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Kinetics of Colorado Oil Shale
Pyrolysis and Hydrolysis

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemical and Petroleum-Refining Engineering)

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ABSTRACT

The kinetics of Colorado Oil Shale pyrolysis and hydrolysis was studied in a downflow, semi-batch tubular reactor. The apparatus was operated isothermally and at ambient pressure. A modified Carlo-Erba Elemental Analyzer (Model 1104) with direct reaction temperature measurement and direct reaction data logging was adapted to this system and the rates of the pyrolysis and hydrolysis reactions were measured directly by monitoring the rate of volatiles evolution with a thermal conductivity detector. Carbon Conversion experiment and pyrolysis rate experiments were run during the course of this study. Organic carbon conversions of the moisture and carbonate free samples (CMF) were of the same order of magnitude in both the hydrolysis and pyrolysis reactions. However, a 10 to 15% reduction in conversion was observed for the hydrolysis reactions of catalyst impregnated (1% Mo loading) CMF samples. About 70% of the organic carbon conversion was completed between 350°C and 450°C; the remaining 10 to 15% was completed between 450°C to 800°C. Pyrolysis reactions occurring at 625°C and above could be considered to be essentially instantaneous, yielding about 90% of the total cumulative conversion in the first 64 seconds of reaction.

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It was found that the overall carbon conversion to oil and gas products could be adequately modeled using a second order irreversible rate expression.

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DEDICATION

This work is dedicated to my parents and my wife in appreciation of their love and understanding.

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1. LITERATURE SURVEY

1.1. Oil Shale

Oil shale can be described as a finely textured, marlestone type sedimentary inorganic material, containing varying quantities of high molecular weight organic material.

Basically, oil shale can be divided into two parts; the organic part and the inorganic part. A small fraction of the organic part, called bitumen, is soluble in organic solvents. The benzene-soluble portion of oil shale is a highly viscous crude hydrocarbon. The major fraction of the organic part is a waxy substance of molecular weight higher than 3000, with a structure consisting of amorphous, highly disordered naphthenic molecules with closely associated aromatics and nitrogen, sulfur, and oxygen heterocycles. This material, called kerogen, is insoluble in common organic solvents and is not a member of petroleum family. However, this insoluble organic fraction is the basic raw material for production of oil from oil shale, and after appropriate treatment is suitable for use as a refinery feedstock. Both aliphatic and aromatic carbon is contained in the organic portion of oil shale(1). Oil shale in the United States is roughly distributed

between deposits in the Western U.S. (the Green River Formation in Colorado, Utah, and Wyoming) and the Devonian shale of Eastern U.S. Eastern shales are very aromatic, while western shales generally contain more aliphatics.

The inorganic part of a typical western U.S. oil shale is a mix of carbonaceous, silicious, and clay-type materials, with nearly half of the inorganic matter being carbonate containing materials. Carbon dioxide (CO_2) may be evolved during heating of oil shale (2). As a result of thermal decomposition of inorganic carbonates.

The chemical characteristics of oil shale can be identified by three different analytical procedures (3).

1. Fischer Assay analysis. This test indicates what volume (liters or gallons) of oil can be produced by pyrolysis per unit mass of oil shale. The mass percentage of organic matter and the mass percentage of aliphatic carbon in oil shale are related to the oil yield by the Fischer Assay analysis. These relationships can be expressed as the following equations (2).

$$\text{Yield (L/t)} = 8.22 * \text{Organic Matter (mass\% of shale)} - 10.8$$

$$\text{Yield (L/t)} = 12.8 * \text{Aliphatic Carbon (mass\% of shale)} - 35.8$$

The "grade" of oil shale is usually characterized by the Fischer Assay analysis (2).

2. X-ray diffraction analysis. This procedure shows the mineral constituents in shale such as carbonates, silicates and pyrite.

3. Elemental analysis. This test determines the main elemental constituents such as total carbon, hydrogen, oxygen, nitrogen, and sulfur. The percentage of inorganic carbon can also be determined by acid digestion, and organic carbon then determined by difference.

1.2. Mechanism of Oil Recovery by Pyrolysis

Past investigations(5) have concluded that kerogen can be decomposed by a consecutive reaction sequence into bitumen which in turn decomposes to oil, gas, and a carbonaceous residue on the spent shale. This mechanism can be represented as follows;

Kerogen-----> Bitumen-----> Oil, gas and carbon
residue

Generally, the reaction rates in this model have been treated as first order with respect to the concentration (weight fraction) of kerogen for formation of bitumen, and also first order with respect to pyrolysis of bitumen in the subsequent formation of oil and gas.

Ekstrom and Callaghan (6) observed from the pyrolysis

of Rundle and Nagoorin shale that the kinetics of hydrocarbon evolution can be described by two simultaneous first order reactions. The fast initial reaction was followed by a very slow decay of the hydrocarbon release rate, whose relative contributions depended on the pyrolysis temperature. At low temperature, a relatively rapid release of low molecular weight products occurred followed by a slower formation of higher molecular weight products.

At high temperature, secondary cracking reactions result in the formation of low molecular weight aromatics which contribute to the total hydrocarbon release. The two simultaneous first order reactions can be expressed as follows,

$$(1-\alpha) = f \cdot \exp(-k_1 t) + (1-f) \cdot \exp(-k_2 t)$$

α : fractional reaction

f : the fraction of total yield by one reaction

The effect of temperature on " f " becomes less significant as the pyrolysis temperature increased.

Hubbard and Robinson (5,7) also reported that a more complex mechanism than a simple first order reaction is required. Critical observations from these researchers are as follows:

1. The weight fraction of the total kerogen appearing

as bitumen plus oil and gas becomes constant at the time the bitumen concentration reaches a maximum. This means little or no carbonaceous matter was formed after this time. At this point all of the kerogen has been converted to bitumen, gas, and carbonaceous residue.

2. The weight fraction of oil and gas combined at the point of maximum bitumen concentration was nearly equal to the weight fraction of bitumen disappearing. Therefore about half of total product was produced during this latter time period. This indicated that the kinetics of bitumen pyrolysis should be directly related to the appearance of volatile matter during the last half of the reaction.

Figure 1 leads to the conclusion that the pyrolysis reaction was proceeding by a somewhat different mechanism than simple first-order kinetics.

A basic concept in kinetics suggests that homogeneous reaction mechanisms are not applicable to the pyrolysis of oil shale kerogen, which involves the reaction of a solid and both gaseous and solid products. Most importantly, concepts such as concentration and reaction order do not have the same physical significance in solid decomposition reactions as they do in solution or gas phase reactions where reacting species are freely mobile

