

Global Kinetics of Primary and Secondary Reactions in Hydrocarbon Gas Evolution from Coal Pyrolysis

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Introduction

The global pyrolysis kinetics of a Pittsburgh No. 8 Seam bituminous coal were studied previously (1,2) in a reactor where volatiles are rapidly diluted and quenched upon exiting the coal, thereby reducing the extent of secondary reactions of primary products. Despite this feature, a significant decrease in tar yield occurs as the pressure is increased, implying that the nascent tar contains reactive components capable of significant secondary reactions under conditions of interest in commercial coal processing. A study was undertaken to systematically determine the effects of temperature (500 to 900°C), residence time (0.6 to 1.1 s), and contacting surfaces (coal char, active carbon, and quartz) on the homogeneous and heterogeneous secondary reactions of tar from a Pittsburgh Seam bituminous coal.

In this paper, results for the formation kinetics of CH₄, C₂H₄, C₂H₆, and C₃'s by primary pyrolysis of the coal and of CH₄ and C₂H₄ by vapor-phase cracking of the tar are presented. An earlier paper (3) focused on the overall kinetics of the homogeneous and heterogeneous cracking of tar.

The kinetic parameters presented in this paper are understood to be global parameters, i.e., they represent the kinetics for the overall reaction A → B rather than any elementary step involving radical species. Consequently, the values obtained for activation energies correlate with the strengths of the bonds which are being broken, but are not equivalent.

Experimental

The apparatus is a reactor containing two independently heated, series-connected stages for controlled generation and reaction of volatiles (3,4,5). A thin bed of coal, diluted with sand to prevent agglomeration, is pyrolyzed in the upstream stage at a low heating rate (3°C/min) in order to produce fresh volatiles at temperatures (<500°C) which are unfavorable to secondary reactions. These volatiles are then rapidly transported by an inert carrier gas to a second (isothermal) stage, held between 500 and 900°C, and then to a collection system. In preliminary experiments (referred to as "base case"), the volatiles generated in the first stage pass directly to the collection system.

In the second (reaction) stage, the separate effects of temperature and residence time (0.6-1.1 s) on the homogeneous secondary reactions of the primary tars are systematically studied. Conditions are chosen such that the cracking reactions of light oils and light hydrocarbon volatiles are relatively unimportant. Consequently, changes in the composition of volatiles within the second stage are attributed solely to secondary reactions of the tar.

Results and Discussion

Kinetics of Tar Formation and Tar Cracking

Cumulative yields of tar as a function of formation temperature are shown in

Fig. 1. Since the heating rate is constant, the abscissa can also be considered a time axis. This figure includes data from base case experiments (no cracking stage) and homogeneous cracking experiments with a gas-phase residence time (V/F, plug flow) of 1.1 s and a temperature ranging from 700 to 900°C in stage 2.

The base case data in Fig. 1 were obtained with a carrier-flow rate equivalent to a nominal stage-2 residence time of 1.1 s. Other base case runs having nominal stage-2 residence times from 0.5 to 3.0 s gave very similar tar yields and evolution profiles (4,5). This result indicates that the evolution of tar from the bed is not limited by mass-transfer into the bulk gas. The independence of tar evolution rate with respect to carrier gas flow rate is important since this parameter is used to control volatiles residence time in the second stage.

The base data also show that the maximum rate of tar formation occurs at relatively low temperatures ($\sim 430^\circ\text{C}$) and that over 90 percent of the tar is formed below 500°C. Consequently, one can assume that the tars being formed in the first stage are "primary," i.e., they have not yet been subjected to significant secondary reactions.

The dotted curve drawn through the base data in Fig. 1 has been generated by fitting with a kinetic model which assumes an infinite set of parallel, first-order decomposition reactions with a Gaussian distribution of activation energies (6). The parameters obtained by fitting this model or a simple, single first-order reaction model to the tar formation data are given in Table 1, below.

