen to obtain estimates for the kinetic parameters, since the method is general and may therefore accommodate virtually any assumed form of the kinetic model.

Coal liquefaction is a complicated process involving reactions in and mass transfer between vapor, liquid, and solid phases; any theoretically based kinetic model must therefore account for the fundamentally different reactions and mechanisms in each phase. Heretofore, kinetic models have failed to incorporate this fact; the reaction mixture was treated as if it were one single phase, with any phase equilibrium effects being incorporated into the empirical kinetic model. Such a treatment is unacceptable, however, since different types of industrial reactors exhibit different types of phase equilibrium behavior. The kinetic model must, therefore, be based on the actual compositions in each phase, which must either be measured or predicted.

Measurements of phase compositions in a coal liquefaction reactor are always difficult and, in the case of the tubing-bomb reactor, may be impossible. However, as shown by Anthony et al. (13), an equation-of-state (EOS) vapor-liquid equilibrium calculation is capable of predicting the phase concentrations of key reactants, such as hydrogen, to a sufficient degree of accuracy. Figures 2 and 3 illustrate the prediction of VLE properties for a hydrogen-coal liquid mixture using an equation-of-state. Figure 2 shows an ASTM D-86 of a SRC-II coal liquid fraction. Bubble points for mixtures of this coal liquid with hydrogen were determined experimentally by Chao (14), as shown in Figure 3, where a VLE calculation using an equation-of-state is also shown. Note that the VLE calculation predicts the mole fraction of hydrogen in the liquid phase well. For this reason, plus the difficulty of sampling, an EOS vapor-liquid equilibrium calculation has been chosen to predict phase compositions in the reactor model. The incorporation of an EOS vapor-liquid equilibrium calculation into the reactor model has the disadvantage that the resulting kinetic model will depend on the particular EOS model chosen; however, the inaccuracies due to such a dependence are not likely to exceed the inaccuracies in the assumed form for the kinetic model. Furthermore, the EOS calculation may be used to find the conditions at which the phase compositions yield the optimum reaction behavior; this predictive function of the reactor model would not be easily available if the phase compositions were obtained by measurement. Hence, reactor conditions of particular interest, consisting of temperatures and pressures at which the liquid-phase reactions may be enhanced (such as the near-critical and supercritical regions), may be investigated.

CONCLUSIONS

The key to an improved coal liquefaction kinetic model is the development of an analytical method capable of separating the reaction products into individual molecular components; The SEC-GC-MS analytical method satisfies this need by providing detailed compositional information, such as the chemical and volatility properties of each component. The tremendous detail provided by the SEC-GC-MS method can then be effectively parameterized using the continuous lumping method, which allows the detailed analytical results to be incorporated into complex kinetic and thermodynamic calculations, such as the equation-of-state VLE calculation described above. Thus, the SEC-GC-MS analytical method and the continuous lumping method, both developed at Texas A&M University, allow the application of advanced theory to the coal liquefaction process.