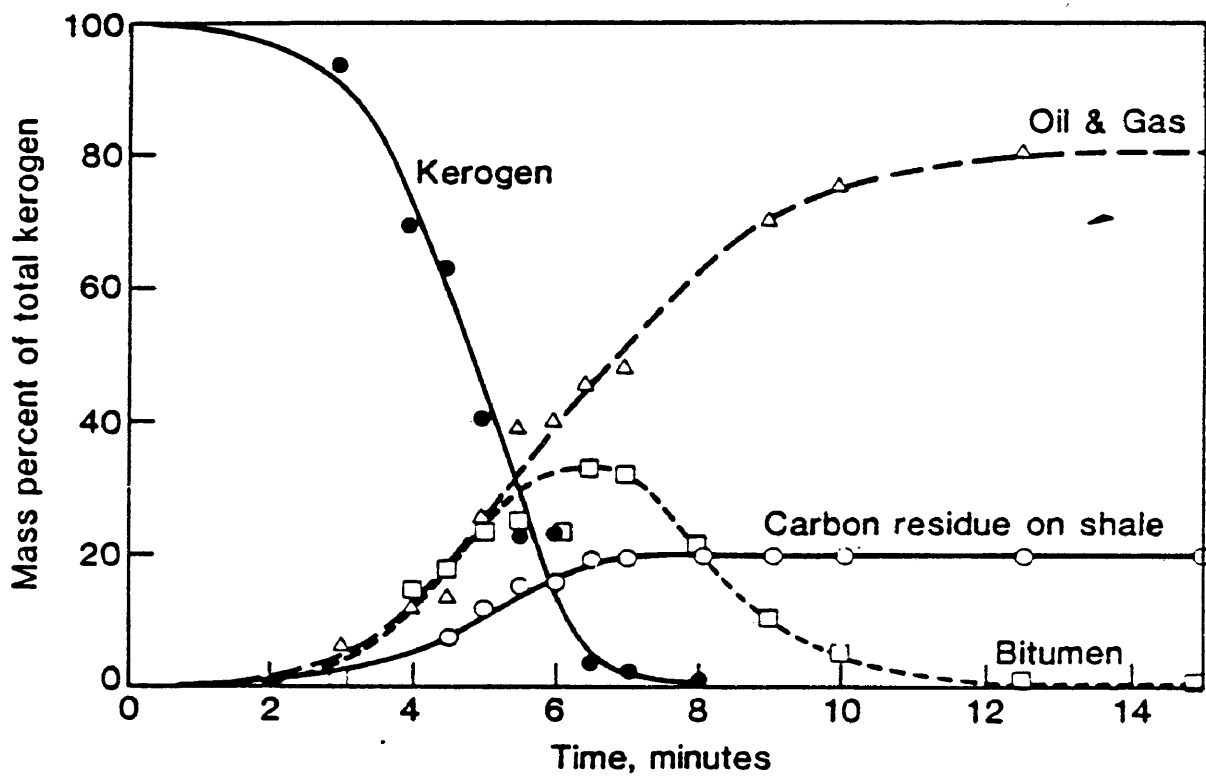
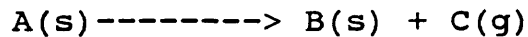


Figure 1

Data for a 111 L/t Colorado Oil Shale on the rate of disappearance of kerogen and the rate of formation of oil, gas and carbon residue on spent shale at 475°C.
(Reproduced from "Synthetic Fuels", McGraw-Hill Book company p 110)

and randomly distributed throughout the system.

Charlesworth (8) used the decomposition of a crystalline solid to explain the pyrolysis reaction mechanism for oil shale.



$$\text{the velocity } \frac{d(\alpha)}{dt} = k(t) * f(1 - \alpha)$$

$k(t)$: rate constant dependent on temperature

$f(1-\alpha)$: depends on the rate limiting step & topochemistry, i.e., geometrical arrangement of chemical species.

Under certain conditions, this rate-limiting step will take place at an interface between the product and reactant phases, and thus determine the speed at which the interface moves into the reactant.

The area of the interface thus becomes analogous to concentration in homogeneous kinetics, and the function $f(1-\alpha)$ is simply the area expressed as a fraction of the original area at $\alpha=0$. In other situations, it may occur that the reaction results in the formation of localized regions of solid product in the bulk of reactant. Under these circumstance the interfacial area, $f(1-\alpha)$, depends on the law of nucleation and growth.

This type of process is likely to happen when

the molecular volume $B(s)$ is greatly different from that of $A(s)$, which leads to a deformation in the structure. The resulting strain energy must be added to the free energy change for the reaction, and depending on the magnitude of the effect, further reaction will take place at the interface between the phases in preference to other sites. Thus the reaction becomes autocatalytic at the points of initial reaction, and the product phase spreads outwards. The factors that determine the rate of growth includes shape of nuclei, the possibility of overlap with other nuclei and the rate of formulating of new nuclei.

1.3. Particle Size

Allred (5) concluded that doubling the particle diameter increased the time required for the same conversion of the pyrolysis reaction.

Willman (17), and Haddadin and Mizyed (18) also suggested that both the rate and extent of pyrolysis were increased upon reduction of particle size.

These effects have been interpreted as indicating a physical process controlling the reaction rate. Particle size effects on the pyrolysis rate are related to the rate of heat transfer rather than to any physical transport

phenomenon.

Ekstrom and Callaghan (6) said that the pyrolysis rate was also strongly dependent on the shale particle size, suggesting that the effect was related to the relatively slow development of a pore structure within the particles to permit the release of the hydrocarbon vapors.

Since oil shale has its organic matter distributed within its inorganic mineral matrix, the kinetics of pyrolysis might be affected by heat and possibly mass transfer limitations.

Intraparticle diffusional resistance will increase as the diameter of the particle increases, giving an inverse relationship between decomposition rates and mean particle size of the sample. The rate of release of volatile products is controlled by the overall temperature gradient inside the particle when larger particles are employed (3,9). When the sample mass is larger than a certain limit, then interparticle transport resistance will decrease the rate of decomposition of kerogen. This is probably due to the fact that temperature gradients develop within the sample (9).

1.4. Hydrogen Effect

Larson & Wen (10) reported that oil shale pyrolysis in an atmosphere of H_2 at pressures up to 4.8 Mpa, have shown that the ratio of hydrogen to carbon (H/C) in the residue is decreased due to preferential cracking of hydrogen-rich fragments of the total organic matter.

Schlinger & Jesse(12) indicated that use of hydrogen at pressure between 68 - 135 ATM resulted in shale oil recovery far in excess of the modified Fischer Assay analysis. These experiments also showed that pyrolysis with hydrogen can have beneficial effects in shale oil yields and product quality.

Fausett and Mikinis (12) have proposed a mechanism in which kerogen pyrolysis can be considered as conversion of most of the aliphatic carbon to oil, while most of aromatic carbon is converted directly to carbon residue. The reactions converting aliphatic kerogen to aromatic oil and continuous cracking to coke are inhibited by hydrogen, and the amounts of aliphatic oil converted to gas and aromatic oil converted to coke are affected by transport processes (13).

The mechanism of carbon residue formation is considered to consist of two pathways,

1. Formation from a fluid intermediate that undergoes

polymerization and condensation reactions,

2. Formation from a material that loses minor fragments but retains its basic three-dimensional structure during pyrolysis.

Secondary reactions that produce coke at slow heating rates from oil aromatic carbon and gas from aliphatic carbon at high temperature compete with the transport process required for recovering of oil. High pressure hydrogen appears to inhibit both the formation of additional aromatic carbon during pyrolysis and coking of aromatic oil. In the absence of high-pressure hydrogen, the total amount of aromatic carbon in the product is nearly twice that in the raw shale, although the distribution of aromatic carbon between the oil and carbonaceous residue changes.

1.5. Effect of Transition Metal and Hydrogen

When pyrolysis is conducted in the presence of transition metal catalysts and hydrogen, reactions involving saturation of aromatic kerogen to form aliphatic kerogen could be promoted. Aliphatic kerogen is responsible for the production of liquid hydrocarbons, while aromatic kerogen is stable during retorting and results mostly in carbon residue.