TABLE 1. TAR FORMATION KINETIC PARAMETERS

Model Type	A 1/s	E (kcal/mole)	σ (kcal/mole)	v^* (wt. % of coal)	RMS Error
Single Reaction	2.56×10^5	27.1	--	23.03	0.026
Multiple Reaction	4.54×10^7 3.80×10^{13}	34.2 52.8	1.1 2.5	23.27 23.41	0.024 0.025

Depending on the initial guess used to initiate the numerical data fitting routine, the multiple reaction model gives two sets of kinetic parameters, which fit the data equally well. Discriminating between these sets will require data from experiments at different heating rates. Since, in all cases, the activation energy for tar formation is higher than would be expected for a physical process, and because of the flow-independence, it is likely that the rate-controlling mechanism for tar evolution is chemical kinetics. This result differs from the study of Unger and Suuberg (7), where evaporation of tar was thought to be rate-limiting. This difference can probably be attributed to the reactor system used in their study, in which a thin layer of coal is heated in the absence of a forced convective flow.

The success of the single reaction model and the small values of σ for the multiple-reaction model indicate that the formation reactions for tar involve only a small range of activation energies, suggesting that primary tar is formed by decomposition of only a few types of bonds in the coal.

The other data sets in Fig. 1 were fitted with an equation with the form of the multiple reaction model but these plots reflect the combined influence of tar generation and tar secondary reactions. Consequently, no kinetic parameters were obtained directly from this fit. However, by using the asymptotic values of tar yield the overall conversion of tar (relative to the base case) was calculated. These data are shown in Fig. 2 for several homogeneous cracking experiments performed at temperatures between 500 and 900°C and nominal residence times of 0.6 and

1.1 s. The data were fit to a model which assumes that the tar consists of three "lumps" of different reactivity, which react independently. The first lump, "A" tar, is the most reactive and is assumed to decompose via a first-order reaction into gases and light oils at relatively low severities. The "B" tar is moderately reactive and decomposes to similar products by a parallel first-order reaction with a presumably higher global activation energy than that of lump "A." The "C" tar is assumed to be unreactive under the present conditions. The percentages of A, B, and C were obtained by inspection of the apparent plateaus in the conversion data (Fig. 2). This resulted in values of 33, 27, and 40 wt. percent for A, B, and C, respectively. Additional details of the model have been discussed previously (3). The kinetic parameters are given in Table 2.

TABLE 2. TAR SECONDARY REACTIONS/KINETIC PARAMETERS FOR 3-LUMP MODEL

LUMP	A 1/s	E (kcal/mole)	T* (wt. % of tar)
A	1.25×10^9	39.4	33.0 (fixed)
B	8.04×10^{12}	65.2	27.0 (fixed)
C	--	--	40.0 (fixed)

Hydrocarbon Gas Formation

The evolution rates of primary hydrocarbon gases (CH_4 , C_2H_4 , C_2H_6 , C_3H_6 + C_3H_8) are presented in Figures 3-6, respectively. The data clearly show that the gas formation kinetics are independent of carrier flow rate. (This same result was observed for the tar).

These data were obtained from base case experiments where the bed temperature in stage-1 is increased at $3^\circ\text{C}/\text{min}$ to 550°C and then held at 550°C for 30 minutes. Only the non-isothermal data have been plotted in Figs. 3-6 and used in the modeling calculations. The gas data are fit to a single reaction first-order model and also to a multiple independent-parallel reaction model, in the same manner as the tar data. The kinetic parameters obtained from a least-squares fit are given in Table 3, below.

TABLE 3. LIGHT GAS FORMATION/KINETIC PARAMETERS

Gas	A (1/s)	E (kcal/mole)	σ (kcal/mole)	v* (wt. % of coal)	RMS Error
- single rxn model					
CH_4	7.52×10^5	30.3	--	1.44	0.073
C_2H_4	2.75×10^5	29.2	--	0.13	0.027
C_2H_6	3.05×10^6	31.6	--	0.51	0.054
C_3 's	8.90×10^{11}	48.6	--	0.12	0.085
- multiple rxn model					
CH_4	4.68×10^{11}	50.0	2.5	1.59	0.064
C_2H_4	2.79×10^{12}	53.1	2.8	0.14	0.020
C_2H_6	$+1.00 \times 10^{13}$	52.9	2.1	0.53	0.047
C_3 's	7.33×10^{13}	55.0	1.2	0.13	0.081

+ indicates a parameter which is fixed during the fitting routine

With the exception of methane, both models describe the data fairly well although the multiple parallel reaction model gives more reasonable parameters (A and E), a better overall fit to the data (smaller RMS error), and a value of V^* that is closer to the experimental value. For methane, it appears that there is an overlapping set of reactions which cannot easily be fit with a single reaction or a Gaussian distribution of reactions. Other studies have fit methane formation data with a set of 2 to 4 parallel first-order reactions (8,9,10). A similar approach has been used for other gases, when necessary.

