

SYMPOSIUM ON PYROLYSIS REACTIONS OF FOSSIL FUELS
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THE MECHANISM OF THE HYDROGEN TRANSFER PROCESS
TO COAL AND COAL EXTRACT

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INTRODUCTION

A rather vast literature exists on the subject of solvent extraction of coal and excellent review articles are available. (1,4) The bulk of the literature deals with the effect of variation of chemical composition of the solvent and the nature of the coal on results achieved. Much less attention has been accorded to kinetic measurements of the dissolution process. H. P. Oele (5) and co-workers, however, studied in some detail the kinetics of coal dissolution in anthracene and β naphthol solvents. No transfer of hydrogen is involved in the process and the term extractive disintegration was coined to describe it.

A process has been under development for the past several years in the laboratories of the Consolidation Coal Company for the production of synthetic gasoline from coal. The first step in the process is the extraction of coal with a process derived solvent which possesses hydrogen donor properties. The process is thus one which involves transfer of hydrogen from the solvent to coal, similar to that studied by Pott-Broche (6) and others. Some literature data (3) were found relevant to the kinetics of this specific type of extraction process as applied to brown coal but little rate data appears to be available with bituminous coals.

Such data were therefore obtained to aid in the rational development of the process. The data reported here were all obtained with chemically pure solvents in order to simplify interpretation of the measurements and were all obtained in a batch system. Kinetic data were also obtained in a continuous system but this will be reserved for later publication.

The significance of the data to the mechanism of the hydrogen transfer process is discussed in some detail in this paper.

EXPERIMENTAL

The experiments were conducted in a micro-autoclave constructed of 316 stainless steel. The dimensions were 0.625" I. D. and 6" long with an internal volume of 30 ml. The autoclave was shaken vertically at 2300 cycles per minute. The shaking device was driven by an electric motor whose rotary motion was converted to reciprocating motion by means of a crank and cross-head linkage. The shaker was supported above a large fluidized sand bed which could be moved up and down rapidly by means of pulleys to immerse or expose the entire autoclave.

The experiments were conducted by first preheating the sand bed to about 40°F above the desired run temperature followed by rapidly immersing the autoclave in the sand bed. Blank experiments showed that the inner temperature of the autoclave rose to within 3°F of the desired temperature 2.5 minutes after immersing the autoclave in the sand bed. Final temperature control was effected by the addition of a dollop of cold sand to the fluidized bed.

At the end of the desired residence time, the sand bath furnace was lowered and a container of cold water was raised to surround the still shaking autoclave. This cooled the autoclave to essentially room temperature in less than 30 seconds. The reaction times reported are taken as the total time from immersion to quenching less one minute for effective heat up time.

All coal runs were made with a Pittsburgh Seam coal from the Ireland Mine in Northern West Virginia. The coal was crushed and screened to give two fractions, i. e., 100 x 200 Mesh and 28 x 48 Mesh with the analyses shown in Table I-A.

Initial runs showed identical results with the two size fractions so that all further work was carried out with the 28 x 48 Mesh coal.

Each run was conducted with 2 grams of coal while the total amount of solvent was varied between 4 and 8 ml. in individual runs.

No attempt was made to remove air from the autoclave before sealing. The oxygen content of the air above the charge varied between 0.3 to 0.7 wt. % of the coal depending on the filling ratio of the autoclave.

The depth of extraction was measured by the amount of filter cake obtained which was insoluble in xylenol at 220°F. The coal conversion was calculated from the weight of dry filter cake and the weight of coal charged as follows:

$$\% \text{ Coal Conversion (MAF)} = \frac{100 (\text{g MAF coal charged} - \text{g dry cake})}{\text{g MAF coal charged}}$$

Experiments were also conducted with a "shallow" coal extract whose composition is given in Table I-B. The extract was prepared by extraction of Ireland Mine coal in a one-gallon stirred autoclave at 650°F for one hour using decalin as solvent. The depth of extraction was 23 percent of the MAF coal.

The bulk of the runs used tetralin as a model for the hydrogen donor liquid, although other pure hydrogen donors were used as will be discussed below.

The amount of hydrogen transferred was determined by analysis of the recovered solvent. The principal product resulting from the transfer of hydrogen to the coal is naphthalene. Appreciable quantities of indane and C₄ benzenes are also formed. Small quantities of cis and trans decalin may also be present.

The weight percent hydrogen in the recovered solvent was determined from the recovered solvent analysis assuming no materials boiling below indane or above naphthalene were formed from the tetralin. The weight of hydrogen transferred was then determined from the difference in weight of hydrogen in the feed tetralin and recovered solvent.

The analysis of the recovered solvent was carried out by first vacuum distilling the product filtrate to recover a cut with a nominal boiling range of 160 x 230°C at 1 atmosphere. The above fraction was extracted with 10% aqueous caustic to remove the tar acids and then analyzed with a Perkin-Elmer Model 154C gas chromatograph.

Separate aliquot portions are analyzed on two different columns as given below:

- Column No. 1 (Polar) - 20% diisodecylphthalate on 60 x 80 M Chromosorb in 1/4" O. D. x 8' stainless steel column at 175°C.
- Column No. 2 (Non-Polar) - 20% DC - Silicone oil on 60 x 80 M Chromosorb in same type column as above maintained at 160°C.

The polar column is used to effect adequate resolution between the naphthalene and tetralin peaks which cannot be achieved with the non-polar column.

Similar gas chromatography analyses were made to define the amount of hydrogen transferred from other pure solvents.

Some experiments were also conducted in either a 300 ml Aminco rocking autoclave or a 1 liter Parr bomb. This was done when the main purpose was not kinetic measurements but to obtain a more complete analysis of the reaction products.

RESULTS AND DISCUSSION

A. Maximum Amount of Hydrogen Transfer

The emphasis in the discussion of the kinetic results will be on measurement of the amount of hydrogen transferred since this is a quantity identifiable with a precise chemical process. Experimental work indicated that there is a "practical" maximum quantity of hydrogen that can be transferred to either coal or extract in a purely thermal process. Some additional hydrogen transfer may be obtained by further treatment at more severe conditions, but little in the way of new useful products are obtained, i. e., very little conversion of asphalt to liquid products occurs. These maximum limits for the coal and extract used in this work are apparently 2.6 and 2.2 wt. % of hydrogen transferred, respectively.

The product distribution resulting from extraction of coal at conditions approaching maximum hydrogen transfer are given in Table II.

B. Basic Nature of Reaction

The hydrogen transfer reaction is first of all a purely thermal process, i. e., attempts to accelerate the reaction with contact catalysts of the hydrofining type (cobalt molybdate on alumina) or with cracking catalysts (silica-alumina) were unsuccessful.

It may be natural to regard the process, also, as a simple second order reaction involving coal or extract molecules and a hydrogen donor molecule.

