

## DEVELOPMENT OF A GENERAL MODEL FOR COAL LIQUEFACTION

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**INTRODUCTION** One goal of coal liquefaction kinetic models is to be able to predict the results of coal liquefaction experiments in order to identify optimal processing conditions. A second goal is to be able to define experimental conditions that provide the greatest amount of information per experiment. This is especially important in comparing catalysts. A third goal is simply to be able to identify those processing variables which will have the greatest effects in a given system. This will reduce the number of actual experiments needed to investigate new systems by focusing on only the most important variables.

Previous investigators have taken into account the effects of a number of variables in development of their kinetic models.<sup>1</sup> These effects include temperature, coal type, solvent type, and hydrogen pressure. Temperature is readily taken into account through determination of activation energies from rate constants found at different temperatures. Coal type and solvent type were sometimes taken into account through ultimate conversions, but most often were included by adjusting the rate constants for each coal or solvent. Hydrogen pressure was included as a separate term in the rate equations in some models.

These models could not fulfill the three goals listed above, because the rate constants determined in each of these models was specific for the conditions of the experiment. Changing conditions in these models meant redetermining the kinetic parameters in the rate expressions. These new parameters could only be obtained by first doing actual experiments under the new conditions. Figure 1 shows the model and rate constants determined by Giralt et al. for a system in which only the solvent was changed.<sup>2</sup> The widely different reaction rate constants for some of the reactions indicate that no predictions of how the system would have performed when the solvent was changed would have been possible.

A model which is to fulfill the above goals must be able to account for the effects which take place when processing conditions are changed without resorting to redetermining the kinetic constants from experimental data. One approach has been to include additional terms directly in the kinetic equations used in the calculations. For example, basing ultimate conversion on coal type provides a way to include the type of coal directly into the models predictions. The ultimate conversion is related to characteristics of the coal being used. Such advances provide a partial answer, but coal type affects more than just the ultimate conversion, as different coals have different solubilities, amounts of mobile phase, numbers of free radicals, and donatable hydrogen. Solvent, solvent/coal ratio, reactor type, heat-up time, mixing speed, coal treatment, and gas phase pressure and composition must also be included in the model. As shown in Table 1, all of these variables have been included in this general model which has been developed.

### GENERAL MODEL

**NEW CALCULATIONS** Two things included in the kinetics of this model, which had not been included in previous models, are the basing of reaction rates on the *concentration* of reactants in the liquid phase and inclusion of an explicit hydrogen concentration. Earlier models used masses of reactants in the reactor, and ignored variable phase volumes and distribution of components between phases. Earlier models also assumed that hydrogen was not limiting in their systems and the hydrogen supply was considered constant. That prevents these models from being applied to systems in which the amount of hydrogen does influence the results of the reactions.

To include the effects of concentration and hydrogen pressure into the kinetic calculations required two additional sets of calculations to be simultaneously carried out. To determine reactant concentrations, both the volume of the liquid phase and the amount of each component in the liquid phase has to be determined. This required that the thermodynamic state of the system be continuously determined in conjunction with the kinetics, as changes in the reactor contents take place. Mass transfer calculations are also required to determine the rate at which solid coal particles dissolve into the liquid phase, and the rate at which hydrogen gas dissolves into the liquid phase. Mass transfer calculations require the thermodynamics calculations to set the maximum solubilities of coal and hydrogen gas in the liquid phase. Mass transfer also depends on kinetic calculations, through the viscosity of the liquid phase which changes as the liquefaction reactions take place. Thus the mass transfer, thermodynamic, and kinetic calculations are completely dependent on each other.

The model was set-up to be as accurate as possible in terms of mass transport and thermodynamic calculations. Figure 2 shows partition coefficients calculated by the model for

the hydrogen/tetralin system along with experimental data.<sup>3</sup> Figure 3 shows calculated and experimental viscosities for a coal liquid at three pressures for a range of temperatures.<sup>4</sup> These figures reflect the different kinds of experimental data which were incorporated into the development of this model. By including thermodynamics and mass transport, the properties of the solvent being used, such as its solubility parameter, vapor pressure, and viscosity became intimately connected with the calculations. The processing variables, solvent/coal ratio and mixing speed, are also directly taken into account through these calculations.

**NEW REACTION SCHEME** As mentioned above, hydrogen concentration was used in the reaction rate equations. To do this, a new scheme had to be developed for the liquefaction mechanism in which hydrogen directly participated in some of the reactions. The reactions were based more on the underlying chemistry which has been determined to take place, through both model compound and liquefaction studies. One of the major improvements in this model was the inclusion of free radical reactions as a significant part of the coal breakdown mechanism. The free radical intermediates could be either capped in reactions in which hydrogen participated, or recombined in retrograde reactions. The numbers of free radicals present was determined from both the coal type and the temperature in the reactor using correlations developed from literature data.

