

ULTRASONIC ENERGY EFFECTS ON COAL EXTRACTION BY A HYDROGEN DONOR SOLVENT

by

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ABSTRACT

The kinetics of a high volatile bituminous coal extracted with 1,2,3,4-tetrahydronaphthalene (tetralin) under the influence of ultrasonic energy has been studied.

The extraction of coal has been carried out at five different temperatures: 47°, 57°, 67°, 77°, and 87°C. Effects of intensity of ultrasonic energy, particle size, and hydrogen content of the coal were also obtained.

Analysis of the data showed that a second order rate reaction followed by a first order rate reaction describes the kinetics of the extraction process.

The enthalpies of the second-order and first-order regions were 8.70 K cal/mole and 2.5 K cal/mole, respectively, which suggests that the extraction process is under essentially physical control. Auxiliary experiments and the kinetic data obtained suggest a model for the extraction process. The mechanism of the overall reaction is undoubtedly complex but the data indicate that weak van der Waals and hydrogen bonding forces are most affected by the ultrasonic energy.

INTRODUCTION

The dissolving of coal in solvents has been studied from many aspects. Since the first systematic experiments by De Marsily in 1860¹ many investigators have extracted coal with a variety of organic liquids.

The work carried out before 1950 has been ably reviewed by Dryden². The first experiments using ultrasonic energy were conducted by Berkowitz³ with some later similar experiments by Littlewood⁴. The influence of solvent properties, experimental conditions and coal types on the yield of extractable material from coal has also been reviewed by Dryden⁵. Very little data have been reported on the kinetics of the extraction process⁶. The influence of ultrasonic energy on the kinetics has also received little attention. Undoubtedly the overall extraction is the result of several types of simultaneous and consecutive reactions due to the complexity of the coal structure involved. However, the results of this study are extremely interesting and, perhaps, can help one to understand the particular effects of ultrasonic waves on the extraction process.

From previous work on coal extraction in the presence of ultrasonic energy the following general conclusions can be drawn:

The amount of material extracted can be significantly increased by the use of ultrasonic energy^{3,7,8}.

The total amount extracted is dependent upon the temperature of the extraction⁶.

The rate of extraction was highest with coal of the smallest particle size⁷.

In this study these conclusions were verified for the coal-tetralin system and some further results were obtained leading to other conclusions regarding the mechanism of the reactions taking place.

MATERIALS AND PROCEDURE

The coal used for this study was from the Spring Canyon Coal Mine, Carbon County, Utah. An analysis is given in Table I. The tetralin used was reagent grade.

TABLE I
ANALYSIS OF SPRING CANYON COAL
(Commercial Testing and Engineering Company)

<u>Dry Ultimate</u>	<u>Weight %</u>	<u>Dry Proximate</u>	<u>Weight %</u>
Carbon	72.88	Ash	8.4
Hydrogen	5.58		
Nitrogen	1.51	Volatile Matter	45.70
Oxygen	10.82	Fixed Carbon	45.90
Sulfur	0.62		
Chlorine	0.119		

Dry Heating Value - 13,240 Btu/lb.

The following procedure was followed in the extraction of Spring Canyon Coal:

The coal was ground and sized to -200+270 Tyler mesh. A portion of the ground coal was removed from stock bottle and put in a beaker. The sample was then dried in a vacuum oven at 110°C for a period of four hours, removed from oven, and then placed in a desicator.

The extraction apparatus used for the experiments was a commercial ultrasonic cleaner which generated waves with a frequency of 25 kc/second. The maximum power output was 300 watts. The ultrasonic energy was directed to a stainless steel tank with a surface area of 80 square inches. Figure 1 is a schematic drawing of the extraction apparatus. A measured

volume of solvent was introduced inside the stainless steel tank and heated. When the selected operating temperature was reached, a weighed amount of coal (solvent to coal ratio = 50 ml/1 gram for tetralin and coal and 60/1 for ethylene diamine and coal) was introduced into the tank and mixed with the solvent; then mechanical stirring started. Stirring assured the uniformity of coal-solvent mixture and eliminated the precipitation of coal. Reaction time = zero for each experiment was taken as the time when the coal was added to the heated solvent. Samples were drawn into glass flasks after 5, 10, 20, 30, 40, 50, 60, 90 . . . 540 minutes. The samples were cooled to room temperature and weighed.

Each sample was then placed in a weighed, double thickness Soxhlet extraction thimble. The thimble containing the sample was placed in the Soxhlet extraction tube and was washed with acetone for 24 hours. The thimble containing the coal residue was dried in a vacuum oven at 110°C for 4 hours. The paper thimble and coal residue was then weighed. The weight of the coal residue or that which was not extracted was found by subtraction.

PRELIMINARY EXPERIMENTS

In order to determine some specific effects of operating conditions several preliminary experiments were conducted. These included the following with the results as indicated.

Decomposition of tetralin: Since it has been shown that ultrasonic energy can cause molecular fragmentation of organic liquids^{9,10} and also degradation of mixtures and organic solvents in the presence of water¹⁰ some experiments were carried out to determine the effects upon tetralin under the extraction conditions to be used for coal.

Tetralin was analyzed by gas chromatography to determine the quantities of other species present (Figure 2). Next tetralin was irradiated for 24 hours in the tank to be used for extraction with ultrasonic waves (3.75 watts/in^2) at 87°C . Samples of the tetralin were taken during the experiment and analyzed. No detectable decomposition was observed for the first 15 hours; the total decomposition after 24 hours was less than 1.0 per cent. Figure 3 is a chromatogram of the irradiated tetralin.

Coal-Solvent Ratio: In order to be sure that neither the rate nor the extent of extraction would be limited by the amount of solvent present for the coal sample some experiments were conducted to determine the amount extracted by various coal/solvent ratio. Figure 4 shows that for a coal/solvent ratio of 1 gram coal/30 ml of solvent or lower the per cent extracted is essentially constant. For subsequent experiments a ratio of 1 gram coal/50 ml solvent was used.

Particle Size: The effect of particle size on the per cent extracted at a particular temperature was found to be negligible. However, as shown in Figure 5 the initial rate of extraction was higher for the coal with a smaller particle size.

Intensity of Ultrasonic Energy: The ultrasonic generator and power control unit was equipped with facility for controlling the mechanical energy to the tank where the experiments were conducted. As shown in Figure 6 the amount extracted was a function of the ultrasonic energy supplied to the system. For all of the experiments conducted after these preliminary tests 100% of the energy available (3.75 watts/in^2) was used.

Some of the coal used in the experiments was reduced with Lithium-ethylenediamine. Calculations indicated an addition of 12.6 hydrogen

atoms per 100 carbon atoms in the coal. Both raw coal and the reduced coal was extracted with tetralin in the presence of ultrasonic energy. As shown in Figure 7 both the amount extracted and the rate of extraction were greater for the reduced coal.

Stirring Effect: Final preliminary experiments were conducted to determine the effects of stirring on the extraction of coal in the system used. Figures 8 and 9 show comparative data for static extraction, stirred extraction and extraction with stirring and ultrasonic energy at 47° and 87°C. Stirring appears to be important in making fresh solvent available to the coal surface.

RESULTS AND DISCUSSION

Conclusions regarding the effects of ultrasonic energy on the extraction rate and yield referred to previously were confirmed. Figure 10 shows kinetic data obtained in experiments with and without the influence of ultrasonic energy.

It was found that most of the data could be fit very well to a second order equation of the form:

$$\frac{dx}{dt} = k_2 (a-x)^2 \quad (1)$$

where k_2 = reaction rate constant

a = maximum fraction of the coal which would dissolve at the temperature studied

x = fraction of the coal extracted after any reaction time, t

Integration of the above equation with the lower limit of $x = 0$ when $t = 0$ leads to:

$$\frac{x}{a(a-x)} = k_2 t \quad (2)$$

A plot of $\frac{x}{a(a-x)}$ versus t should yield straight lines with the slope k_2 for each temperature if equation (1) adequately describes the reaction kinetics. Figure 11 shows the second order plot to be in agreement with the above conditions.

The second order equation was very adequate to describe the first hour of reaction at each of the temperatures studied from 47° to 87°C. However, after 60 minutes the data no longer fit the second order curves. Table II shows the extent of the second order reaction at the temperatures studied.

TABLE II
EXTENT OF SECOND ORDER REACTION

Temperature °C	Time at End of Second Order (min.)	Maximum Potential Yield (a)	"X" at End of Second Order	Percent of "a" During Second Order
47	60	0.1782	0.1221	69
57	60	0.1899	0.1473	80
67	60	0.1985	0.1663	84
77	60	0.2098	0.1863	89
87	60	0.2240	0.2077	94

The data after 60 minutes were found to be simple first order for the remainder of the extraction reaction. The first order equation to describe the portion of the reaction taking place after 60 minutes was:

$$\frac{dx}{dt} = k_1 (a-x) \quad (3)$$

Integration and setting the limits as for equation (2)

$$\ln \frac{a}{a-x} = k_1 t \quad (4)$$

The data for this portion of the reaction are plotted in Figure 12 to show the agreement of equation (4) to the data obtained.