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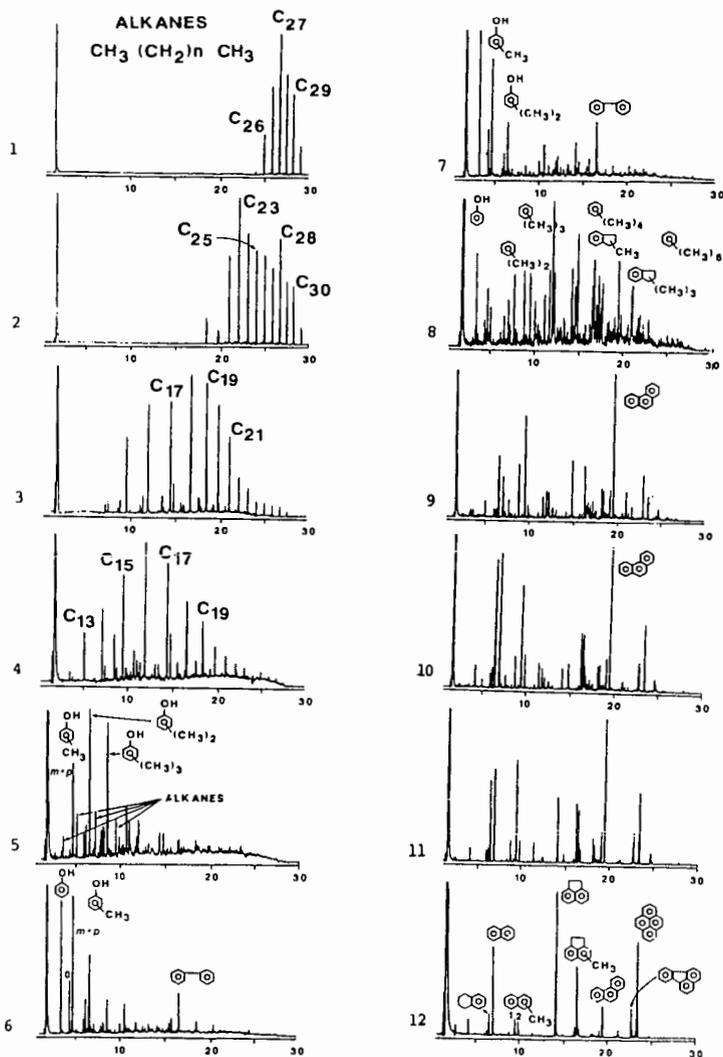


Figure 1 – SEC-GC-MS Material Distribution

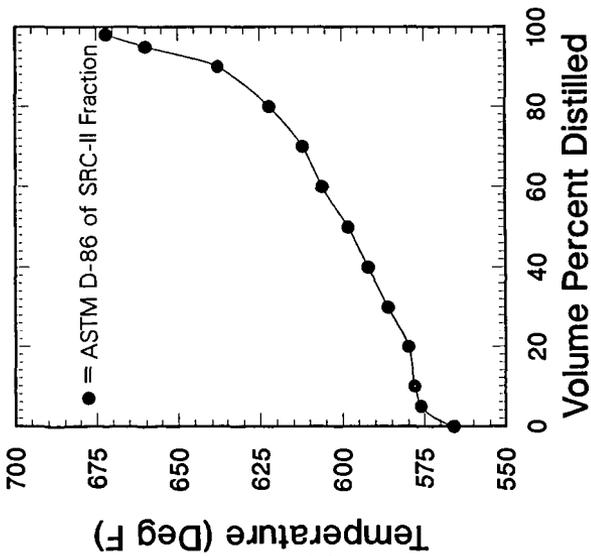


Figure 2 - ASTM D-86 of SRC-II Coal Liquid Fraction.

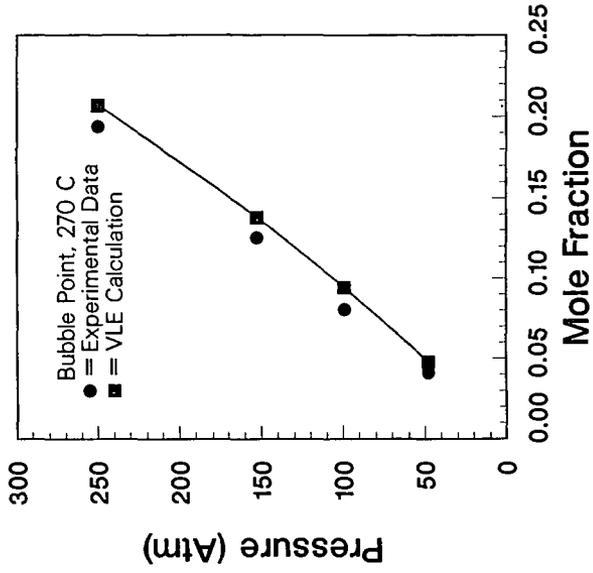


Figure 3 - Bubble Points of Hydrogen / SRC-II Coal Liquid Mixture