As in some earlier models, we assume a fixed fraction of the coal is unreactive. This amount is based on the coal type, but it does not have to be experimentally determined in this new model. Instead, a literature correlation of maximum conversions based on coal characteristics has been adapted to provide this value for any coal used in the model. In addition to the unreactive coal, the retrograde reactions form some material which will be unreactive; some fraction of the preasphaltenes and asphaltenes produced in the liquefaction are also considered to be stable. Empirical correlations were developed to determine the stable fractions also based on the coal characteristics. Data from a large number of liquefactions run under different conditions was used to determine the final coefficients in these correlations.

Both parallel and serial reactions were included in the scheme to allow for the production of asphaltenes and oils directly from the coal. Two separate coal breakdown reactions were specified, representing the two types of bonds which are normally broken in the coal structure, ether bonds and alkyl linkages between aromatic structures. The amounts of each fraction formed by these initial reactions was also set up to be dependent on the type of coal used in the model. The series reactions, including preasphaltenes to asphaltenes to oils and preasphaltenes to oils, were also made hydrogen dependent since hydrogen addition is a big part of the conversion to lower molecular weight products. In the model, hydrogen for these reactions comes from three sources: the coal, the solvent if it has donatable hydrogen, and hydrogen gas if present. The amount of hydrogen available from the coal is also determined from a literature derived correlation.

**COMPUTER PROGRAM** To make the model useable, a computer program was written to carry out all of the simultaneous kinetic, mass transport, and thermodynamic calculations. Including all of the various correlations for stable fractions, free radicals, coal solubility parameter, and the amount of donatable hydrogen from coal, allows the user to specify only the type of coal without having to first do all of these calculations to use the model. This required storing default values of the coal characteristics for each type of coal within the program. Solvent characteristics were also stored within the program for use in both the thermodynamic and transport calculations.

The final computer program which was produced is designed such that the user does not have to understand the inner workings of the model or the calculations included in the model. The user interacts with the program answering questions about the processing conditions which are to be used. Variables which must be input to the program include the reaction temperature, the type and amount of coal, the coal particle size and if the coal has been dried, the type and size of the reactor, the mixing speed and heat-up time, the type and mass of solvent, and the type of and pressure of the gas phase. The computer program calculates all necessary parameters which are dependent on the users input, then simulates the experiment using the model's calculations. Results of the simulation are given as preasphaltene, asphaltene, oil, gas, and THF insoluble material.

**PARAMETER FITTING** As with other kinetic models, the activation energies and frequency factors for each of the reactions had to be determined from experimental data. This model had a number of additional parameters which also had to be fitted. What is unique about this model is that data from experiments run under widely varying conditions was combined to carry out this parameter fitting. The data covered temperatures from 300 to 480 °C, 6 different types of coal, 4 different solvents, in both stirred autoclave and microautoclave reactors; short and long heat-up time experiments were included. Both hydrogen and inert gas phases were represented at pressures from 0 to 2000 psi, and solvent to coal ratios from 1/1 to 8/1 were covered.

Figure 4 shows a parity plot of experimental versus predicted coal conversions for 100 data points. Figure 5 shows a parity plot of the oil yields for those same data points. Because these points were used in fitting the model parameters, it is not surprising that the model predicts these results well. The diversity of conditions under which these simulations were run using the same set of kinetic constants, however, shows that the model has been able to incorporate a wide variety of processing conditions.

**RESULTS** The real test for this model was to show that the effects reported in the literature for changes in processing conditions could be reproduced by the model. A simulation was run using a set of conditions selected as the base case. The processing variables were then varied one at a time and the simulation results compared with experimental results for similar changes. The effects of temperature and solvent to coal ratio are predicted by this model. An effect of solvent is predicted, but comparison with experimental data shows that all properties of the solvent have not been fully incorporated into the model. Changes in product yields due to changes in coal type are predicted by the model, but do not follow the exact pattern seen in experimental studies. This was not completely unexpected, as the literature correlations used for taking coal characteristics into account in the model were determined over limited ranges of coal types. The effects of changing hydrogen pressure are predicted by the model, with less of a hydrogen effect seen in good hydrogen donating solvents as expected.

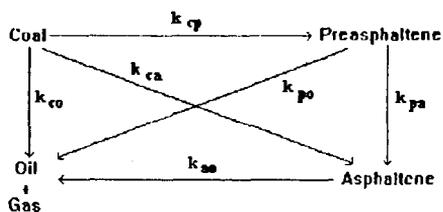
**CONCLUSIONS** A first generation general model for coal liquefaction has been developed in which the model parameters are not dependent on the liquefaction conditions. This allows the effects of changes in processing variables to be modelled without having to first run experiments to get the necessary kinetic parameters. Inclusion of both mass transport and thermodynamic calculations, along with the kinetic calculations, was needed to incorporate these processing variables into the model predictions. Development of a computer program proved to be the best way to carry out all of the simultaneous calculations which are needed in the model. The interactive nature of the computer program makes the model accessible for use by those unfamiliar with the underlying concepts on which the model was designed.