Applying the absolute reaction rate theory to the second order and first order portions of the extraction process the rate constant, k' (or k_2 and k_1) would be of the form:

$$k' = \kappa \frac{kT}{h} e^{-\Delta F^\ddagger/RT} \quad (5)$$

where κ = transmission coefficient (usually = 1.0)

k = Boltzman's constant

h = Planck's constant

T = absolute temperature ($^\circ\text{K}$)

R = universal gas constant

ΔF^\ddagger = activation free energy (also can be expressed as $= \Delta H^\ddagger - T\Delta S^\ddagger$)

The rate constants were expressed by the expression

$$k' = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (6)$$

and plots of equation (6) are shown in Figure 13 and 14. Since $\ln \frac{k'}{T}$ is plotted against $1/T$ the slope is then $-\frac{\Delta H^\ddagger}{R}$ and the activation entropy ΔS^\ddagger can be obtained from the intercept. The values for the activation enthalpy and apparent activation entropy for the two portions of the reaction were:

	ΔH^\ddagger	ΔS^\ddagger
2nd order	8.7 kcal/mole	-44 e.u.
1st order	2.5 kcal/mole	-70 e.u.

With the values of the activation enthalpies obtained the extraction process appears to be under essentially physical control. Forces being affected if this is the case would include van der Waals or hydrogen bonding forces which are generally of the order of 1-10 kcal/mole. Freundlich and Gillings have demonstrated the breaking of the loose gel network of van der Waals bonds in gelatin-water¹² by ultrasonic waves. However, many other degradation and depolymerization reactions have also been effected by ultrasonic energy when the bonds involved were chemical bonds of 50-100 kcal/mole. Some polymers which have been depolymerized by ultrasonic waves are polystyrene¹³, polyvinyl acetate, polyacrylates and nitrocellulose¹⁴, and rubber¹⁵.

An interesting and quite plausible explanation for the depolymerization of polystyrene solutions has been proposed by Crawford¹⁶. According to his calculations ultrasonic waves of 300 kc/s at 10 watts/cm² could easily furnish sufficient energy to break the C-C or C-O bonds. Forces from ultrasonic waves could be set up simply as friction between a polymer molecule and the surrounding liquid. In the case of polystyrene in toluene only 5 bonds in 1000 were broken at 70°C.

The structure of coal is, at best, very complex and the bonding forces are not well defined at present. There are, however, some general facts concerning the products of coal extraction, pyrolysis and hydrogenation which can be of great assistance in determining the types and magnitude of some of the important bonding forces in coal. Coal pyrolysis and coal

dissolution (solvent extraction) have been visualized by Wiser as similar processes, with similar reaction kinetics (second order) and activation enthalpies (35.6 kcal/mole and 28.8 kcal/mole respectively)¹⁷. The products resulting from coal pyrolysis and dissolution are high in aromatics, exhibiting even higher aromaticity than the original coal. From this and other work on the structure of coal the strongest bonds in the "coal macromolecule" appear to be aromatic carbon-carbon bonds. Aliphatic C-C bonds, C-O, C-H, and C-S bonding are also present and important in the coal structure¹⁸. Weaker forces such as van der Waals forces and hydrogen bonding would naturally be expected since coal can be considered as a polymer and other polymers containing C, H, S, N and O are at least partially held together by such bonding forces^{19,20}. Pimental and McClellan²⁰ give values of hydrogen bond strengths of 3.0 to 7.7 kcal/mole.

The results of any kinetic study on a complex substance such as coal will indicate only average values of the activation enthalpies and entropies involved in the process being studied.

Since the value of "a", the maximum part of the coal extractable, varies systematically with temperature it appears that at any particular temperature the quantity (a-x) represents a potential in the form of a concentration. The rate at any particular time, t, depends only upon this concentration. As "x" approaches "a" the rate approaches zero. The value of "a" is much smaller when ultrasonic energy is not used in the extraction. From this study and others the effect of this energy appears to be the actual breaking of bonds in the coal structure which cannot be broken by the solvent. The breaking of these bonds then results in fragments from the coal which are soluble in the solvent liquid. Another possible effect of the ultrasonic energy is the transfer of kinetic energy

to the coal structure in such a way that would be the same as raising the "effective" temperature of the coal to some value much higher than the temperature measured by a thermometer or thermocouple in the solvent. According to Dognon and Simonot^{21,22} the temperature of dispersed particles in an ultrasonic field is raised several degrees above the average temperature of the solution or suspension. The cavitation taking place in liquids subjected to ultrasonic waves (formation and violent collapse of small bubbles in the liquid due to pressure changes) has been credited with practically all observed chemical effects in liquid systems⁹. The violent collapse of cavitation bubbles may generate local pressures of thousands of atmospheres and/or local temperatures of hundreds of degrees above that of the environment²³. The intensity of ultrasonic energy used in this study was several times that required to produce cavitation.

The results of this study may be interpreted in two different ways based on the above information:

(1) The extraction of coal with ultrasonic energy results in the dissolving of species present in the pores of the coal structure. Extraction also takes place by breaking van der Waals and hydrogen bonds in the coal structure. The extraction yield is higher with ultrasonic energy because these weak bonding forces are severed by the energy of the ultrasonic waves. The rate controlling step in the second order portion of the reaction is the reaction between the solvent molecules and the available van der Waals or hydrogen bonds in the coal. The activation enthalpy for this second order reaction is 8.7 kcal/mole. The second order dependence is most likely due to a rate controlling step involving both a solvent molecule and a van der Waals or hydrogen bond. When most of the extraction has taken place the slow step becomes solution diffusion

either of solvent molecules to the soluble species in the coal matrix or of dissolved extraction products from the coal into the bulk solution. This part of the reaction is first order and has an activation enthalpy of 2.5 kcal/mole.

(2) Assuming that the ultrasonic effect to the coal-tetralin system is to raise the "effective temperature" of the reacting species to some higher value leads to some very interesting conclusions. To obtain the "effective temperature" (T_e) corresponding to the measured temperatures of 47°, 57°, 67°, 77° and 87°C used in this study is not difficult if "a" values at these temperatures is used to obtain the temperature necessary for the same yield in a coal-tetralin system without ultrasonic energy. In previous work by Charlot²⁴ tetralin was used to extract Spring Canyon coal without ultrasonic energy. T_e values corresponding to 47, 57, 67, 77 and 87°C are found to be 258°, 261°, 263°, 267° and 269°C. Values of the activation enthalpies for the second order and first order portions of the reaction became 31.5 and 9.1 kcal/mole respectively. With these values the second order portion of the reaction would undoubtedly involve the same type of bond rupture that occurs with pyrolysis and dissolution as previously referred¹⁷. The first order portion of the reaction would then appear to be controlled by either the breaking of van der Waals and/or hydrogen bonds or possibly solution diffusion.

CONCLUSIONS

Kinetic data of solvent extraction with tetralin and ultrasonic energy over the temperature range 47-87°C have been obtained. The kinetic data indicate that the rate determining step for most of the process is a second order reaction probably involving tetralin molecules and van der Waals or hydrogen bonds in the coal. The activation enthalpy for this

second order reaction is 8.7 kcal/mole with an activation entropy of -44 e.u. The second order reaction is followed by a first order reaction with an activation enthalpy of 2.5 kcal/mole and entropy of -70 e.u. The rate controlling step for the first order portion of the reaction is probably solution diffusion. The high negative values for the activation entropies obtained are not surprising since similar results have been obtained by others working with complex reactants such as coal, coal tar, petroleum, and some pure aromatic compounds^{25,26}. Such values are usually obtained when the number of reaction sites changes with the amount of reaction as would be the case for extraction²⁷.

No exact mechanism for the reactions taking place can be concluded. The interaction of the ultrasonic energy, tetralin, coal and environment cannot be completely understood until much more is known about such phenomena as the exact effects of ultrasonic waves upon organic solvents and suspended solids and extraction of coal; in particular how each type of bonding in coal is affected by the solvent molecules.