TABLE II
Hydrogen Donor Extraction of Ireland Mine Coal
at Severe Conditions

	100 x 200 Mesh		Tetralin/Coal, Wt. Ratio		1
	28 x 48 Mesh	4.66	1.5	3.0	
<u>Time-Temperature History, Mins.</u>					
		715-825°F	10	13	715-750°F
		Hold 825°F	60	60	Hold 750°F
		825-715°F	11	4	750-715°F
		2.25			
		6.25			
<u>Yields, Wt. % MAF Coal</u>					
H ₂			0.3	0.5	0.1
H ₂ S + CO ₂ + CO			1.6	1.0	0.9
H ₂ O			5.0	3.3	3.5
C ₁ -C ₃ Hydrocarbons			4.5	3.1	1.3
C ₄ x 400°F Distillate			5.4	18.4	14.2
400°F x 750°F Distillate			16.2		
Heavy Oil ⁽¹⁾			26.4	29.0	20.9
Asphaltenes ⁽²⁾			18.4	35.0	42.1
Benzene Insolubles ⁽³⁾			16.6	4.8	10.9
Cresol Insolubles			8.0	7.4	7.5
Total			102.4	102.5	101.4
% H ₂ Transferred			2.4	2.5	1.4

(1) Soluble in cyclohexane.
(2) Soluble in benzene - Insoluble in cyclohexane.
(3) Soluble in cresol - Insoluble in benzene.

TABLE I

A. Analysis of Feed Coal

% by Wt. Dry Basis	28 x 48 Mesh	100 x 200 Mesh
H	4.86	4.66
C	71.77	70.21
N	1.25	1.48
O (diff.)	7.12	6.51
Organic S	2.48	2.25
FeS ₂	3.70	6.25
Other Ash	8.82	8.64
Total Ash	12.52	14.89

B. Analysis of Feed Extract

	Wt. %
H	6.52
C	83.39
N	1.23
O	6.28
S	2.58
Heavy Oil	22.6
Asphaltenes	47.0
Benzene Insolubles	30.4

There are two objections to this point of view. First of all, if this were so the process should follow a simple second order rate law

$$\frac{dH}{dt} = \frac{k(E)(H_T - H)(H_1^0 - H)}{100} \quad (1)$$

The definition of terms used in equation (1) is given in the appendix. The integrated form of equation (1) is

$$kt = \left(\frac{100}{H_1^0 - H_T} \right) \cdot \frac{1}{E} \ln \left[\frac{H_T(H_1^0 - H)}{H_1^0(H_T - H)} \right] \quad (2)$$

where H_T is assigned the value of 2.6 in the case of Ireland Mine coal. The justification for this will be presented later. It should be remembered here that $H_1^0 = 400/132$ (T/E).

It is undoubtedly naive to consider that simple second order kinetics would hold in this case where one is dealing with a non-homogeneous system. However, if the true mechanism is of this type, the second order rate law should hold at least approximately.

The results of such a test of the validity of the second order mechanism are given in Table II. Since the rate constant varies by a factor of 5 over the limited range of conditions tested, it is justifiable to discard the second order mechanism.

Another clue pointing in the same direction is the behavior of different solvents. A true second order reaction would naturally involve very specific stereochemical effects. Thus, it would be expected that only solvents that are very similar in structure would function at all, and that the rate of hydrogen transfer would depend markedly on the chemical structure of the donor.

Data summarized in Table IV again show that these properties of a second order process are not found. A wide diversity of solvents function as hydrogen donors as long as they contain mobile hydrogen bonds. The rate of hydrogen transfer with the more active donors appears to be about the same and independent of their structure.

It would seem, therefore, that the rate of thermal decomposition of the coal determines the extent of hydrogen transfer once a sufficiently reactive donor is used.

These observations would point to a free radical mechanism. The coal is dissociated into free radicals by thermal decomposition which are stabilized by capture of a hydrogen atom from a donor molecule. The hydrogen saturated radicals are now stable molecules and are sufficiently low in molecular weight to be soluble in cresol. Thus, a direct relationship exists between solvent extraction depth and hydrogen transfer. This subject will be discussed in more detail later.

Thus, if donor of sufficient activity or concentration is used, one in effect is studying the rate of thermal decomposition of coal or extract into free radicals.

C. Coal Conversion Kinetics

It is therefore logical to test the above proposition by treating the hydrogen donor extraction process as a first order reaction. The above treatment should apply under conditions where a high ratio of donor to coal is used such that change in concentration of donor during the course of the reaction may be neglected. Such a series of kinetic runs were made using a ratio of 4 cc tetralin per gram coal.

Figure 1 shows a first order rate plot for these runs for coal conversion where $\log \left(\frac{1}{1-\alpha} \right)$ is plotted against time. It is noted that the points of longer residence times fall reasonably well onto a straight line, but that short time points fall well below the line.

The treatment of coal conversion per se as a first order process assumes that only a single thermal decomposition process occurs with a characteristic rate constant. As a matter of fact, it appears more reasonable to assume that two or more decomposition processes occur simultaneously with different rate constants. The rate of coal pyrolysis on this model is given by the expression

$$C_T - C = \sum_{i=1}^n C_i e^{-k_i t} \quad (3)$$

where C_i is the weight percent of the coal which decomposes with the characteristic rate constant k_i .

After a relatively long reaction time, all terms with the higher rate constants decay rapidly such that only the last or slowest rate remains important. The coal conversion rate under these conditions reduces to

$$C_T - C = C_n e^{-k_n t} \quad (4)$$

TABLE III
Second Order Rate Constants in
Hydrogen Transfer to Coal at 730°F

Vol. % Tetralin in Solvent	$E \left(\frac{\text{gms MAF Coal}}{\text{cc}} \right)$	(T/E)	H_0	H_T	H	t (min.)	$k \text{ (min.}^{-1} \text{ cc gm atoms}^{-1}\text{)}$
100	0.178	4.5	13.6	2.6	0.48	10	0.85
↓	↓	↓	↓	↓	0.71	20	0.67
↓	↓	↓	↓	↓	1.22	60	0.36
25	0.178	1.12	3.39	2.6	0.16	5	2.12
↓	↓	↓	↓	↓	0.32	20	1.12
↓	↓	↓	↓	↓	0.47	60	0.56

TABLE IV
Comparison of Hydrogen Donor Activity of
Various Organic Substances
 Ireland Mine Coal Used in All Cases

Solvent	Temp., °F	Residence ⁽¹⁾ Time, Min.	% Hydrogen Transferred to MAF Coal
A - Perhydrophenanthrene	716	60	0.21
Decalin	734	↓	0.28
Indane	716	↓	0.33
o-Cyclohexylphenol	716	↓	0.98
Tetralin	716	↓	1.12
Dihydrophenanthrene	716	↓	1.21
<hr/>			
B - Tetralin	620	60	0.22
Cyclohexanol	620	↓	0.42
<hr/>			
C - 50% Tetralin-50% Decalin	800	20	1.36
50% Isopropanol-50% Decalin	800	↓	1.14

(1) Excludes heat-up time.