Gas Formation from Tar Cracking

A determination was made of how well the kinetics for "secondary" CH_4 and C_2H_4 formation in the volatile cracking experiments agreed with the kinetics for disappearance of tar based on the three-lump model. Only CH_4 and C_2H_4 were examined because these gases are the most stable, being resistant to secondary cracking at temperatures below 800°C. For the same reason, only low-temperature (<800°C) tar cracking and secondary gas formation were considered. This regime corresponds to decomposition of the "A" lump in the 3-lump cracking model discussed above (see also Fig. 2).

These two gases account for about 1/3 of the products of low temperature decomposition, while an additional 1/3 is estimated to be light oil (4,5). However, the light oil (primarily benzene, toluene, and xylenes) is not as easily quantified due to difficulties in collection, so it was not considered in this analysis.

The yields of secondary CH_4 and C_2H_4 were determined by subtracting their corresponding base case yields (no cracking stage) from their yields in a homogeneous cracking experiment. These results are plotted in Figs. 7 and 8, for CH_4 and C_2H_4 , respectively.

The kinetic analysis was done by fixing the preexponential factor at the value obtained for the "A" lump of tar. Then the V^* was fixed at a value corresponding to the yield at 750°C and a regression analysis was done to calculate the value of the activation energy. The results are given in Table 4.

TABLE 4. SECONDARY REACTION KINETIC PARAMETERS

SPECIES	A (1/s)	E (kcal/mole)	T^* (wt % of tar)	V^* (wt. % of coal)
- Secondary Formation				
CH_4	$+1.25 \times 10^9$	40.2	+4.6	+1.1
C_2H_4	$+1.25 \times 10^9$	39.4	+5.8	+1.4
- Secondary Decomposition				
"A" tar	1.25×10^9	39.4	+33.0	+8.0

⁺indicates a parameter which is fixed during the fitting routine.

In both cases, the value of the activation energy was very close to that for decomposition of lump "A."

These results indicate that:

- 1) The additional ethylene and methane formed in secondary reactions are predominantly from tar cracking rather than cracking of other gases. This

result supports one of the key assumptions of the reactor system:

- 2) The two gases are formed from tar by breaking bonds of similar strength and/or type, which supports the concept of dividing the tar into "lumps" containing bonds of similar reactivity.

Comparison of Gas Formation from Coal Pyrolysis and Tar Decomposition

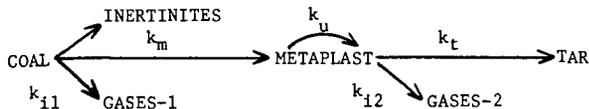
It is instructive to compare the rate constants for the formation of CH_4 , C_2H_4 , C_2H_6 , C_3 's, and tar from the primary pyrolysis of coal with those for the low-temperature (vapor-phase) decomposition of tar to form CH_4 and C_2H_4 (among other products). These are plotted in Fig. 9 for the temperature range of 300 to 700°C. The rate constants were calculated from the Arrhenius parameters in Tables 3 and 4. Because of the similarity of the parameters for secondary formation of CH_4 and C_2H_4 from tar with those for the overall decomposition of tar (lump "A"), only the latter values were used.