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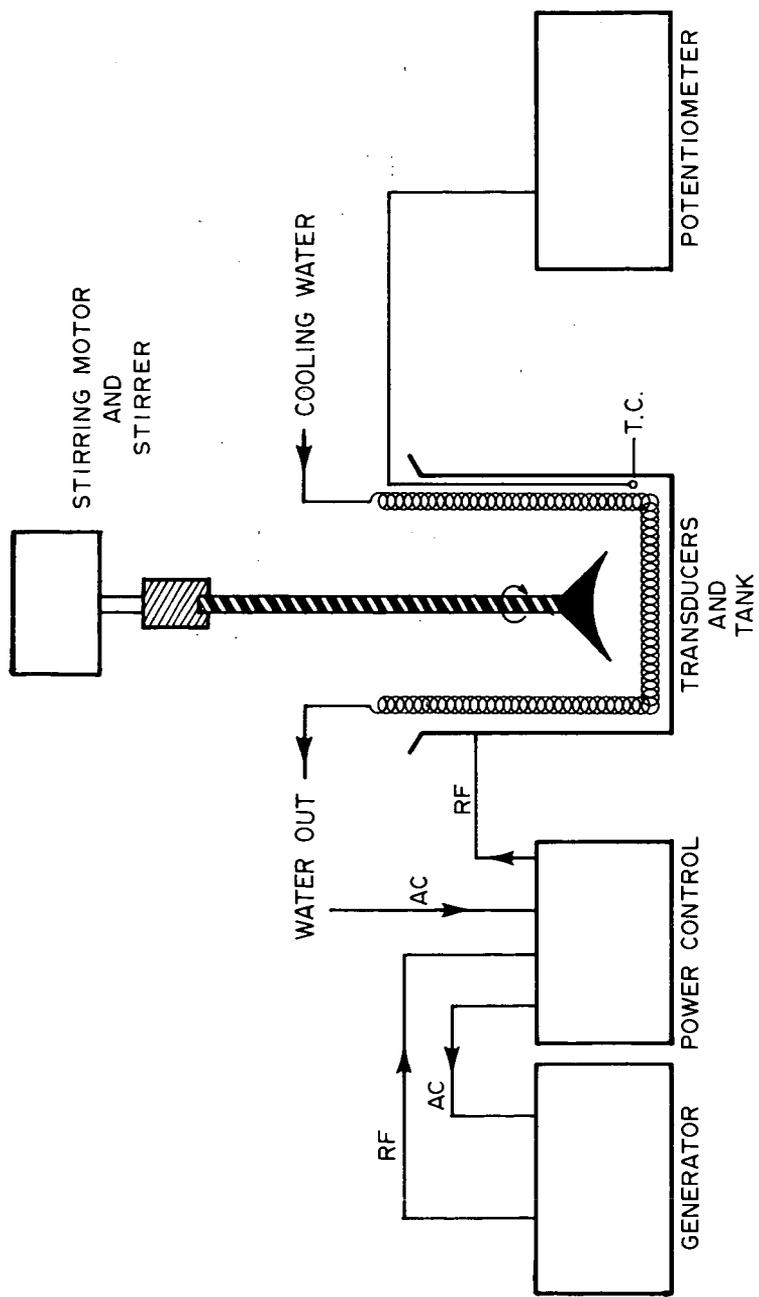


Figure 1. Schematic drawing of ultrasonic extraction apparatus.

Pure Tetralin

Column 8 ft. Carbowax

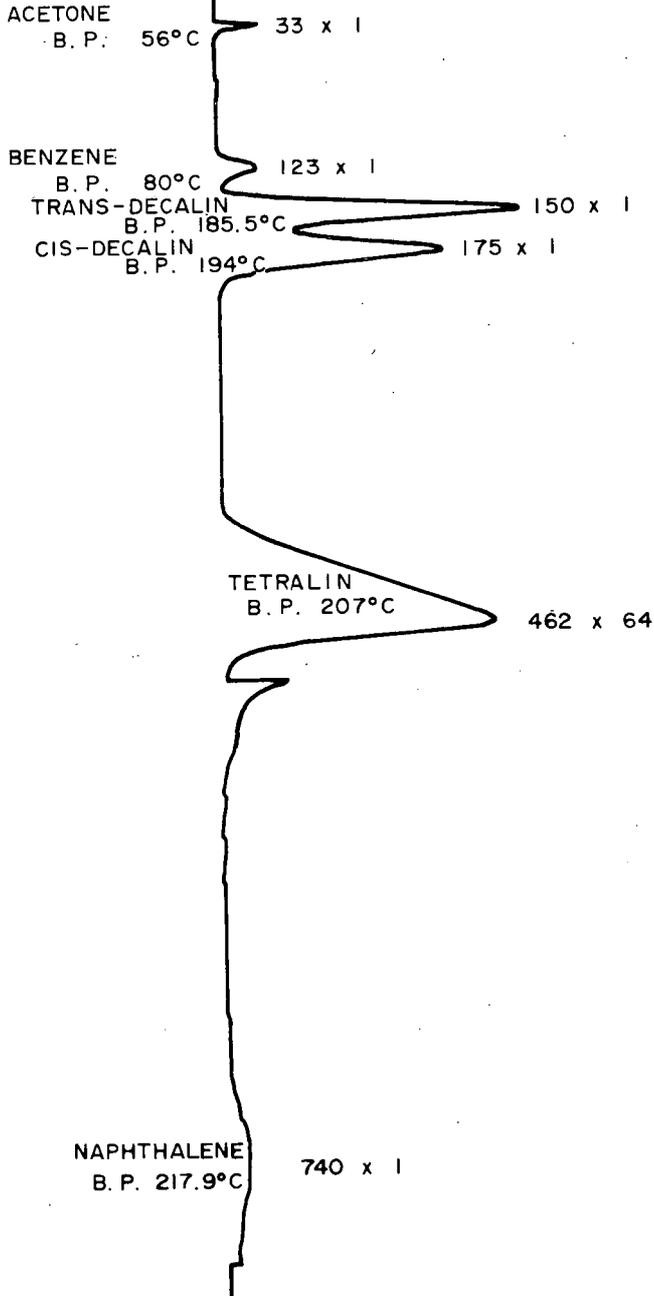


Figure 2. Chromatogram of Tetralin.

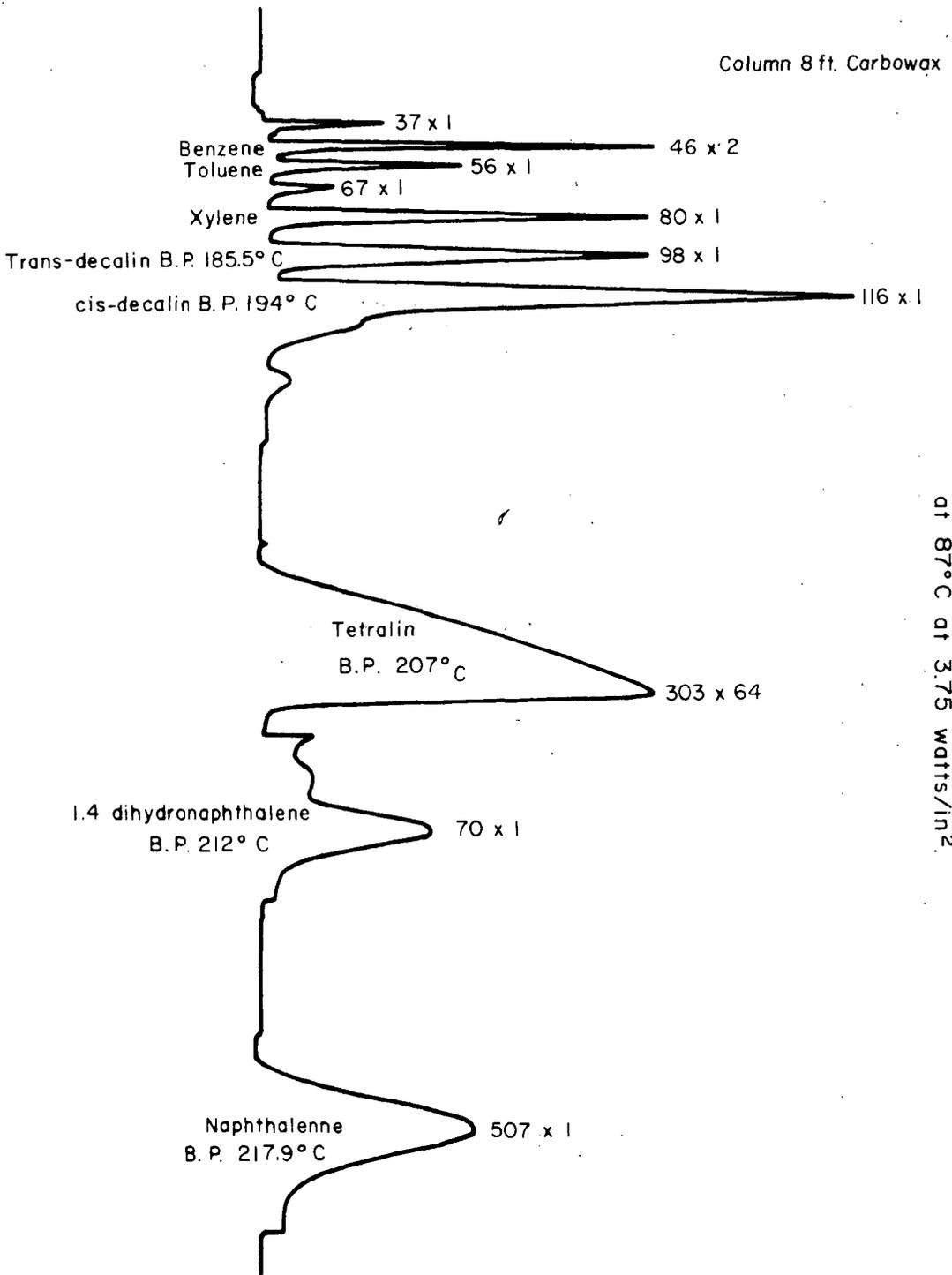


Fig. 3 Chromatogram of Tetralin Irradiated for 24 hours at 87°C at 3.75 watts/in².