Equation (4) may be rearranged to the form

$$\ln \frac{1}{1-\alpha} = -\ln \left(\frac{C_N}{C_T} \right) + k_N t \quad (5)$$

Thus, in a first order plot such as shown in Figure 1, the slope is the value k_N of the smallest rate constant and the intercept $-\ln (C_N/C_T)$ may be used to determine the weight fraction of the coal (C_N/C_T) which decomposes at the low rate.

The above treatment leads to values of .52 and 0.38 for the ratio C_N/C_T at 670 and 730°F, respectively. It is clear that this ratio must be constant and not a function of temperature if it represents the true physical picture.

A more accurate analysis of the situation was made on the analog computer. It was assumed here, as shown in Figure 2, that one is dealing here with only two first order rates occurring in parallel, i. e., a relatively fast and a relatively slow rate. The best fit, which is the one shown in Figure 2, was made on the assumption that $\gamma = 0.50$, i. e., half the coal decomposes at a fast rate.

The fit obtained with this model is eminently satisfactory. The values of the rate constants obtained from the analog computer are given in Table V. It is seen that the high conversion rate is of the order of ten times the slow rate.

D. Relationship Between Coal Conversion and Hydrogen Transfer

The kinetic treatment of the coal conversion process is far from rigorous, since it is not possible to identify it with a precise chemical change. The above kinetic treatment presupposes that in essence two types of coal co-exist, i. e., refractory and labile material.

Hydrogen transfer can on the other hand be identified with a more definite chemical process. On the basis of the free radical picture outlined above, each gram mole of hydrogen transferred can be identified with the dissociation of a specific chemical bond into two free radicals.

The relationship between coal conversion and hydrogen transfer, therefore, might be helpful in throwing some light on the mechanism of the coal extraction process itself. The graphical relationship between the two quantities at 670 and 730°F is shown in Figure 3 and 4, respectively. In this work the solvent consisted of pure tetralin, or tetralin diluted with various quantities of another solvent of which decalin, paraffin hydrocarbons and xylene were used. Surprisingly enough, the coal conversion from these data alone appears to be little affected by the composition of the solvent and is determined primarily by the amount of hydrogen transfer. It is seen that the first 50 percent coal conversion is obtained with very little hydrogen transfer, i. e., < 0.2 wt. %. On the other hand to approach the ultimate possible coal conversion C_T which is approximately 91%, a relatively large amount of hydrogen transfer, i. e., 1.4% is required.

No substantial difference in the above relationship is apparent as the temperature is changed from 670 to 730°F. The 670°F data do, however, indicate a somewhat higher coal conversion at the same level of hydrogen transfer for the more polar solvents.

E. Kinetics of Hydrogen Transfer to Coal

The hydrogen transfer process was treated kinetically in the same fashion as coal conversion. As was pointed out above, there is less uncertainty in this case in identifying the process with a definite chemical change. The kinetic treatment can therefore be more rigorously applied.

It is necessary, in the kinetic treatment of the hydrogen transfer process, to assign a value to the maximum amount of hydrogen that can be transferred, i. e., H_T . A value of $H_T = 2.6$ was assigned. This is based on the fact that experimentally one approaches the same level of H_T under widely different conditions with 100 percent tetralin solvent as cited below:

<u>% H Transferred</u>	<u>Time, Minutes</u>	<u>Temperature, °F.</u>	<u>Unit</u>
2.0	120	730	Kinetics
2.5	60	800	Kinetics
2.4	94*	825	Batch Autoclave

*Total time above 700°F.

The first order type of rate plot is illustrated in Figure 5. The same tendency of the early time points to fall below the straight line remarked earlier in the case of coal conversion is noticed here likewise. Again, an initial first rate followed by a slow rate is indicated. The general kinetic treatment as a series of simultaneous first order reactions applies here likewise.

TABLE V
Summary of Rate Constants Derived from
Analog Computer

Temp., °F	Process	γ	First Order Constants, Min. ⁻¹	
			K ₁	K ₂
616	Coal Conversion	0.50	0.0089	--
670	" "	↓	0.248	0.0167
730	" "	↓	0.895	0.0916
<hr/>				
670	H ₂ Transfer to Coal	0.12	0.047	0.0013
700	"	↓	0.096	0.0040
730	"	↓	0.248	0.0084
800	"	0.149	1.85	0.0437
<hr/>				
670	H ₂ Transfer to Extract	0.15	0.0050	0.0008
700	"	↓	0.0135	0.0018
730	"	↓	0.0195	0.0043

TABLE VI
Energies and Entropies of Activation in Coal
Conversion and Hydrogen Transfer Rate Processes

Process	Energy of Activation, Kcal/Mole		Entropy of Activation, e.u.	
	Mean Value	Prob. Error	Mean Value	Prob. Error
Coal Conversion - - Fast Rate	28.1	1.4	-23.5	2.0
Hydrogen Transfer to Coal - Fast Rate	45.1	1.4	-4.6	2.0
- Slow Rate	41.7	1.5	-21.0	2.1
Hydrogen Transfer to Extract				
- Fast Rate	33.8	5.7	not calculated	
- Slow Rate	47.4	1.2	-9.2	1.7

$$H_T - H = \sum_{i=1}^n h_n e^{-k_n t} \quad (6)$$

The extrapolation technique based on the long time points leads to the expression

$$\ln \left(\frac{1}{1-\alpha} \right) = -\ln \left(\frac{h_n}{H_T} \right) + kt \quad (7)$$

The ratio h_n/H_T here is the fraction of the total hydrogen which is transferred at the slow rate.

Again, a model was chosen based on only two types of bonds, one relatively strong and the other relatively weak. The extrapolation technique as applied in Figure 5 leads to values of the fraction h_n/H_T varying from 0.96 at 670°F to 0.89 at 730°F.

A more accurate appraisal of the dual first order model was made on the analog computer as illustrated in Figure 6. The fraction of weak bonds present γ was assigned the value $\gamma = 0.12$ which appeared to give the best fit. A value of $\gamma = 0.149$ was assigned to the 800°F. points although in the strict sense of the word γ should be independent of temperature.

The rate constants derived from the analog computer are given in Table V. It is seen from Table V that the fast hydrogen transfer rate corresponds roughly to the slow coal conversion rate though it is 2-3 times higher.

The above identification is reasonable since the fast coal conversion rate is associated with little or no hydrogen transfer. The fast hydrogen transfer rate apparently takes over in the coal conversion range of 50-90 percent which corresponds to the slow coal conversion rate. The slow hydrogen transfer rate corresponds in all likelihood to continued transfer of hydrogen to coal extract.

F. Kinetics of Hydrogen Transfer to Extract

The extract used in this work was a shallow extract, i. e., obtained with decalin solvent at 650°F with total coal conversion of only 23 percent.