One conclusion from this plot is that, even at relatively low temperatures (350-500°C), the intrinsic rate of tar decomposition to form CH_4 , C_2H_4 , etc., is greater than or equal to the intrinsic rate of formation of these gases from primary pyrolysis of the coal. This result is not surprising, in light of the fact that these gases are formed from cracking of side chains of aromatic units in either case. The only difference is that the side chains are attached to a volatile species in the case of tar. The fact that the rate of gas formation from tar is actually somewhat greater than that from the coal can be explained based on the sequence of product evolution indicated in the composite plot shown in Fig. 10. It is apparent that significant light gas formation occurs after the maximum rate of tar evolution has ended. Consequently, it would be expected that the viscosity of the coal melt would be increasing as the evolution of light gas proceeds. It is known that the rates of bond homolysis reactions in the gaseous and liquid phases are generally the same within a factor of 2, but the latter tend to decrease with increasing melt viscosity due to so-called "cage" effects (11).

Comparison of the Rates of Tar Formation and Tar Decomposition

From Fig. 9, it is also apparent that the intrinsic rate of tar cracking is comparable to or greater than that of tar formation over a wide range of temperature. This fact underscores the necessity of removing the tar quickly from the generation zone in order to prevent cracking of side chains and aliphatic (or etheric) linkages. Failure to do so will result in increased yields of light gases (e.g., CH_4 , C_2H_4) and light oil at the expense of tar. Consequently, it would be expected that, in coal pyrolysis, factors which affect the time-temperature history of the tar and/or the escape of tar from the coal will also affect the yield of light hydrocarbon products. These factors would include the heating rate, which can affect both the time-temperature history and the evaporation rate of the tar. (Note: For the purpose of this discussion, it is assumed that the coal of interest is a softening bituminous coal and that the tar does not react further once it escapes from the melt.)

The phenomenon is best understood by first considering the behavior of tar during pyrolysis according to the model proposed by Unger and Suuberg (12) for a softening bituminous coal:



In this scheme, which is well supported by the body of evidence in the literature, the metaplast is the tar precursor. It can be evaporated as tar (k_t), undergo repolymerization to form char (k_c), or give rise to additional gas formation via side-chain cracking (k_{12}). In the case where formation of tar is rate-limiting ($k_t \gg k_m$), it would be expected that an increased heating rate would lead to increased light gas formation since the temperature interval of tar formation would be shifted upward (13) to temperatures where the rate of tar cracking becomes greater than the formation rate (see Fig. 9).

If the evaporation rate of tar is rate-limiting ($k_m \gg k_t$) the light gas yields would be increased over the case of no mass-transfer limitations but would not be sensitive to heating rate, provided that the final temperature is the same in every case. This is a result of the fact that, while the tar is formed at lower temperatures as the heating rate is reduced, it still cannot escape until relatively high temperatures are reached. Consequently, there is ample opportunity for side-chain cracking at any value of the heating rate.

The above hypotheses can be tested by examining some recent work from the literature. Suuberg (13,14) used a captive sample, screen-heater apparatus to study changes in volatiles composition with heating rate for the Pittsburgh No. 8 Seam coal. Over a range from 350-15,000°K/s, no significant effect was observed. Conversely, Stangeby and Sears (15) studied a comparable Canadian coal using a similar system and found a significant increase in CH_4 and C_2H_4 yield as the heating rate was raised from 250 to 6000°K/s. Desypris et al. (16) found the same result for an Australian bituminous coal over the range from 450 to 1800°K/s. In all of the above studies the reactor system, final temperature ($\sim 1000^\circ C$), and pressure (~ 1 atm) were similar. However, in the latter two studies a gas flow was superimposed on the screen-heater during pyrolysis to enhance mass-transfer of the volatile species.

This disagreement can be explained based on the presence or absence of mass-transfer effects. In Suuberg's experiment it is likely that the rate of tar evolution was limited by tar evaporation. This conclusion is based on recent studies, using gel permeation chromatography, of tars from a similar experiment (17). In the work of Stangeby and Sears and Desypris et al., it is likely that such limitations were not a factor. This concurs with results from the present study (discussed above) for a gas-swept fixed-bed and explains the sensitivity to heating rate.

While high heating rates can promote tar cracking in experiments where tar evaporation is rate-limiting, they are not always detrimental. If the heating rate is too slow, the low volatility of the tar will cause it to accumulate, thus providing an opportunity for repolymerization reactions to occur. In practice, the reduction in tar yield by this mechanism may be more important than by side chain cracking as evidenced by the dramatic reduction in tar yield and corresponding increase in char yield observed when tar escape is inhibited by increasing the ambient pressure (13,14).