The presence of hydrogen alone in the retorting atmosphere does not influence any kinetic parameter of kerogen decomposition (3).

The most probable mechanism for hydrogen participation in the kerogen decomposition reaction in the presence of metal catalysts would involve dissociative adsorption of hydrogen on the metal surface. The adsorbed and activated hydrogen atoms could then diffuse into the interior of the oil shale and react with the organic matter saturating and/or cracking large hydrocarbon molecules.

Baldwin and Chen (14) reported that hydrogen availability to the primary pyrolysis reaction is the rate-limiting step in hydroxyrolysis. Use of an impregnated catalyst for hydrogen dissociation was shown to be effective in facilitating high conversion of organic carbon and oil yield, but only at elevated hydrogen partial pressures. The catalyst (MoS_2) was not effective at ambient pressure, and was found to be detrimental to conversion if the metal loading was sufficient to introduce mass transfer limitations, due to pore mouth blockage, or structural changes brought about by the chemistry of the impregnating solution.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

2.1. Reactor System Description

The pyrolysis/GC system was constructed by modifying an existing Carlo-Erba Elemental Analyzer (Model 1104). A schematic of the experimental equipment is presented in Figure 2. The micro-reactor unit is a quartz tube packed with two layers, and was operated in the downflow mode. The top layer consists of quartz chips used for supporting the sample in the isothermal zone, while quartz wool on the bottom layer was used for support of the quartz chips.

Hydrogen or Helium carrier gas, divided into two paths, separately passes through a filter for oxygen and water removal and a Porter Instrument Co. A-125-3 rotometer at a flowrate of 30 cc/min. The calibrated carrier gas, at a pressure slightly higher than atmospheric then flows into the top of each reactor tube.

The pyrolysis system consists of two identical quartz tubes, 18"-long x 3/8"-outside diameter x 1/32"-wall thickness. One is empty, and was operated at ambient temperature. The carrier gas passes through this empty tube and into the reference side of a thermal conductivity detector. The other tube, supported in a

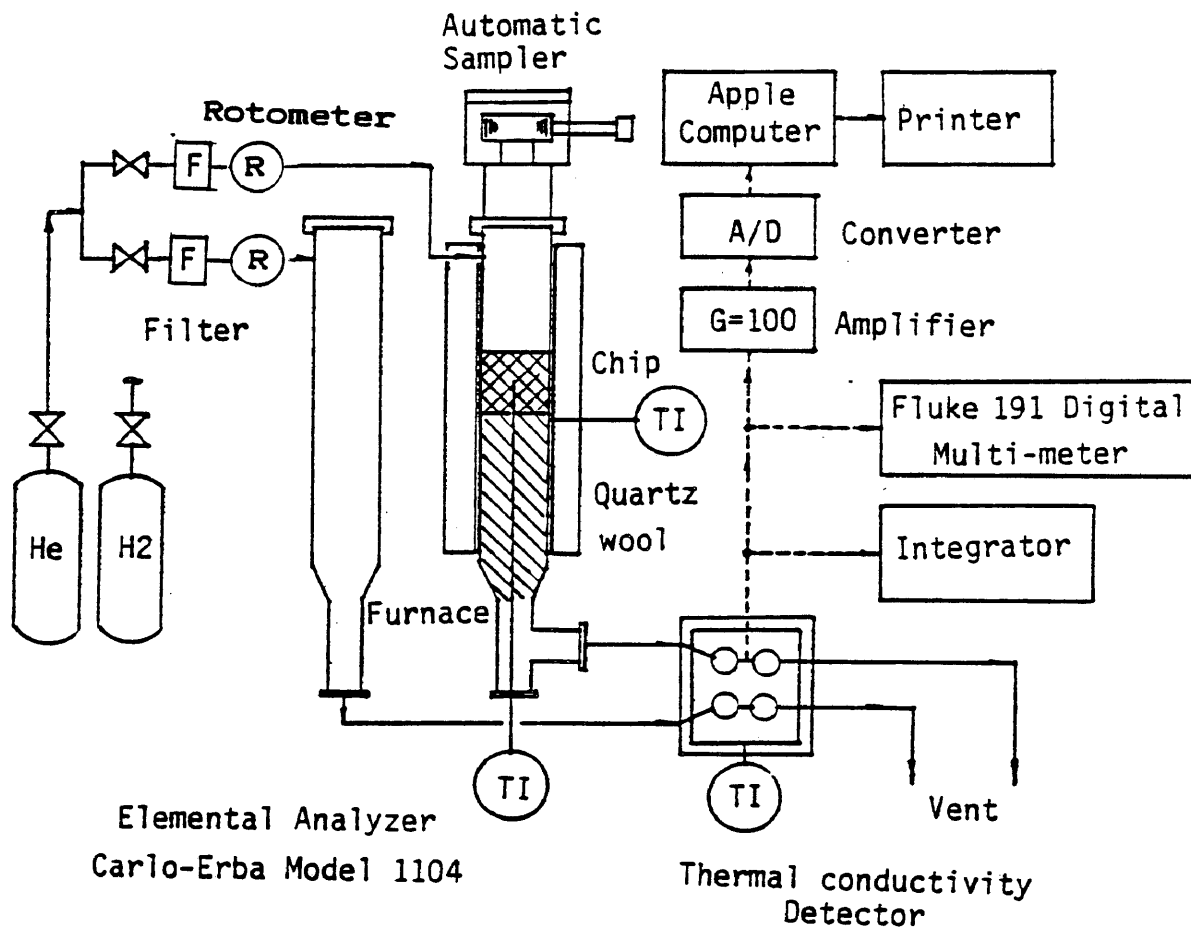


Figure 2
Schematic Diagram of Experimental Appartus

furnace, had a thermocouple inserted from the bottom and located at the hot spot in the pyrolysis tube. The reaction zone was located at 8-13/16 inch distance from top, and was approximately 1 inch long.

The sample for pyrolysis was placed in a small quartz cup, 1/4"- long x 1/8"- outside diameter x 1/32"- wall thickness, and injected into the pyrolysis tube from an autosampler. The cup containing the sample was permitted to fall freely down to the top of isothermal zone. The carrier gas then swept the reactants through the rest of the tube and into the sample side of the thermal conductivity detector in the GC.

The signals, 0.05 mv to +35 mv, produced from the thermal-conductivity detector, varied linearly with the reactor effluent flow and pyrolysis gas composition. A thermocouple was located inside the detector box, and the temperature of the detector was controlled around 110 °C.

A HP-3380A integrator and a Fluke 191 digital multi meter were used to monitor the variation of signals from the detector, and also for establishment of baseline zero prior to starting a run.

A Lawson Labs, Inc. amplifier (gain=100) was used to magnify the detector's signal from the millivolt to

volt range. The amplified signal was then passed to a Lawson Labs, Inc. analog-to-digital (A/D) converter (Model 14). An Apple IIe computer logged the digital signal, and stored data in a disk file. An Epson printer was used to print out the results.

2.2. Sample Preparation

Three different oil shale samples were used in these experiments. A flow chart of the sample preparation scheme used is provided in Figure 3 and the procedures followed to make each sample are explained below.

2.2.1. MF (moisture free)

Initially, a one kilogram chunk of Colorado oil shale was broken into small (1/2 inch) pieces with a hammer. These shale pieces were next processed in a ball mill in order to grind the 1/2 inch lumps to 100% -74 micron (200 mesh) material. The powdered shale was vacuum dried at 333 °K and stored in a dessicator until used. In the following discussion, this sample is named MF, meaning moisture free.