The kinetic treatment followed the pattern set forth for the coal work. The first order rate plots are shown in Figure 7. The values of γ calculated by the extrapolation technique show that γ ranges from .09 to .13 at 730°F. The analog computer treatment is illustrated in Figure 8. In this case a value of $\gamma = 0.15$ gave the best fit.

The rate constants from the analog computer are given in Table V. It might be expected that the slow rate in the case of coal would correspond to the fast rate in the case of extract. This is seen not to be the case since the fast extract rate is of the order of 3 to 4 times greater than the slow coal rate. The lack of agreement is partly due to the fact that shallow rather than deep extract was used where the comparison would be more valid. Data obtained with deep extracts were insufficient for calculation of rate constants but showed that the rate is indeed slower.

G. Activation Energy, Entropy of Activation in Coal Conversion and Hydrogen Transfer to Coal and Extract

The activation energies were derived by a least squares analysis of the standard Arrhenius type plot as shown in Figures 9 and 10. The resulting equations of the line and the values of the activation energies are given on the figures. The probable error in the activation energy is listed, also.

The activation energies and entropies of activation are summarized in Table VI. Insufficient data are available to estimate the activation energy corresponding to the slow coal conversion rate.

The entropy of activation was estimated by use of the Theory of Absolute Reaction Rates. (2)

$$\text{Rate Constant} = e \left(\frac{kT}{h} \right) e^{-E_{\text{exp}}/RT} e^{\Delta S^\ddagger / R} \quad (8)$$

where ΔS^\ddagger is the entropy of activation.

The exact quantitative value of ΔS^\ddagger is of little significance but its sign and order of magnitude is significant relative to the structure of the activated complex and hence the mechanism of the process.

The low activation energy for the high coal conversion rate of 28 Kcal/mole is well below that of most "reasonable" chemical bond strengths. Thus, it appears doubtful that the reaction involves rupture of a conventional covalent bond. This is consistent with the fact that the fast rate (approximately half of the total conversion) occurs with no significant hydrogen transfer. The energy of activation likely may be attributed to the breaking of non-valence bonds, i. e., hydrogen bonds and the like. The high negative value of the entropy of activation indicates

Figure 1

COAL CONVERSION vs TIME

1st Order Rate Plots

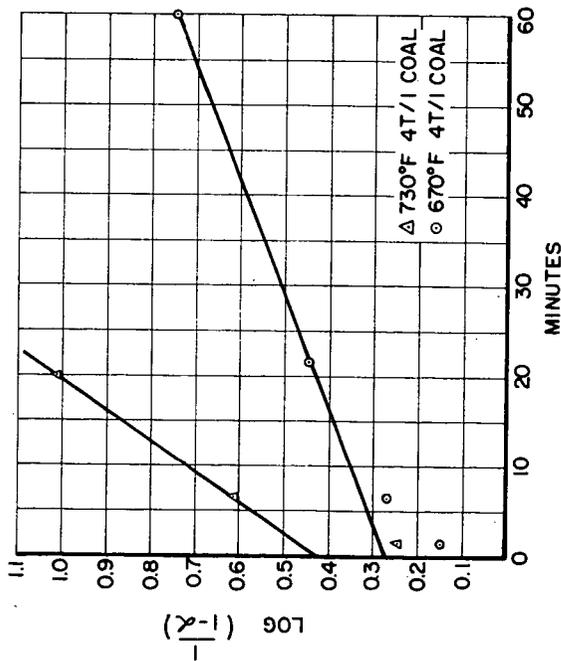
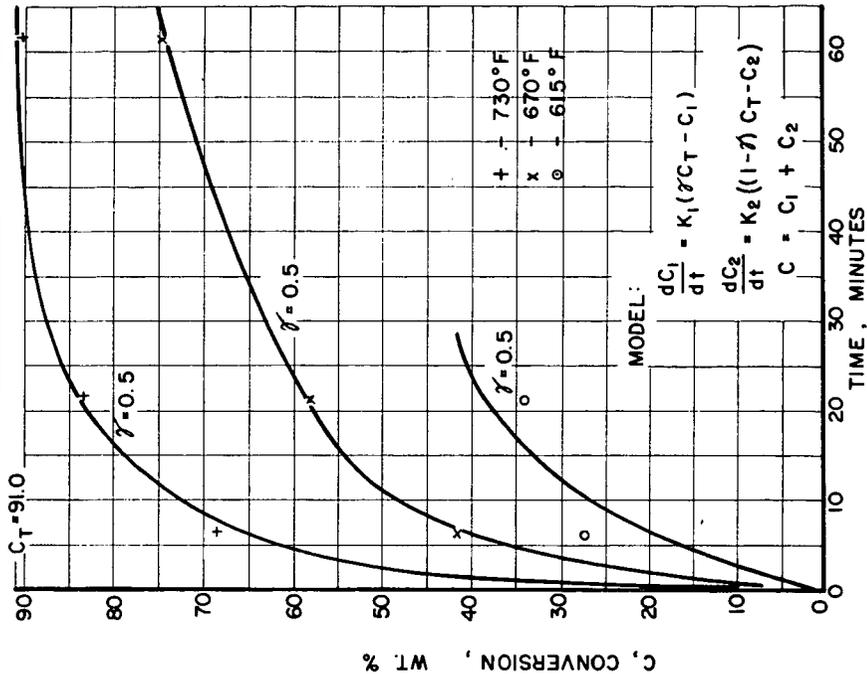


Figure 2

RATE PLOTS - COAL CONVERSION



a much more ordered structure in the activated complex than in the original coal molecule. This may be rationalized as meaning that the surrounding coal molecules must be oriented in a very specific manner to permit escape of the small coal molecule into the surrounding solvent medium.

The hydrogen transfer rates for both coal and extract were also treated in the same manner. The values of the energies and entropies of activation for the initial fast rates is probably of little significance since the accuracy of determination of the characteristic rate constants is not high.

The accuracy for determination of the values for the slow rates is much better since this corresponds to 85-90 percent of the total observed reaction.

The activation energy of the slow rate in the case of extract is higher than in the case of coal. This is to be expected since somewhat stronger bonds are involved. The energy of activation in both cases is somewhat low, however, i. e., ca. 45 Kcal/mole for most normal covalent bonds. The heat of dissociation of carbon-carbon bonds for example varies for most simple molecules between 65-85 Kcal/mole. The low value is indicative of a highly resonating structure in the free radicals produced by bond rupture which stabilizes them. This is analogous to the well-known stable free radicals of organic chemistry such as triphenyl methyl which are stabilized by the same mechanism.

The entropies of activation are again negative. In the case of simple known unimolecular reactions where dissociation to free radicals is involved a positive entropy of activation is usually observed. Thus, in this particular instance the proposed model does not appear to be wholly consistent with the facts.