An example of how the heating rate can affect such reactions is the work by Warren (18,19,20), who did a series of studies on pyrolysis of packed beds of coal. It was found that the yield of tar increased at the expense of gas and coke when the heating rate was increased from 0.7 to 21.80°K/min.

A theoretical basis for this phenomenon can be found in the model compound work of Van Krevelen (21). An increase in heating rate was observed to increase the yield of volatiles from pyrolysis of a hydroxyl-substituted polycondensed aromatic system, but had no effect on the unsubstituted polycondensate. Van Krevelen theorized that, in the former case, evaporation of tar competed with repolymerization via hydroxyl groups.

It should be noted that in the high heating rate studies discussed above (14,15,16) the total yield of volatiles was found to be independent of heating rate in all cases. This result implies that the repolymerization reactions are not influenced by heating rate at values above $\sim 100^\circ\text{K/s}$.

Conclusions

The above discussion would indicate that there is an optimum heating rate for tar yield. This has been found by Freihaut and Seery (22), who studied the vacuum pyrolysis of a variety of coals in a captive sample reactor at heating rates of $1-10^3^\circ\text{C/s}$. They found a variation in tar yield for two high volatile bituminous coals, with an optimum value of 10^2°C/s (for maximum tar yield). Other coals were not nearly as sensitive to heating rate.

In theory, if the rates of tar formation, tar evaporation (which depends on the molecular weight distribution), tar cracking, and tar recombination reactions are well-known, the optimum time-temperature path to maximize tar yield could be predicted. The model proposed by Unger and Suuberg (12) does incorporate most of the important features of the chemistry and transport of tar, but requires better information on the tar molecular weight distribution and the kinetics of tar formation and secondary reactions. The overall objective of the present study is to provide some of the information on tar which is now lacking.

Acknowledgements

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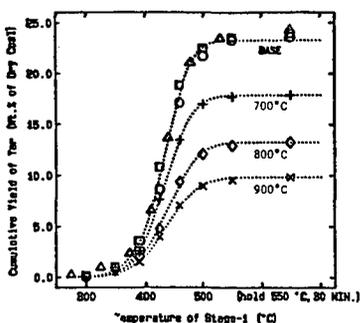


Figure 1. CUMULATIVE YIELD OF TAR vs. FORMATION TEMPERATURE
 Data for base case and homogeneous reaction at 1.1 s residence time; (---) Multiple reaction model; Parameters for base case are given in Table-1.

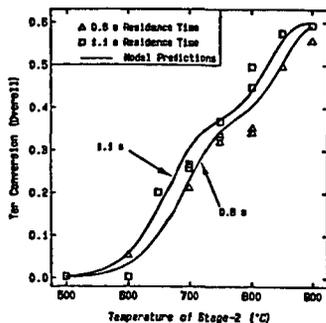


Figure 2. TAR CONVERSION FOR HOMOGENEOUS REACTION
 Parameters for model are given in Table-2.

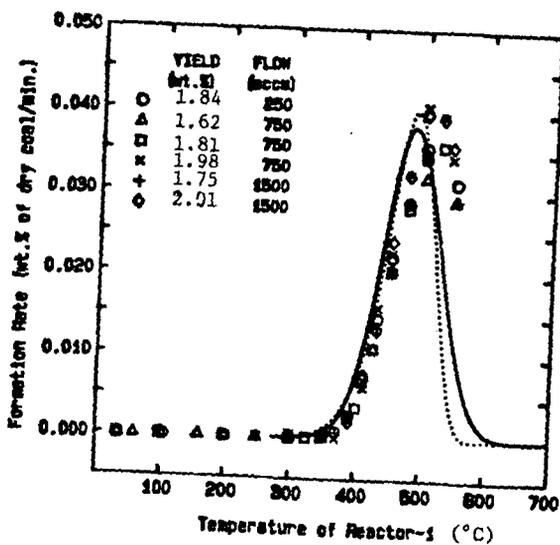


Figure 3 FORMATION RATE OF PRIMARY METHANE
 (.....) single reaction model
 (————) multiple reaction model
 Parameters are given in Table 3.
 Yields are experimental values.