2.2.2. CMF (carbonate and moisture free)

The MF sample was leached with concentrated HCl to

dissolve all the carbonate carbon. The resulting slurry was filtered, washed with hot water, dried in the vacuum oven at 333 ° K overnight, and stored in a dessicator.

2.2.3. CCMF (catalytic carbonate and moisture free)

Ammonium heptamolybdate $(\text{NH}_4)_6 \cdot \text{Mo}_7 \cdot \text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in distilled water. Hydrogen sulfide was then bubbled through this solution at room temperature. The conversion to the thio-salt, $(\text{NH}_4)_2\text{-MOS}_4$, takes place quickly and is accompanied by a color change; the solution turns succesively from colorless to orange to dark red. The CMF shale sample was next placed in this dark red solution and impregnated with Ammonium tetra thio molybdate (about 1 % Mo loading). The sample was then dried in a vacuum oven at 333 ° K overnight, and stored in a dessicator.

2.3. Chemical Analysis

2.3.1 Carbon Analysis

A Coulometrics Inc. Carbon Dioxide Coulometer (Model 5010), total carbon apparatus (Model 5020) and Carbonate carbon (CO_2) apparatus (Model 5030) were used to analyze the total carbon content and inorganic carbon content of the MF & CMF samples. The results are provided

Table 1
Carbon analysis of MF & CMF samples

	MF	CMF
Total carbon (wt%)	26.96	33.23
Inorganic carbon (wt%)	4.0004	0
Organic carbon (wt%)	22.9002	33.23

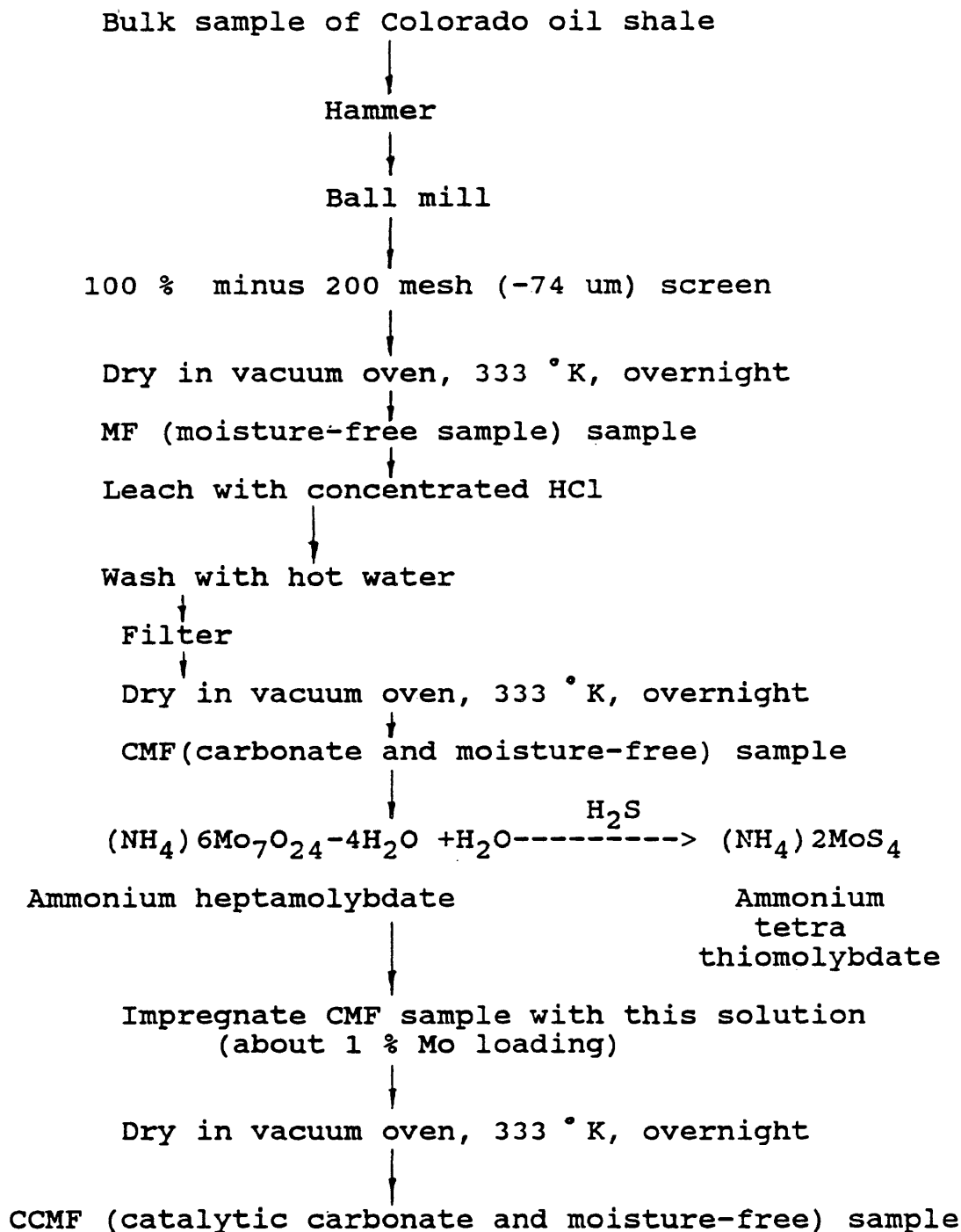


Figure 3

Sample preparation

in table 1.

2.4. Experimental Operating Procedures

Two different kinds of experimental procedures were used. The first was to run the pyrolysis experiment in order to measure the rate of pyrolysis in the pyrolysis/GC system. The second was to measure the carbon conversion with the Coulmetrics system in order to determine the final conversion data.

Each run was performed at a given set of operating conditions: reaction temperature, sample weight, and carrier gas flow rate. The run matrices used are shown in Table 2 and Table 3.

2.4.1. The standard operating procedure for each pyrolysis run was as follows;

1. Select the correct carrier gas; H₂ or He.
2. Set and balance both carrier gas flow rates at 30 cc/min.
3. Turn on the furnace and stabilize at the desired temperature.
4. Weigh out the specified sample (MF, CMF, CCMF) to the desired weight and put in the autosampler.
5. Turn on the bridge current to the GC, and set the GC oven temperature at 110 °C.
6. Balance and stabilize the analyzer's zero point (0.050 mv reading from digital multi meter).
7. Turn on the amplifier and computer.

8. Run program A/D-18, and inject the sample from the auto sampler into the reactor.
9. After 636 seconds, the A/D-18 program has logged 2000 points from analyzer. The program (A/D-18) will stop automatically, and transfer the 2000 points of reaction data to a disk file.

2.4.2. The standard operating procedures for each conversion run is listed as follows.

1. Select the correct carrier gas (H₂ or He).
2. Set & balance both carrier gas flow rates at 30 cc/min.
3. Turn on the heater and stabilize at the specified temperature.
4. Place the specified sample (MF, CMF, CCMF) into the quartz sample cup (a large sample of 50-100 mg was generally used)
5. Turn on the main switch, set the oven temperature at 110 ° C.
6. Balance and stabilize the analyzer's zero point (about 0.050 mv reading on the digital multi meter)
7. Turn on the integrator, set the specified points such as timer, area reject, speed, slope sensitivity, attenuation.
8. Inject the sample from autosampler into the reactor.
9. After one hour when the recorded data on the integrator has stabilized near the starting point, turn off the main switch.
10. Take the reactor tube out of the furnace, cool to atmospheric temperature, and pull out the sample cup and its residue.
11. Weigh the reacted sample on a electronic scale.
12. With the Coulometrics system, measure the total carbon and/or the inorganic carbon wt % in the

reacted sample.