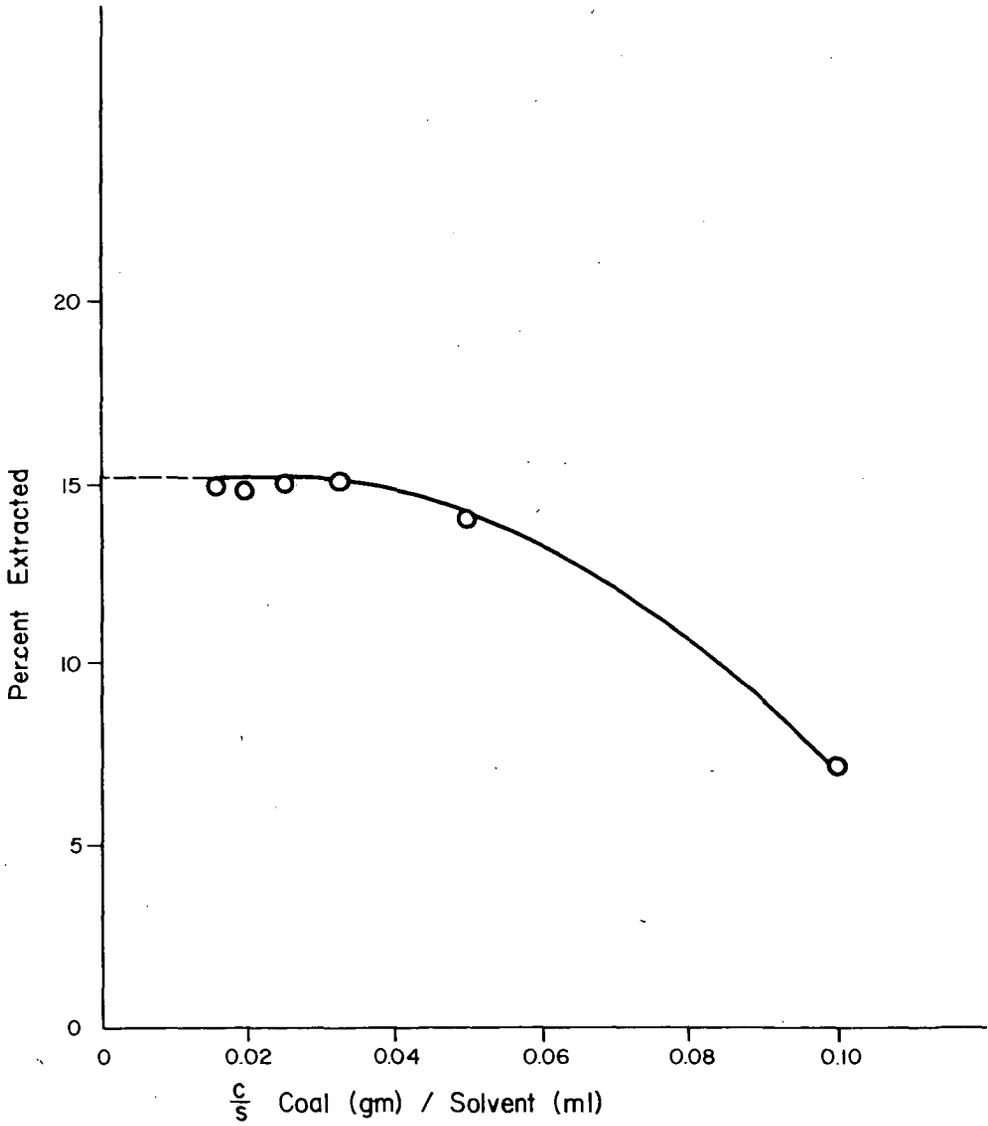


Fig. 4 Percent of extracted vs. $\frac{\text{coal}}{\text{solvent}}$ ratio
Temperature = 47°C; Time = 3 hours;
Coal size = -200 + 270 mesh
Solvent = tetralin

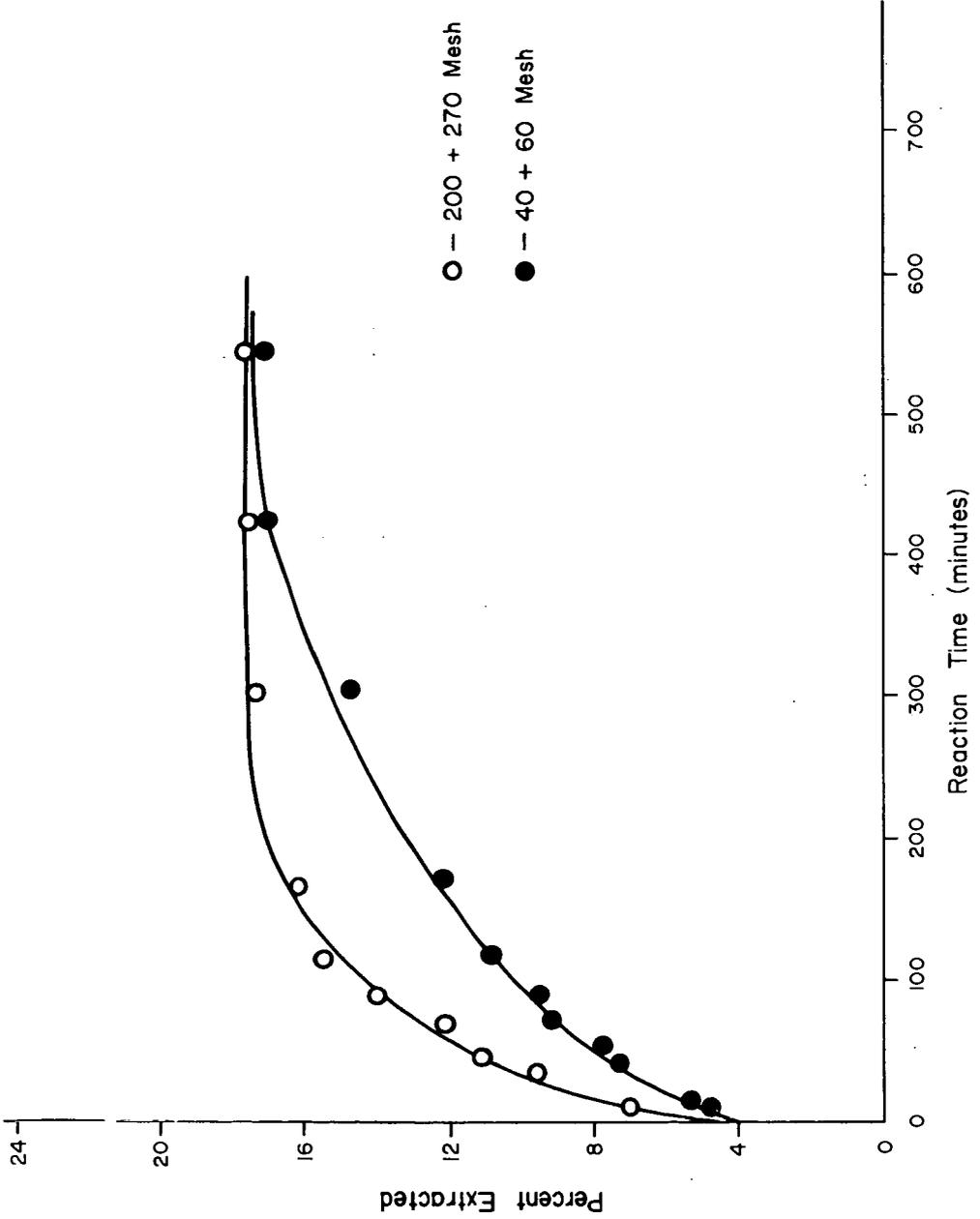


Fig. 5 - 40 + 60 and -200 + 270 mesh coals. Effect of coal particle size on ultrasonic extraction with tetralin.