H. H₂ Transfer Rate as Effected by Tetralin Concentration and Tetralin/MAF Coal Ratio

The above kinetic treatment applies only to the case where high solvent to coal and/or extract ratios are employed and where high tetralin concentrations are used. The hydrogen transfer rate falls off when either of the above quantities are reduced, although it is much more sensitive to a reduction in the latter than to the former quantity. A wholly consistent kinetic model must predict the effect of variation of the above parameters.

Experimentally only sufficient data are available in the case of coal for testing the applicability of kinetic models. Even here most of the data revolves about variation only of the tetralin concentration. The testing of kinetic models in the case of coal is difficult as mentioned above since the system is not truly a homogeneous one.

A number of models were considered to represent the kinetics, but the one given below was chosen by reason of simplicity.

This model considers that the extract or MAF coal has built in hydrogen donor structures which compete for the radicals produced in thermal dissociation. Thus, the kinetic model consists of the following sequence of reactions:

<u>Reaction</u>	<u>Rate Constant</u>
$E \rightarrow 2R$	k_0
$R + T \rightarrow RH + T^-$	k_1
$R + E \rightarrow RH + E^-$	k_2
$R + T^- \rightarrow RH + D$	k_3
$R + E^- \rightarrow RH + DE$	k_4

where T⁻ and E⁻ in the above correspond to radicals produced by abstraction of a hydrogen atom from tetralin (tetralyl radical) and extract, respectively. D and DE are, respectively, dihydro naphthalene and the corresponding dehydrogenated structure derived from extract.

Dihydro naphthalene is undoubtedly a much more reactive hydrogen donor than naphthalene itself, and rapidly undergoes similar reactions wherein it is converted to naphthalene. It thus is present in a very small steady-state concentration such that its activity for hydrogen transfer is equivalent to that of tetralin. From the kinetic point of view it is appropriate to disregard its presence. Experimentally, we have at the present time no definite evidence for or against the presence of dihydro naphthalene. Dihydro naphthalene boils between naphthalene and tetralin and thus is likely difficult to separate even on a gas chromatograph. It would, however, be of interest in the future to prove definitely the presence or absence of this compound as an intermediate.

The above mechanism can be used to derive an expression between the amount of hydrogen transferred from tetralin H₁ and the total amount of hydrogen transferred by all

Figure 3

COAL CONVERSION
vs
PERCENT H TRANSFER AT 730°F

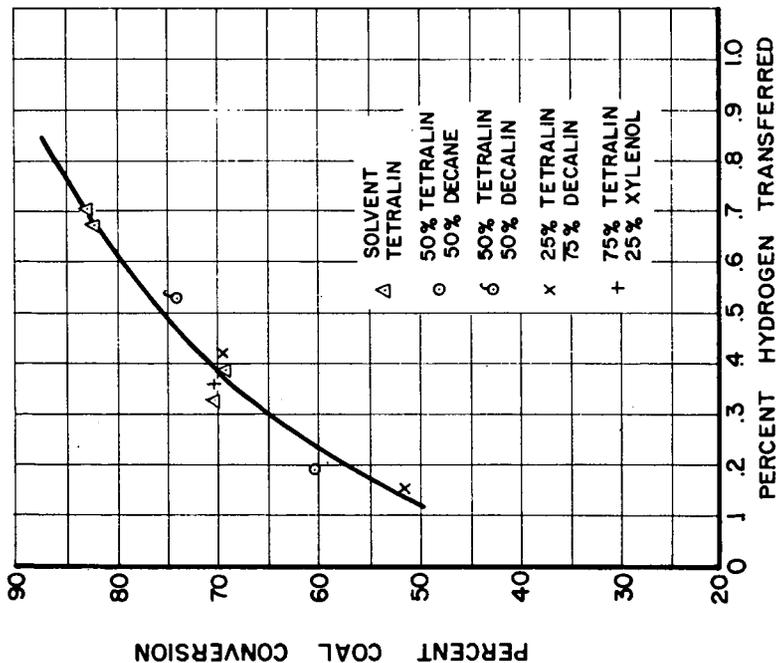
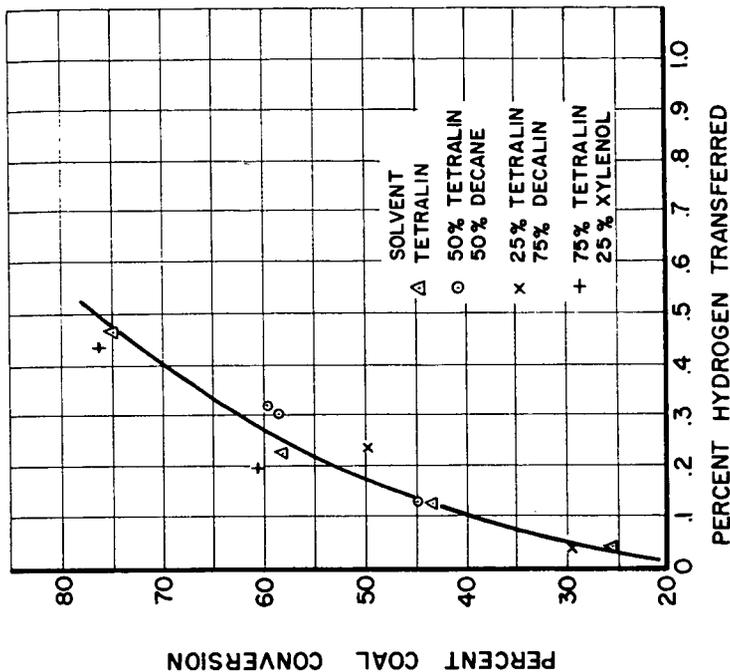


Figure 4

COAL CONVERSION
vs
PERCENT H TRANSFER AT 670°F



mechanisms H as shown below:

$$\frac{dH_1}{dH} = \frac{(H_1^0 - H_1)}{(H_1^0 - H_1) + k \{H_E^0 - (H - H_1)\}} \quad (9)$$

where $k = (k_2/2 k_1)$

Integration of equation (9) leads to the equation

$$\left(1 - \frac{H_1}{H_1^0}\right)^k = 1 - \left(\frac{H - H_1}{H_E^0}\right) \quad (10)$$

The left hand side of equation (10) may be expanded by the binomial theorem. As an approximation only the first term of the expansion is used since $H_1/H_1^0 < 1$. The result, after rearranging and collecting terms and noting that $H_1^0 = 400/132 (T/E)$, is

$$\frac{1}{H_1} = \frac{1}{H} \left[1 + C \left(\frac{E}{T}\right)\right] \quad (11)$$

where

$$C = kH_E^0 \left(\frac{132}{400}\right)$$

Experimental data obtained at 670°F and 730°F using 4 cc total solvent/gm coal were used to test equation (11). The test consists of plotting $1/H_1$ versus E/T . Each series of points at constant temperature and residence time should lie on a straight line. The slope (C/H) divided by the intercept $(1/H)$ should be a constant, i. e., C for each residence time series at constant temperature.