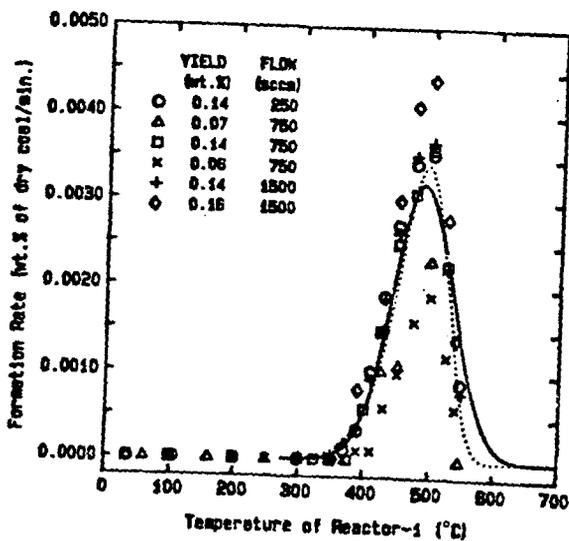


Figure 4 FORMATION RATE OF PRIMARY ETHYLENE
 (.....) single reaction model
 (————) multiple reaction model
 Parameters are given in Table 3.
 Yields are experimental values.

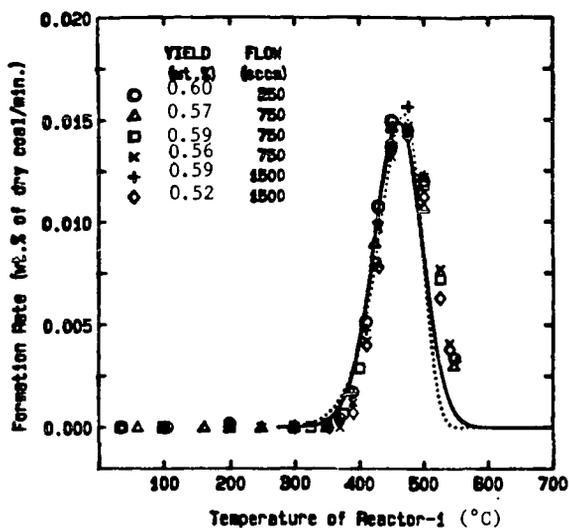


Figure 5 **FORMATION RATE OF PRIMARY ETHANE**
 (.....) single reaction model
 (—) multiple reaction model
 Parameters are given in Table 3.
 Yields are experimental values.

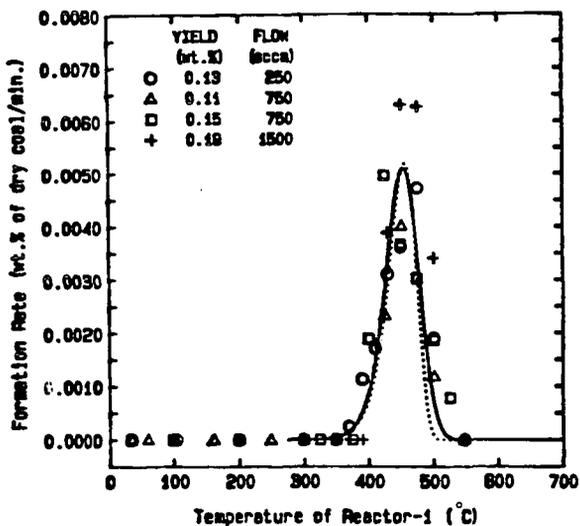


Figure 6 **FORMATION RATE OF PRIMARY PROPANE (AND PROPYLENE)**
 (.....) single reaction model
 (—) multiple reaction model
 Parameters are given in Table 3.
 Yields are experimental values.