13. Calculate the conversion, based on organic carbon, via following formula.

A. For CMF ,HCMF and HCCMF samples:

$$\% \text{ conversion} = \frac{33.23 - X}{33.23}$$

B. For MF samples:

$$\% \text{ conversion} = \frac{22.9002 - (X-Y)}{22.9002}$$

X: Wt % total carbon in the reacted sample.

Y: Wt% inorganic carbon.

Table 2

Matrix for Pyrolysis Experiments

Temperature Deg C	Samples	Sample weight (Milligram)
805	MF	0.4
765	CMF	0.6
625	HCMF	0.8
542	HCCMF	1.0
425		
458		

Table 3

Matrix for Conversion Experiments

Temperature Deg C	Samples
805	MF
765	CMF
625	HCMF
542	HCCMF
458	
425	
400	
372	

2.5. System Calibration and Pre-Treating

Initially, the individual components of the system were calibrated and tested within their respective operating range. A calibration curve for the reactor temperature distribution is presented in Figure 4. The purpose of this calibration was to find the highest temperature point and the length of isothermal zone around the hot spot, which was subsequently used for the actual reaction zone.

A series of preliminary checks on the function of the analyzer, A/D converter and computer independently and linked together with the system were performed in order to:

1. Determine the maximum and minimum operating range for the system, such as sample weight, GC attenuation, and span of the digital signal in the A/D-18 computer program used to log data.

2. Set up the sequences of the operating procedure.

The specification and conversion formula for the Lawson Lab, Inc. amplifier are as follows:

Amplifier gain : 100

Input range: 0 to 95 mv

Output range: -4.75 to +4.75 v

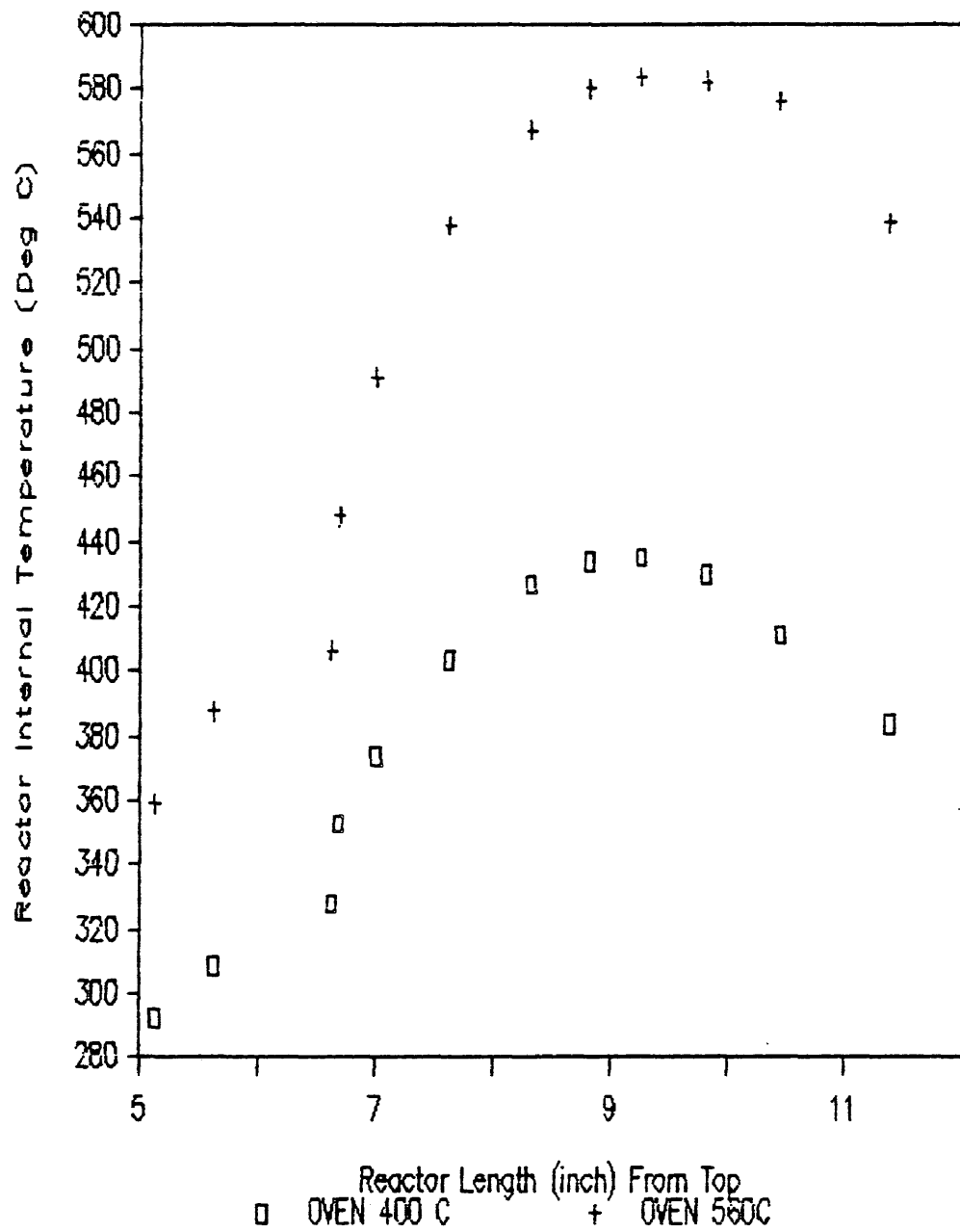


Figure 4
Reactor internal Temperature Profile

$$\text{Voltage in} = \frac{\text{Voltage out} + 4.75}{100}$$

The testing results for the amplifier are shown in Figure 5. The span of the A/D converter was from -32000 to +32000. However, the range used in this experiment was only from -9500 to 0.

The absolute digital signal was converted into a relative percentage via the following formula;

S (zero point) : close to -9500

FN (digital signal): in the range of -9500 to 0

ABS(S) (range): 9500

W = FN + ABS(S)

$$Y = 1.0 - \frac{W}{\text{ABS}(S)} = 1.0 - \frac{\text{FN} + \text{ABS}(S)}{\text{ABS}(S)} = - \frac{\text{FN}}{\text{ABS}(S)}$$

The following modifications of the Carlo-Erba Elemental Analyzer (Model 1104) were made to meet the actual requirements of this experimental program.

1. Remove the oxidation and reduction catalyst tubes in the analyzer, by-pass the selecting switch, and pass the effluent from the pyrolysis reactor to the thermal-conductivity detector directly. Hence, peak area from the TCD will vary linearly with the rates of evolution of total pyrolysis gas.