The tests for validity of equation (11) at 670 and 730°F are shown in Figures 11 and 12. Constant values of $C = 3.7$ and 4.2 were used for all the 670°F data and 730°F data, respectively.

The fit to the experimental data is quite good for 21.5 and 61.5 minute points but is poor for the 6.5 minute points. The accuracy of the experimental data points themselves are poor at the shorter times, however, due to the small amount of hydrogen transferred.

The equations derived above must be regarded as semi-empirical and are useful for estimating the effect of tetralin concentration at constant total solvent-to-coal ratio. They cannot be safely used to estimate hydrogen transfer rates at lower solvent-to-coal ratios.

Equation (11) predicts that the amount of hydrogen transfer obtained should be the same at the same tetralin-extract ratio irrespective of the tetralin concentration in the initial solvent. The experimental facts are not in accord with this, since the amount of hydrogen transfer increases at constant (T/E) with increasing tetralin concentration.

A few data points, for example, are available at 730°F and a lower solvent/coal ratio, i. e., 2 cc/gm. The experimentally determined amount of hydrogen transfer as compared with that estimated by means of equation (11) is shown below:

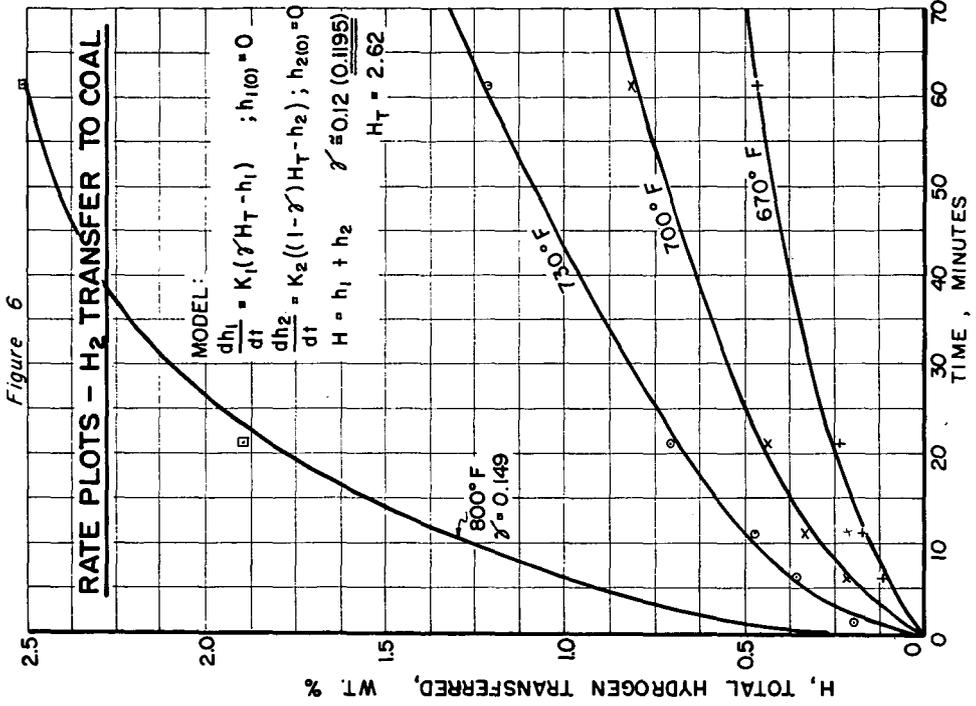
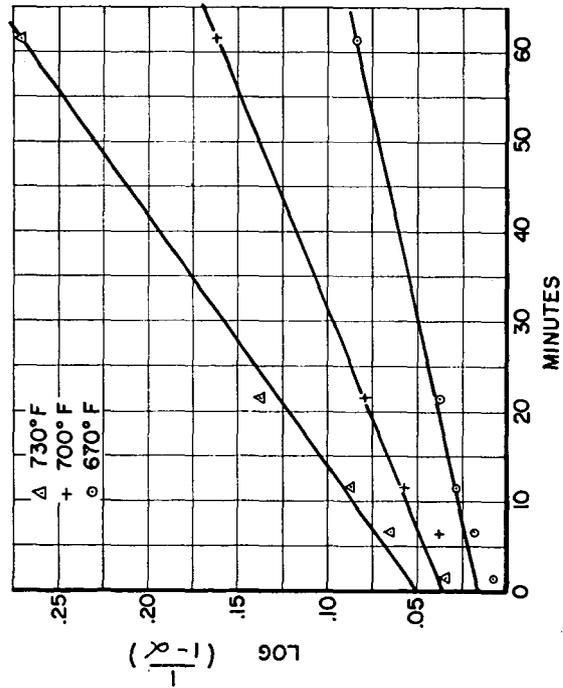
Res. Time Minutes	Solvent/Coal cc/gm	Volume % Tetralin	Hydrogen Transfer	
			Observed	Predicted
6.5	2	100	.33	.26
21.5	2	100	.68	.52

J. Evolution of Free Hydrogen

It has been observed under severe operating conditions, i. e., high temperatures and/or long residence times, that a considerable fraction of the hydrogen released from the tetralin appears as free hydrogen (cf. Table II). Under mild operating conditions little free hydrogen is produced. These facts are also in accord with the general mechanism outlined above. The mechanism at high tetralin concentrations where the recombination of radicals and hydrogen donor properties of the acceptor may be neglected may be written as follows:

Reaction	Rate Constant
$E \rightarrow 2 R$	k_0
$R + T \rightarrow RH + T^-$	k_1
$R + T^- \rightarrow RH + D$	k_3
$T^- \rightarrow D + H$	k_5
$H + T \rightarrow T^- + H_2$	k_6

Figure 5
H₂ TRANSFER TO COAL VS TIME
 1st Order Rate Plots



Thus, molecular hydrogen may be formed by thermal decomposition of the tetralyl radical by way of reactions 5 and 6. High operating temperatures will favor this reaction since reaction 5 will have a higher activation energy than reactions 1 and 3. This is seen from the differential equation corresponding to the above reaction sequence.

$$\frac{dH_2}{dH_1} = \frac{k_1 k_5}{2 k_0 k_3} \left[\frac{\left(\frac{T}{E}\right) \frac{400}{132} - H_1 - 2 H_2}{(HT - H_1)} \right]$$

where H_2 corresponds to moles of free hydrogen produced and H_1 corresponds to gram atoms of hydrogen actually transferred to the extract.