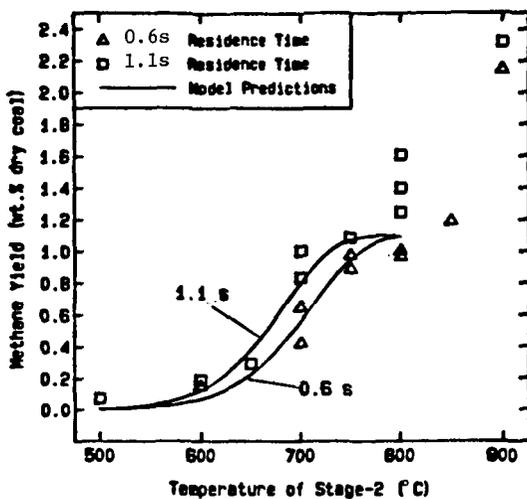


Figure 7 METHANE YIELD FROM SECONDARY REACTIONS
Parameters for model are given in Table 4.

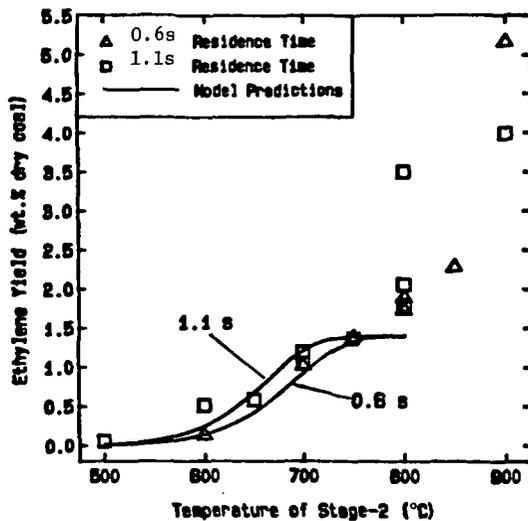


Figure 8 ETHYLENE YIELD FROM SECONDARY REACTIONS
Parameters for model are given in Table 4.

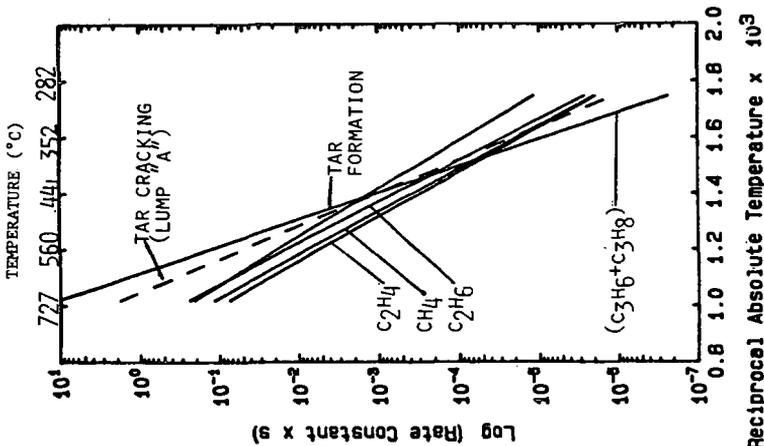


Figure 9
RATE CONSTANTS FOR PRIMARY GAS AND TAR FORMATION AND TAR CRACKING

Calculated from parameters in Table 3 and 4.

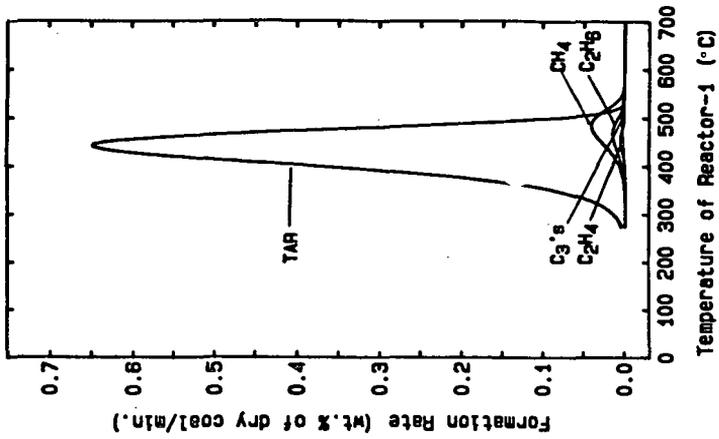


Figure 10
FORMATION RATE OF PRIMARY GAS AND TAR

Calculated from parameters in Tables 1 and 3.