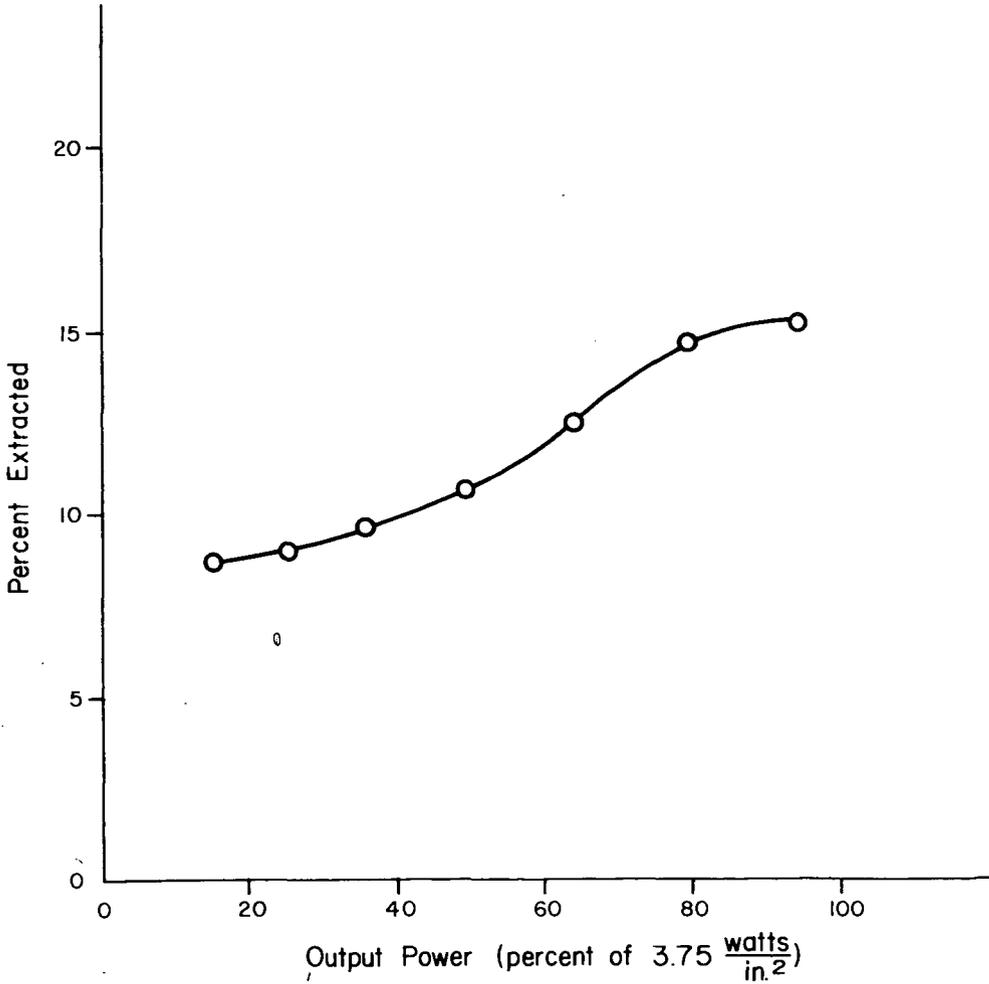


Fig. 6 Output vs. percent extracted at 47°C, and 3 hours reaction time in tetralin. Coal size = -200+270 mesh.

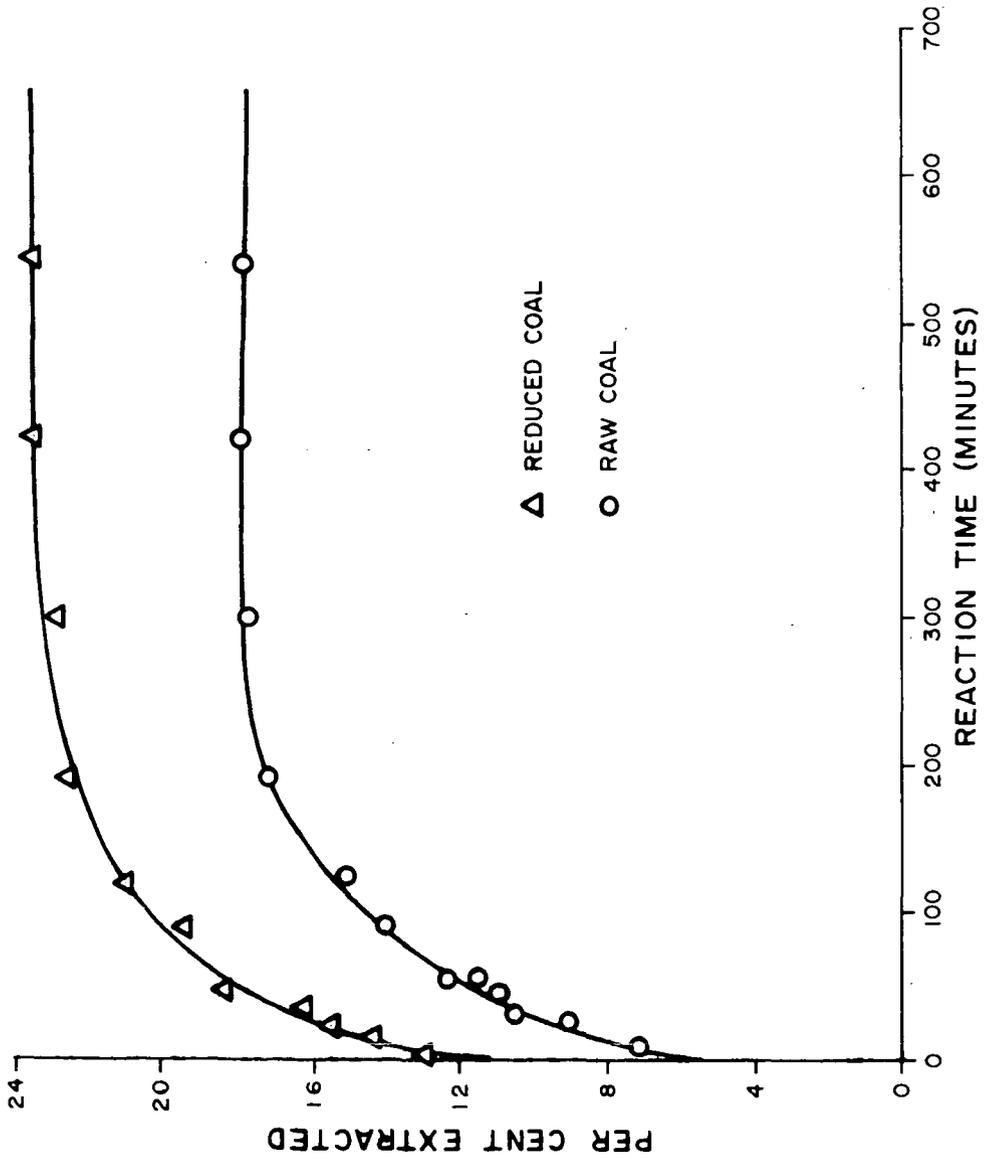


Fig. 7 Percent extracted versus time for raw and reduced coal.