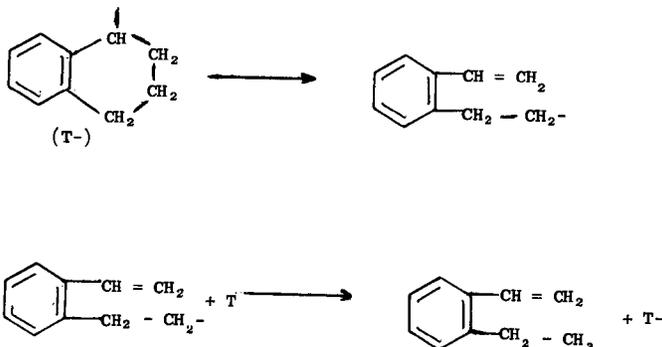
Equation (12) likewise predicts that the relative proportion of free hydrogen will increase at constant temperature with increasing residence time due to decrease in rate of production of free radicals from the coal or extract. This is also in accord with other experimental data which will be presented in a future publication.

K. Sensitized Thermal Decomposition of Tetralin

It has been observed that decomposition of tetralin is enhanced when it is used as a hydrogen donor. This is illustrated by the data in Figure 13 where the decomposition products as a function of time at 800°F are plotted. The tetralin decomposition products other than naphthalene are found largely in two peaks in the gas chromatograph which are labeled arbitrarily as C_4 benzenes and indane, respectively. These do not necessarily correspond to actual compounds produced since these were not definitely identified. The peaks in the gas chromatograph labeled as C_4 benzenes and indanes have, however, the same retention time as those of the corresponding pure compounds.

Thus, unsaturated compounds such as o-ethyl vinyl benzene and o-methyl allyl are not excluded as possible major decomposition products.

Increased yields of these decomposition products would be expected as a result of thermal decomposition of the tetralyl radical produced from the coal radicals as follows:



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- (3) Jostes, F., and Siebert, K., Oel, Kohle, Erdoel, Teer 14, 777-83 (1938).
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- (5) Oele, H. P., Waterman, H. I., Goedkoop, M. L., and Van Krevelen, D. W., Fuel 30, 169 (1951).
- (6) Pott, A., and Broche, H., Fuel 13, 91-5, 125-8, 154-7 (1934).

Figure 7

H₂ TRANSFER TO EXTRACT

1st Order Rate Plots

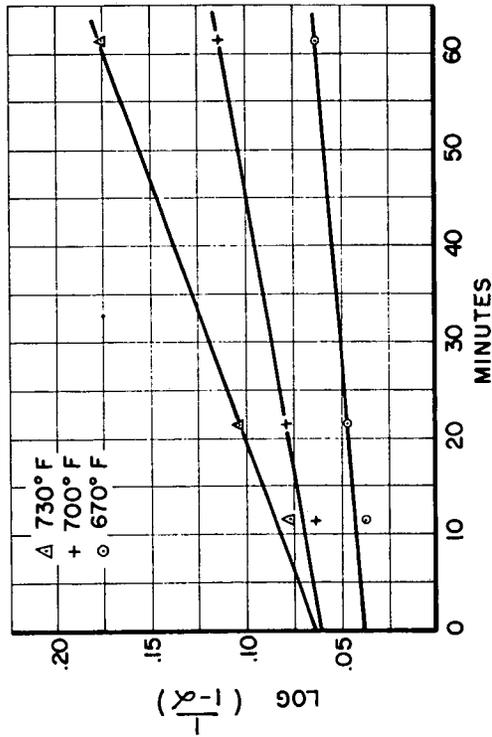


Figure 8

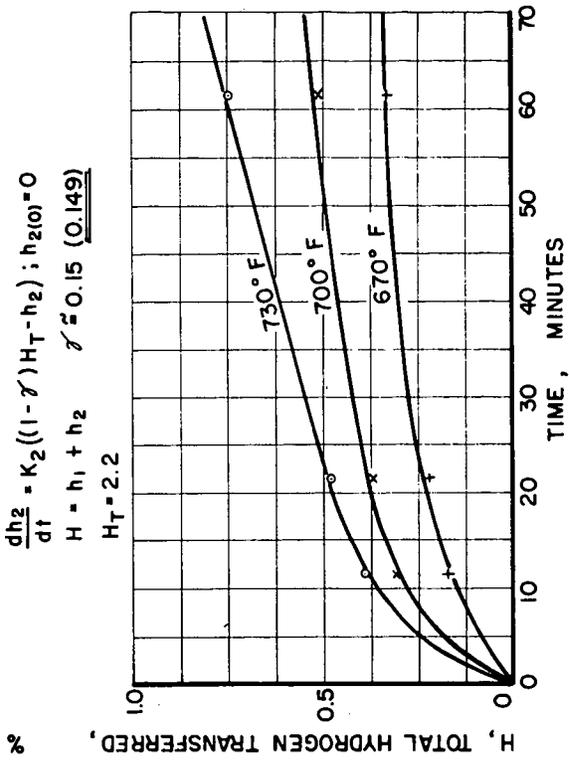
RATE PLOTS - H₂ TRANSFER TO EXTRACT

$$\frac{dh_1}{dt} = K_1(\gamma H_T - h_1) \quad ; \quad h_{1(0)} = 0$$

$$\frac{dh_2}{dt} = K_2((1 - \gamma) H_T - h_2) \quad ; \quad h_{2(0)} = 0$$

$$H = h_1 + h_2 \quad \gamma \approx 0.15 \quad (0.149)$$

$$H_T = 2.2$$



APPENDIX

Definition of Terms

- T = gms Tetralin/cc reaction mixture.
- E = gms Extract or MAF coal/cc reaction mixture.
- H₁ = gm atoms of H transferred from tetralin/100 gm extract or MAF coal.
- H = gm atoms of H transferred from all sources/100 gm extract or MAF coal.
- H_E = gm atoms of H transferred from extract/100 gm extract or MAF coal.
- H_T = Total gm atoms H transferred at infinite time/100 gms extract or MAF coal due to rupture of all bonds.
- H₁^o = Hydrogen transfer capacity of tetralin in gm atoms/100 gms extract or MAF coal.
= 400/132 (T/E).
- H_E^o = Hydrogen transfer capacity of extract in gm atoms/100 gms extract or MAF coal.
- γ = Fraction of "weak" bonds in coal or extract.
- C = Coal conversion in percent of MAF coal.
- C_T = Coal conversion in percent of MAF coal achieved at ∞ time.
- α = Fraction of ultimate conversion.
- α = C/C_T for coal conversion.
- α = H/H_T for hydrogen transfer.
- R = Free radical concentration, moles/cc.
- T- = Concentration of tetralyl radical, moles/cc.
- H₂ = gm moles free hydrogen produced/100 gms of extract or MAF coal.