2. Use the CHN section of the analyzer only for the

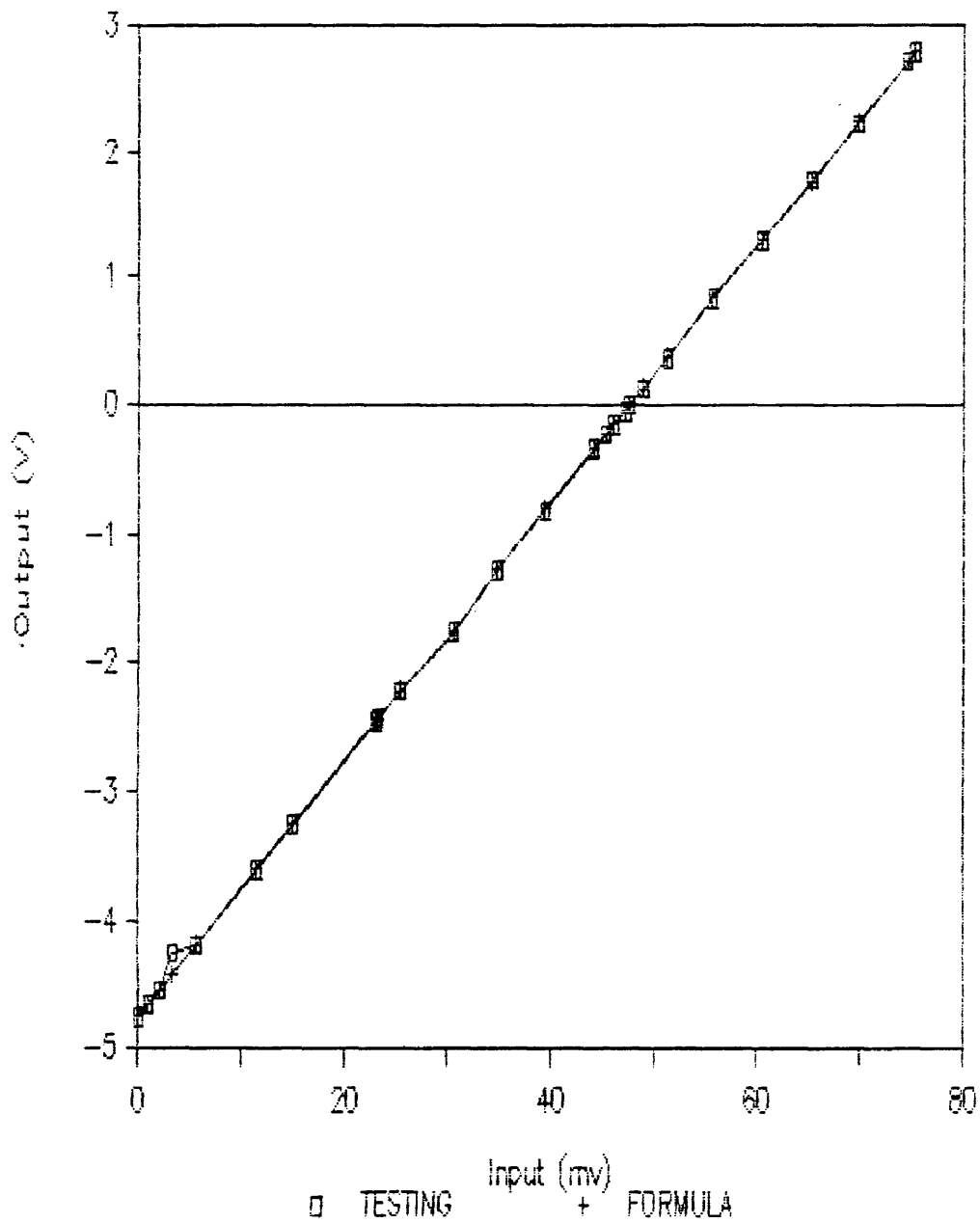


Figure 5
Lawson Labs, Inc. Amplifier

reference, and operate this zone at ambient temperature.

Some procedures were carried out at regular intervals in order to keep the system functioning properly.

1. Check the position (8-13/16 inch from top) and length (1 inch) of isothermal reaction zone.
2. Check for leakage of carrier gas.
3. Screen the chips and remove any residue from the sample after reaction from the chip layer.
4. Wash the reactor tube and dissolve the deposited shale oil via THF. Refill with new chips and quartz wool.
5. Bake-out the pyrolysis tube (keep the system at 875 C, for 8 hours).

2.6. Data Treatment

The flow sheet of the analyzer's raw data treatment is shown in Figure 6. The function of each program is explained as follows.

A: Show the analyzer's raw data:

Text 66: plot the raw data in one screen and print out.

Text 11: show raw data in percentage format.

Text 12: show raw data in coordinate system 0-160

Text 17: plot raw data in continuous screen.

B: Average:

Average: find the average value of first 20 and

last 250 points, and also the first point which is close to the average of the last 250 points.

C: Integration and Normalization:

Text 14: without normalization

Text14b: the procedures of normalization explain on section 4.3.

D: Show the normalized data;

Text100: plot normalized data in one screen and print out.

Text 13: show the normalized data.

A print-out of each of these programs is provided in Appendix A.