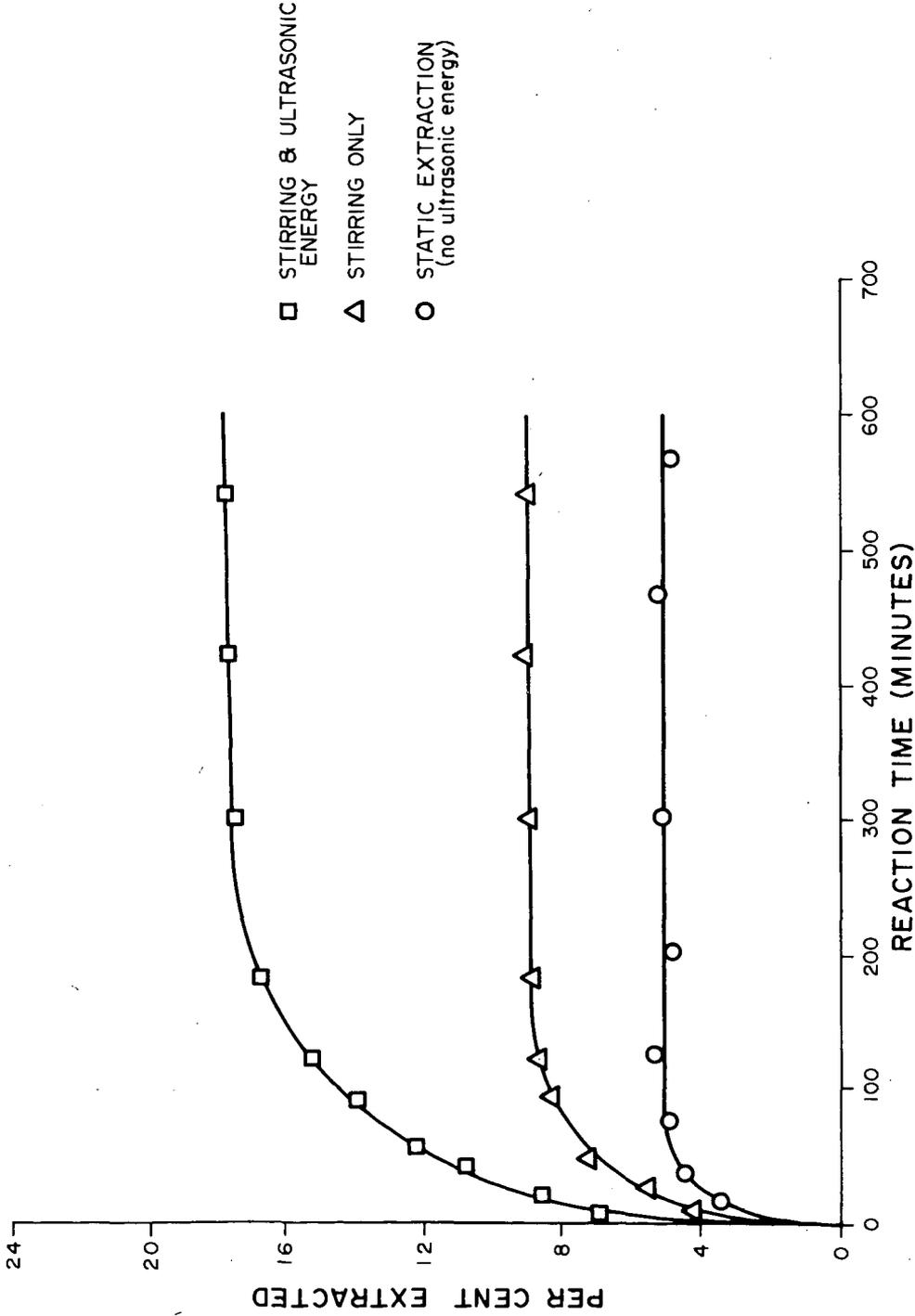


Figure 8. Percent extracted versus time at 47°C. Solvent = Tetralin, Power output = $\frac{3.75 \text{ watts}}{\text{in.}^2}$, Coal size = -200 + 270 mesh.

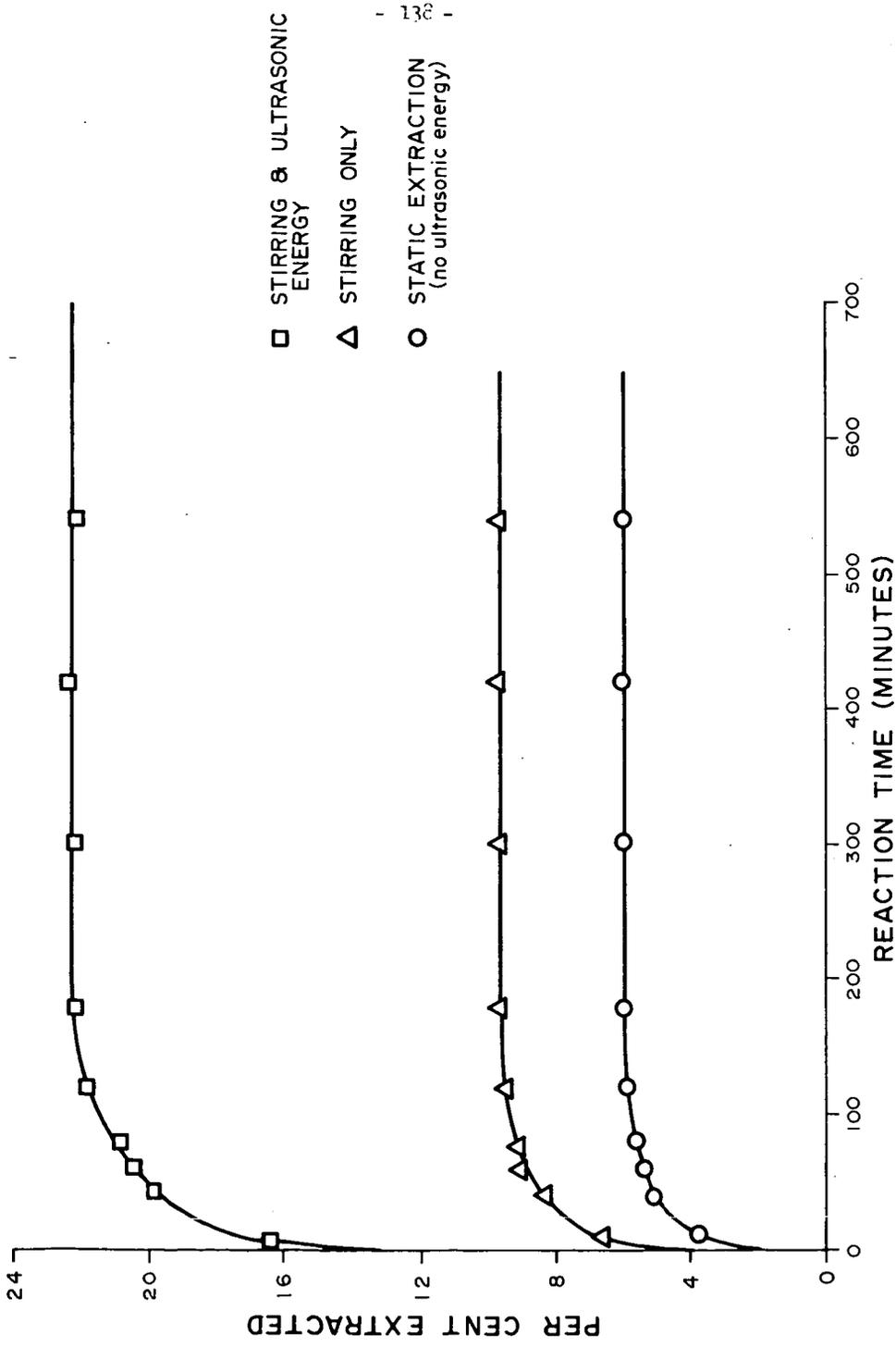


Figure 9. Percent extracted versus time at 87°C. Solvent = Tetralin, Power output = $\frac{3.75 \text{ watts}}{\text{inch}^2}$, Coal size = -200 + 270 mesh.