Figure 9

ARRHENIUS PLOTS

A.) HYDROGEN TRANSFER RATES TO COAL
B.) COAL CONVERSION RATE

A) \circ $\text{LOG } K_1 = 14.362 - 9.879 \times 10^3/T$ $E_1 = 45.1 \pm 1.4 \text{ K Cal/mol.}$

+ $\text{LOG } K_2 = 11.717 - 9.134 \times 10^3/T$ $E_2 = 41.7 \pm 1.5 \text{ K Cal/mol.}$

B) Δ $\text{LOG } K'_1 = 9.230 - 6.147 \times 10^3/T$ $E_1 = 28.1 \pm 1.4 \text{ K Cal/mol.}$

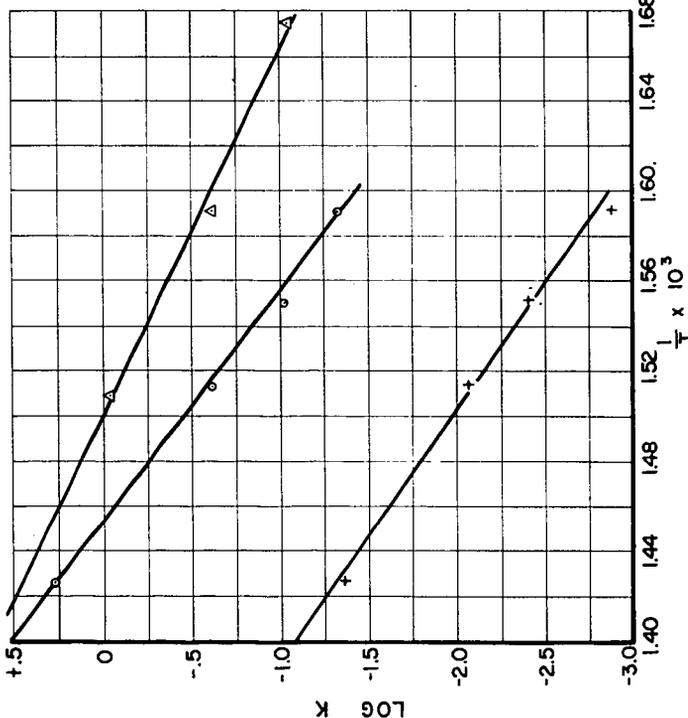


Figure 10

ARRHENIUS PLOTS FOR HYDROGEN
TRANSFER RATES TO EXTRACT

+ $\text{LOG } K_1 = 9.532 - \frac{7.402 \times 10^3}{T}$ $E_1 = 33.8 \pm 5.7 \text{ K Cal/mol.}$

\circ $\text{LOG } K_2 = 13.348 - \frac{10.38 \times 10^3}{T}$ $E_2 = 47.4 \pm 1.2 \text{ K Cal/mol.}$

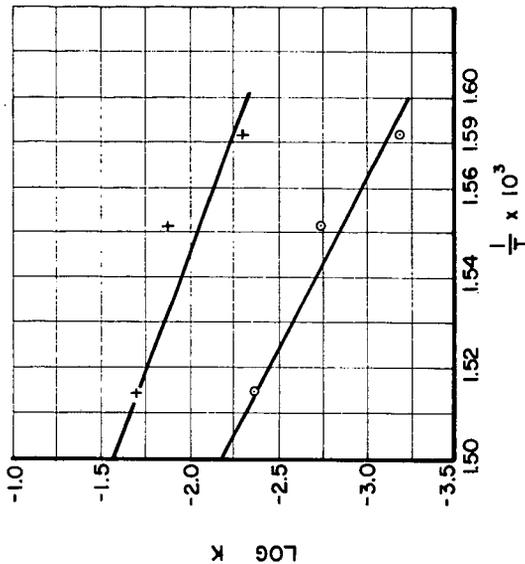


Figure 12

HYDROGEN TRANSFER RATE AT 730°F
AS AFFECTED BY MAF COAL/TETRALIN RATIO

cc Total Solvent/gm MF Coal = 4.0

$$\frac{1}{H_1} = \frac{1}{H} [1 + c(E_T)]$$

C = 3.7

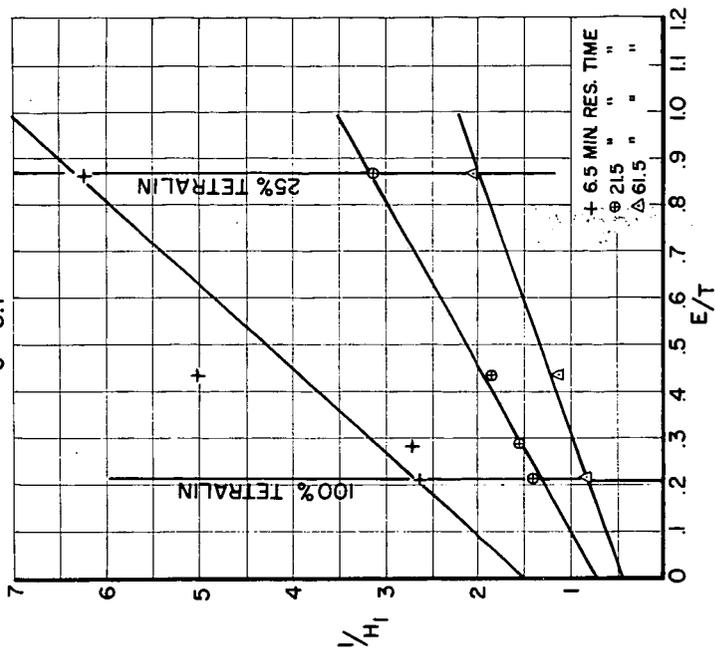


Figure 11

HYDROGEN TRANSFER RATE AT 670°F
AS AFFECTED BY MAF COAL/TETRALIN RATIO

cc Total Solvent/gm MF Coal = 4.0

$$\frac{1}{H_1} = \frac{1}{H} [1 + c(E_T)]$$

C = 4.2

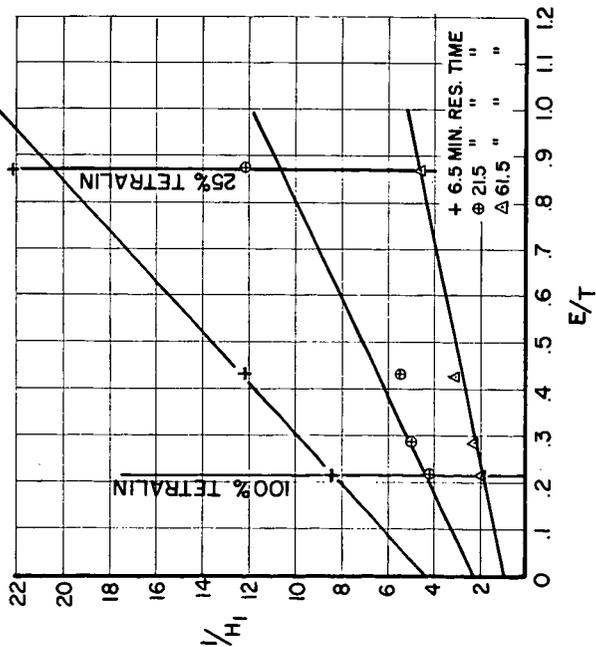


Figure 13

**THERMAL DECOMPOSITION OF TETRALIN
AT 800° F**