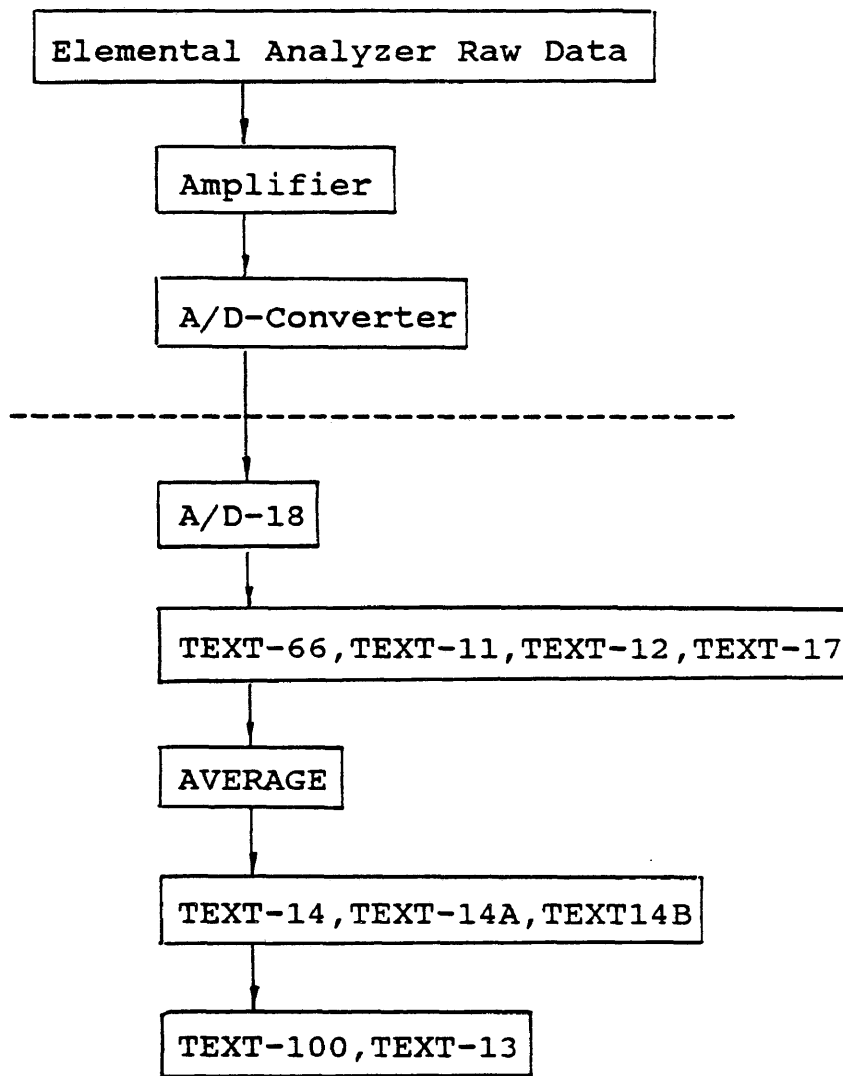


Figure 6

The Flow Sheet of Raw Data Treatment

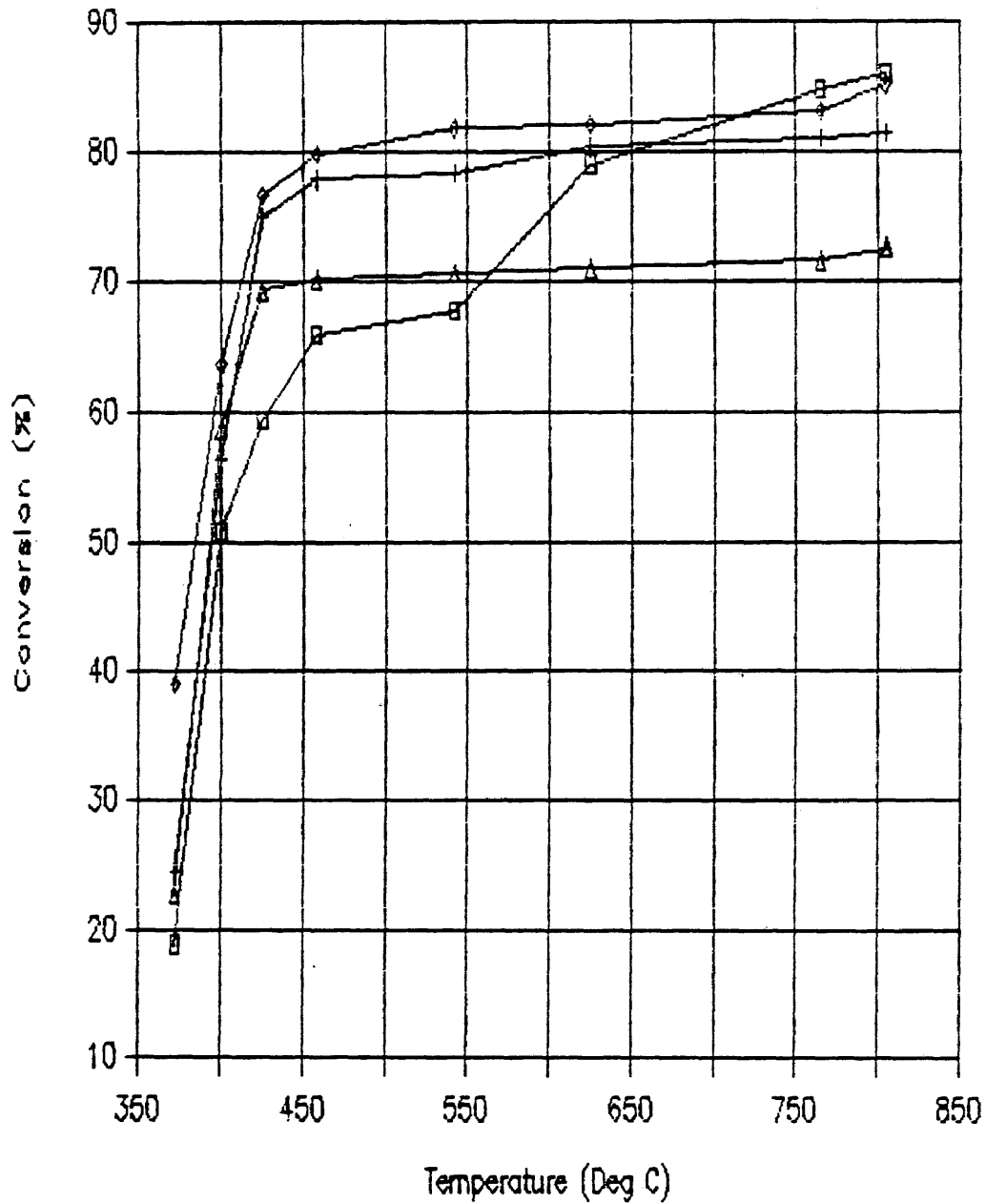
3. EXPERIMENTAL RESULTS

3.1. Conversion Experiments

A total of 32 data points for carbon conversion were used to construct the oil shale conversion curves. Each point was confirmed by three to five independent replicate experiments. The details of each experimental run are provided in Appendix C.

The oil shale conversion curves are presented in two different ways; total carbon conversion vs temperature (Figure 7) and organic carbon conversion vs temperature (Figure 8). Figure 7 and Figure 8 are identical for the CMF, HCMF, and HCCMF samples, since these samples are carbonate free. Only the MF sample which still contains carbonate (inorganic) carbon is described differently in Figure 7 and Figure 8.

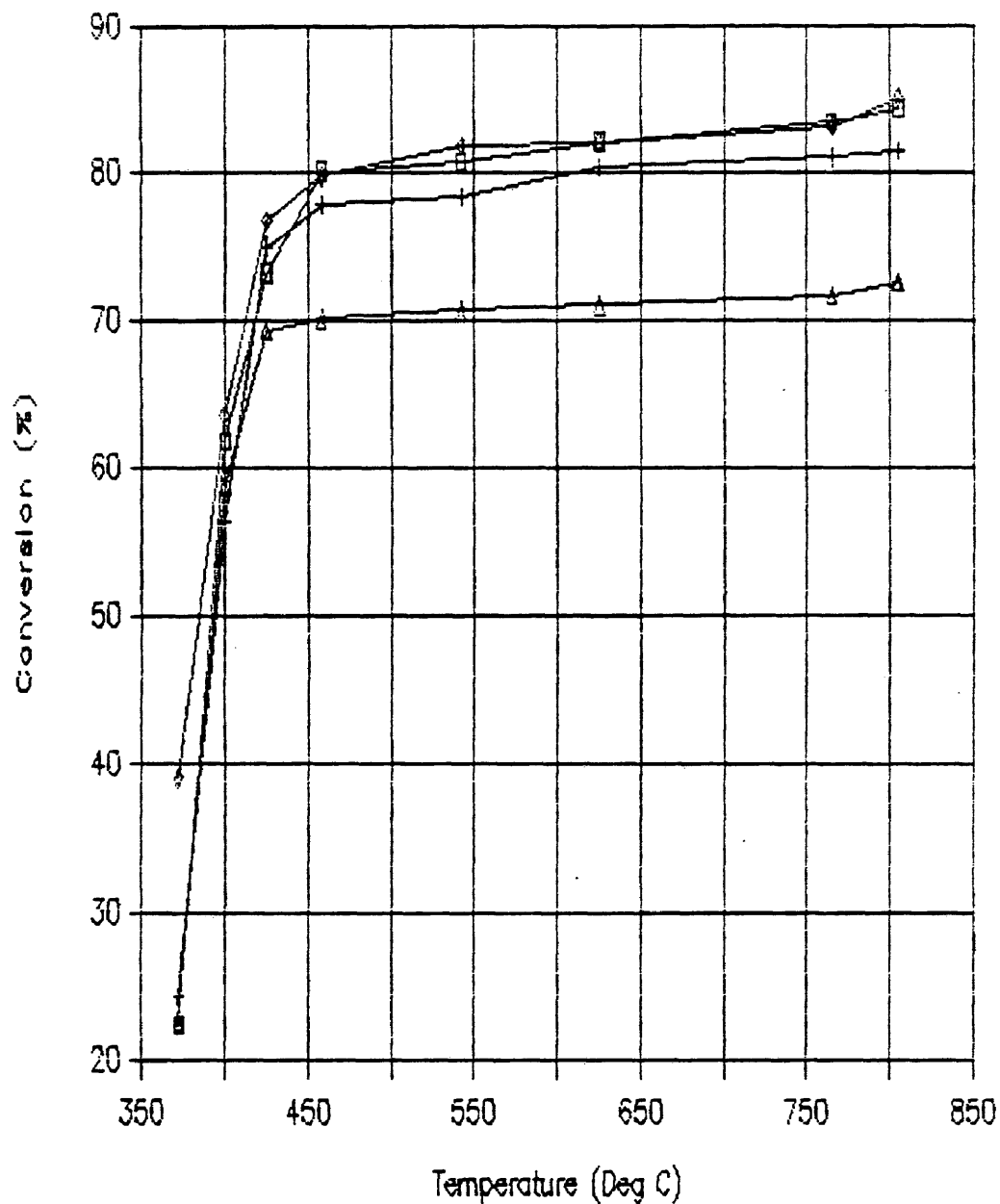
From the conversion experiments on the dry shale (MF), it was found that the carbonate decomposition reaction increased rapidly when the reaction temperature exceeded 550 °C. This is shown graphically by the discontinuity in the MF conversion curve (Figure 7) at approximately 550 °C, and meant that more carbon dioxide would be produced from carbonate decomposition at higher temperatures. This rapid increase in carbonate conversion is shown graphically in