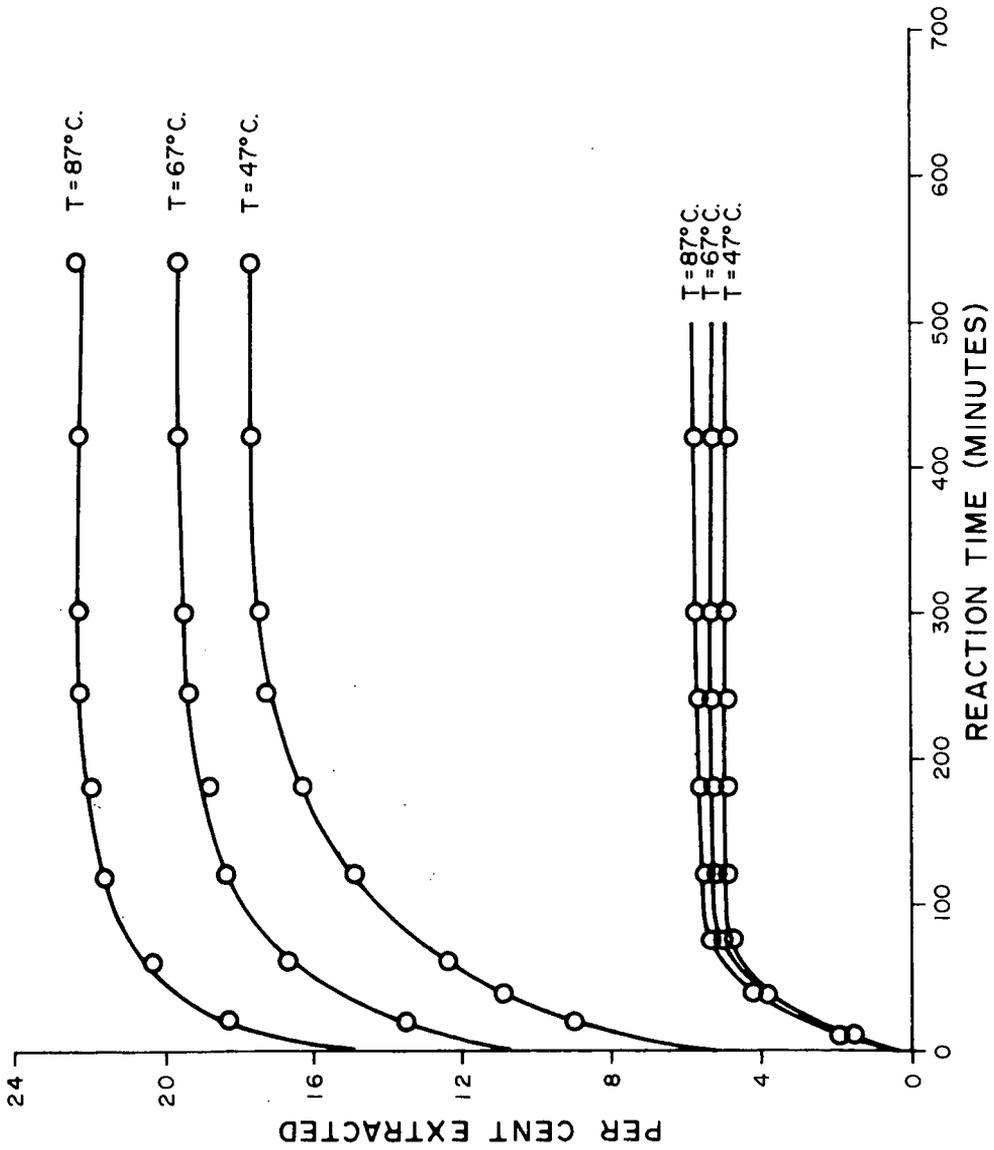


Figure 10. Kinetics of coal extraction with Tetralin.

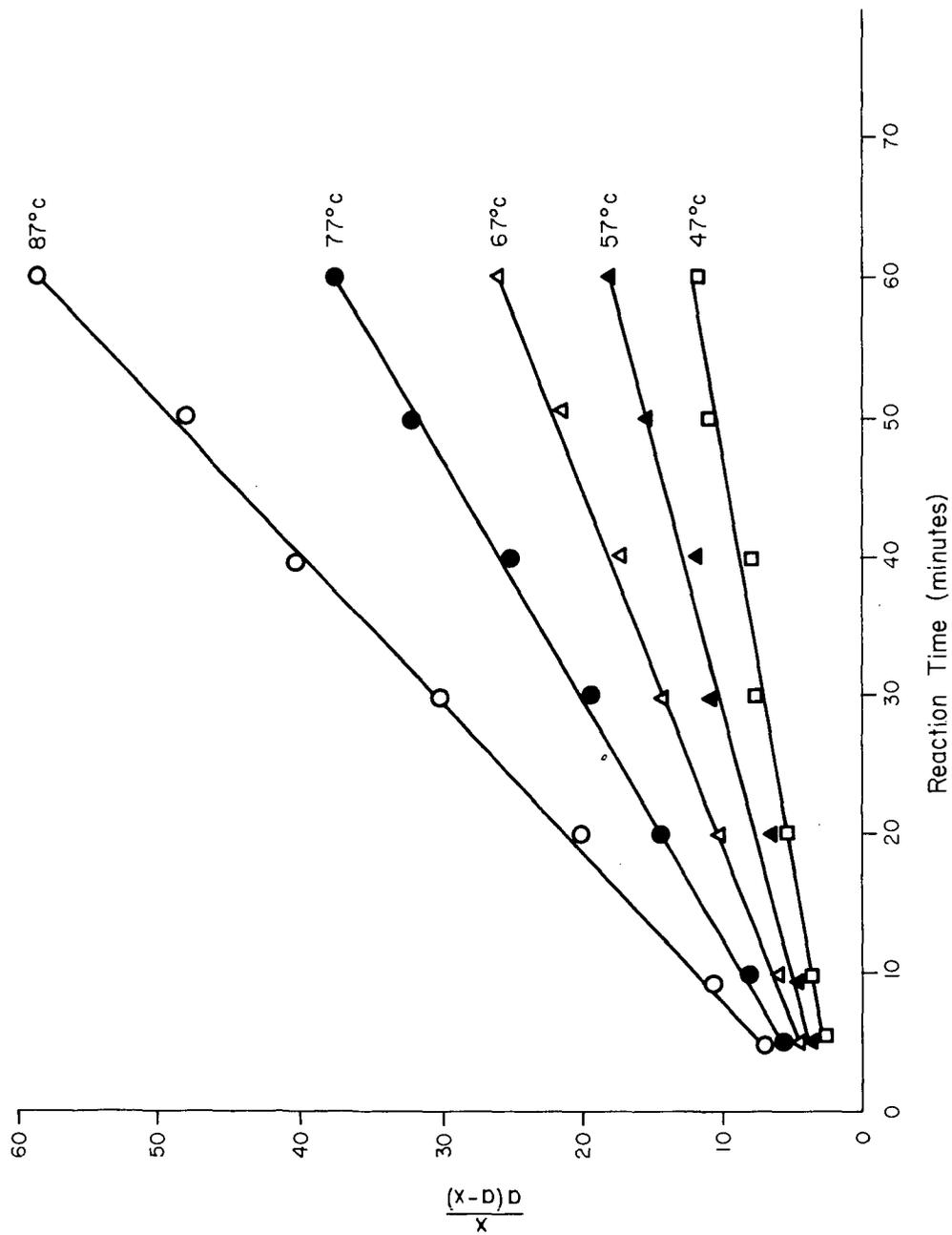


Fig. 11 Plot of $\frac{x}{a(a-x)}$ vs. time for second order reaction

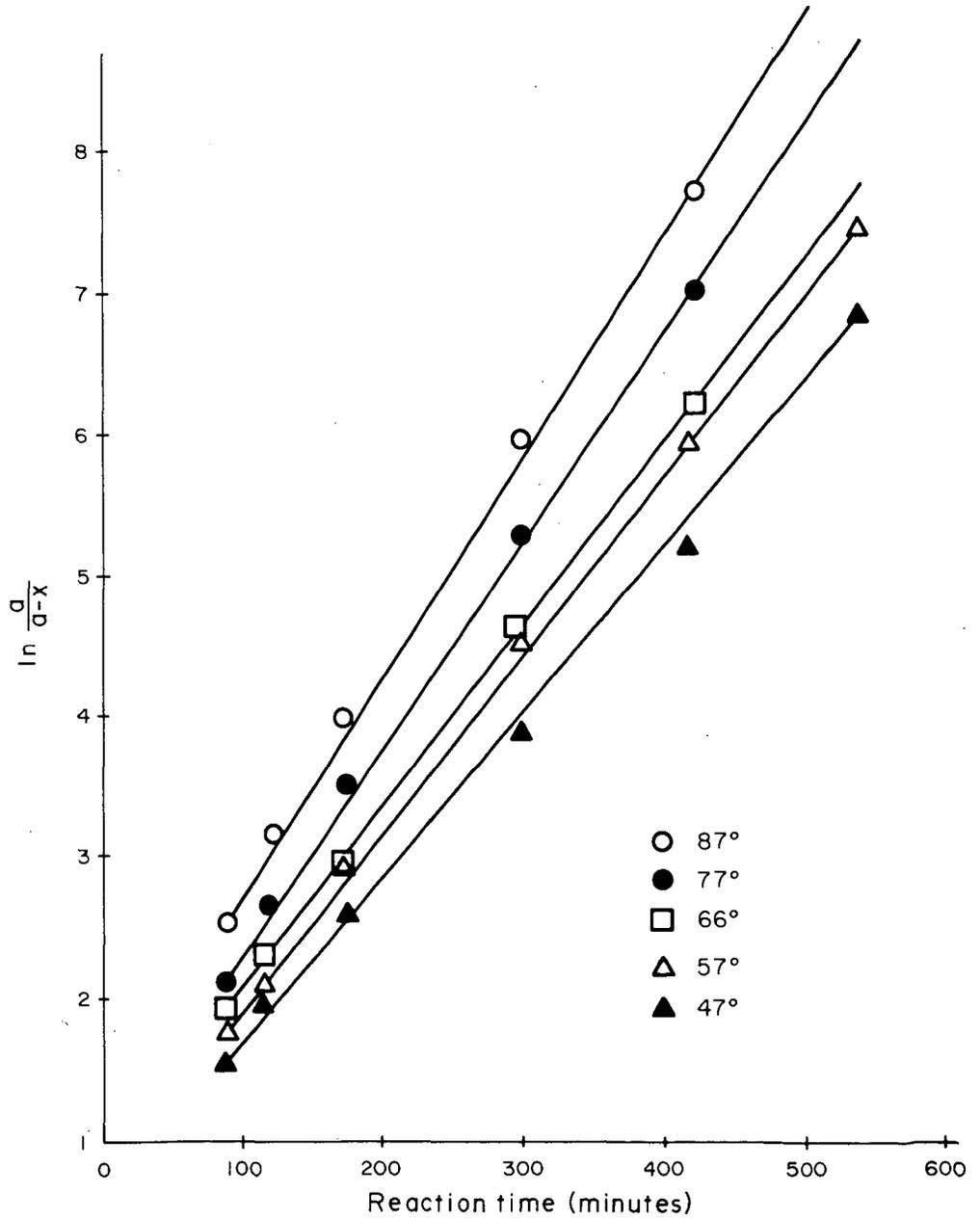


Fig.12 $\ln \frac{a}{a-x}$ versus time for first order reaction.