#### REFERENCES

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Table 1 Processing variables included in the model

Variable	Incorporated into model through:
Temperature	Influence on reaction rates Influence on ultimate conversion Influence on hydrogen availability from the coal and solvent Influence on the thermodynamics of the system
Coal type	Influence on ultimate conversion Influence on hydrogen available from coal Influence on initial production fractions Influence on the number of free radicals Influence on coal solubility
Solvent (type and amount)	Influence on the amount of available solvent hydrogen Influence on the system thermodynamics Influence on the coal and hydrogen gas solubilities Influence on the concentrations of reactants Influence on the viscosity
Pressure and gas phase composition	Influence on the system thermodynamics Influence on the amount of hydrogen available from the gas phase Influence on the hydrogen solubility
Reactor (type, size, and mixing speed)	Influence on the thermodynamics of the system Influence on the cold volume in the reactor Influence on the coal and hydrogen dissolution rates
Heat-up time	Reaction rates change during non-isothermal operation Amount of available hydrogen changes with temperature



	400°C		350°C	
	Tetralin	Anthracene oil	Tetralin	Anthracene oil
$k_{cp}$	.0964	.0978	.0575	.0766
$k_{ca}$	.0540	.0044	.0283	.0022
$k_{co}$	.0241	.0235	.0191	.0195
$k_{po}$	6.2E-6	.0066	2.7E-6	.0039
$k_{pa}$	1.8E-4	0	7.4E-5	0
$k_{ao}$	.0080	.0125	.0027	.0054

Figure 1 Reaction scheme and rate constants in two different solvents for a kinetic model by Giralt et al.

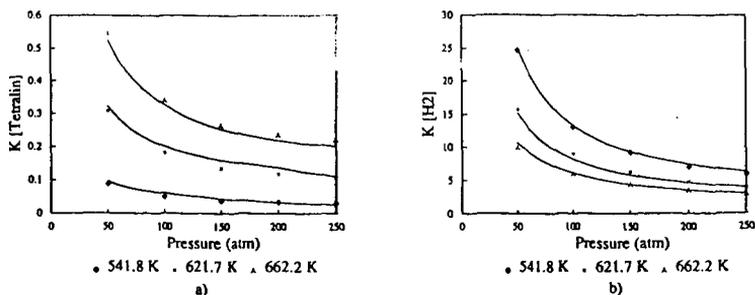


Figure 2 Predicted and experimental partition coefficients for hydrogen/tetralin system: a) tetralin, b) hydrogen.

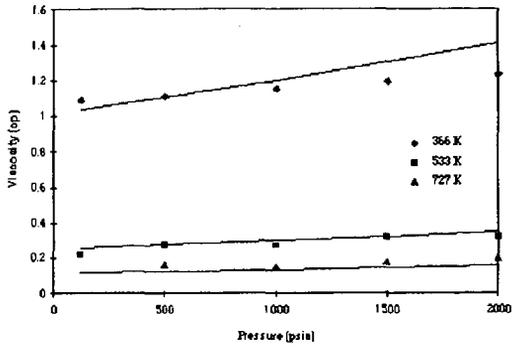


Figure 3 Viscosity of a coal liquid versus pressure at three different temperatures.

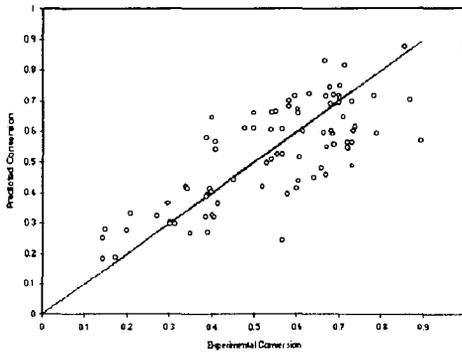


Figure 4 Parity plot of experimental and predicted coal conversions.

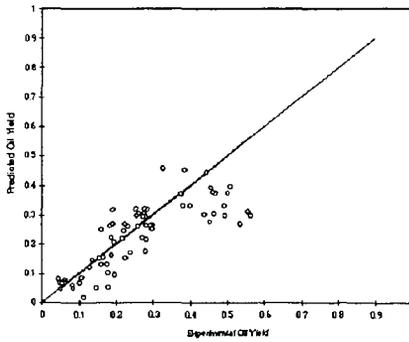


Figure 5 Parity plot of experimental versus predicted oil yields.