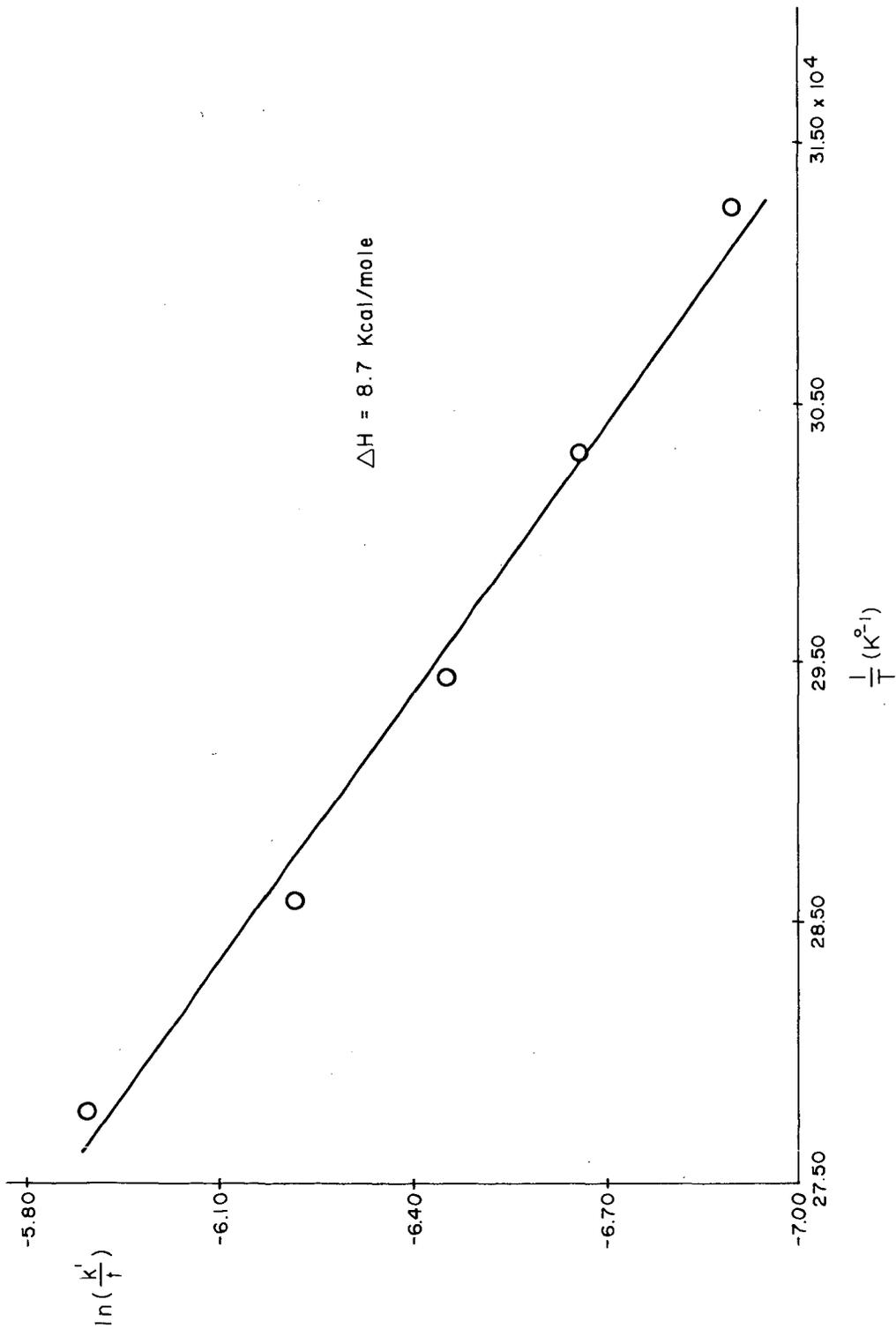


Fig. 13 $\ln \frac{k'}{T}$ versus $\frac{1}{T}$ for evaluation of the activation enthalpy and entropy for second order portion of reaction.

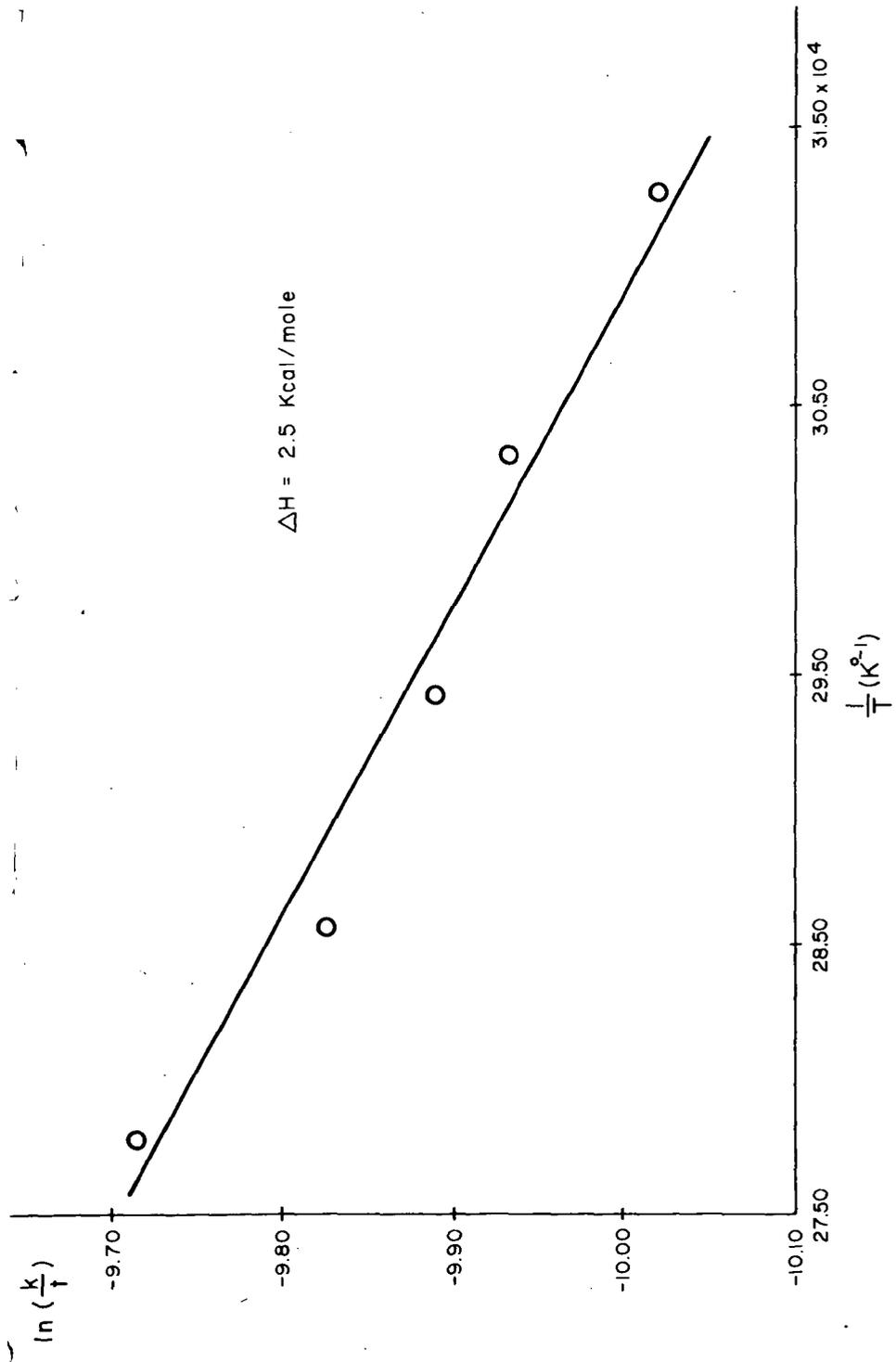


Fig. 14 $\ln \frac{k}{T}$ versus $\frac{1}{T}$ for evaluation of the activation enthalpy and entropy
(first order reaction)