- MF : Moisture free
 + CMF : Carbonate and moisture free
 ◇ HCMF : Hydropyrolysis of CMF sample
 Δ HCCMF : Metal impregnated HCMF sample

Figure 7

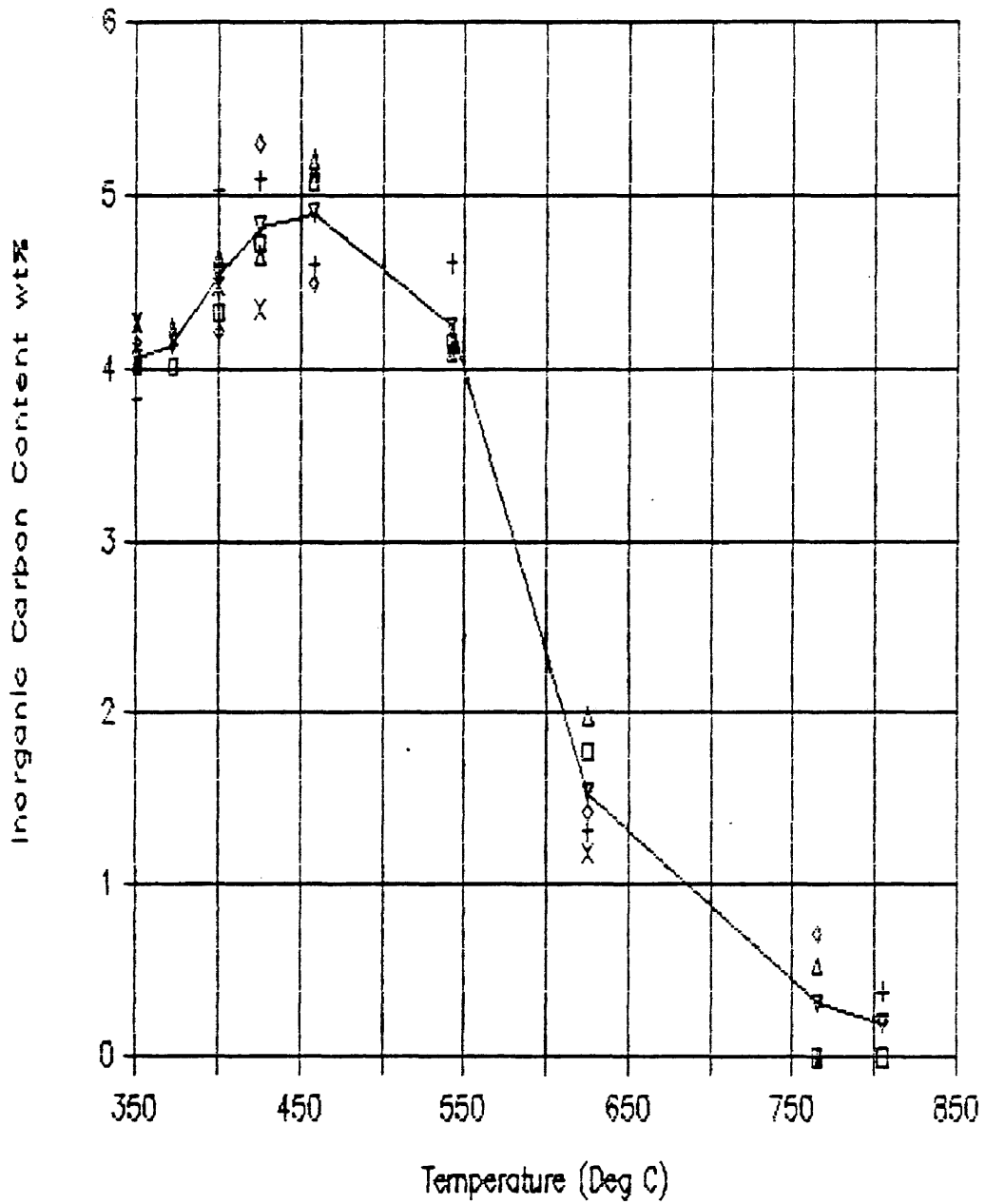
Total Carbon Conversion
 (Summary of MF, CMF, HCMF, HCCMF Samples)



- MF : Moisture free
- + CMF : Carbonate and moisture free
- ◇ HCMF : Hydropyrolysis of CMF sample
- △ HCCMF: Metal impregnated HCMF sample

Figure 8

Organic Carbon Conversion
(Summary of MF, CMF, HCMF, HCCMF Samples)



□ , +, ◇, △ Different of experimental runs
 ▽ Average of all runs

Figure 9

Inorganic Carbon Conversion

Figure 9.

The conversion experiments showed no carbon conversion at 332 °C and about 20 % conversion at 370 °C. Extrapolation of the low temperature data indicated that the organic carbon conversion reaction would start around 350 °C.

3.2. Pyrolysis Experiments

A total of 96 runs were made during this study. Two runs were aborted due to a signal overscaling problem. Several runs had high noise on the tail of the GC signal, and thus were inconsistent with other data. These runs were also not used for kinetic modeling.

A typical curve for the pyrolysis rate experiments is shown in Figure 10. The curve had a very long tail that exhibited considerable "noise". Figure 10 shows the pyrolysis rate were plotted using only a total of 400 data points, however when these curves were integrated, 2000 data points were employed.

The width and height of each pyrolysis rate curve was influenced by the reaction temperature and sample weight. Generally speaking, for runs with the same sample weight, increasing reaction temperatures made the reaction peak higher and decreased the width of the peak. This comparison is shown in Figure 11. Compared with the same reaction temperature, larger sample weights would give

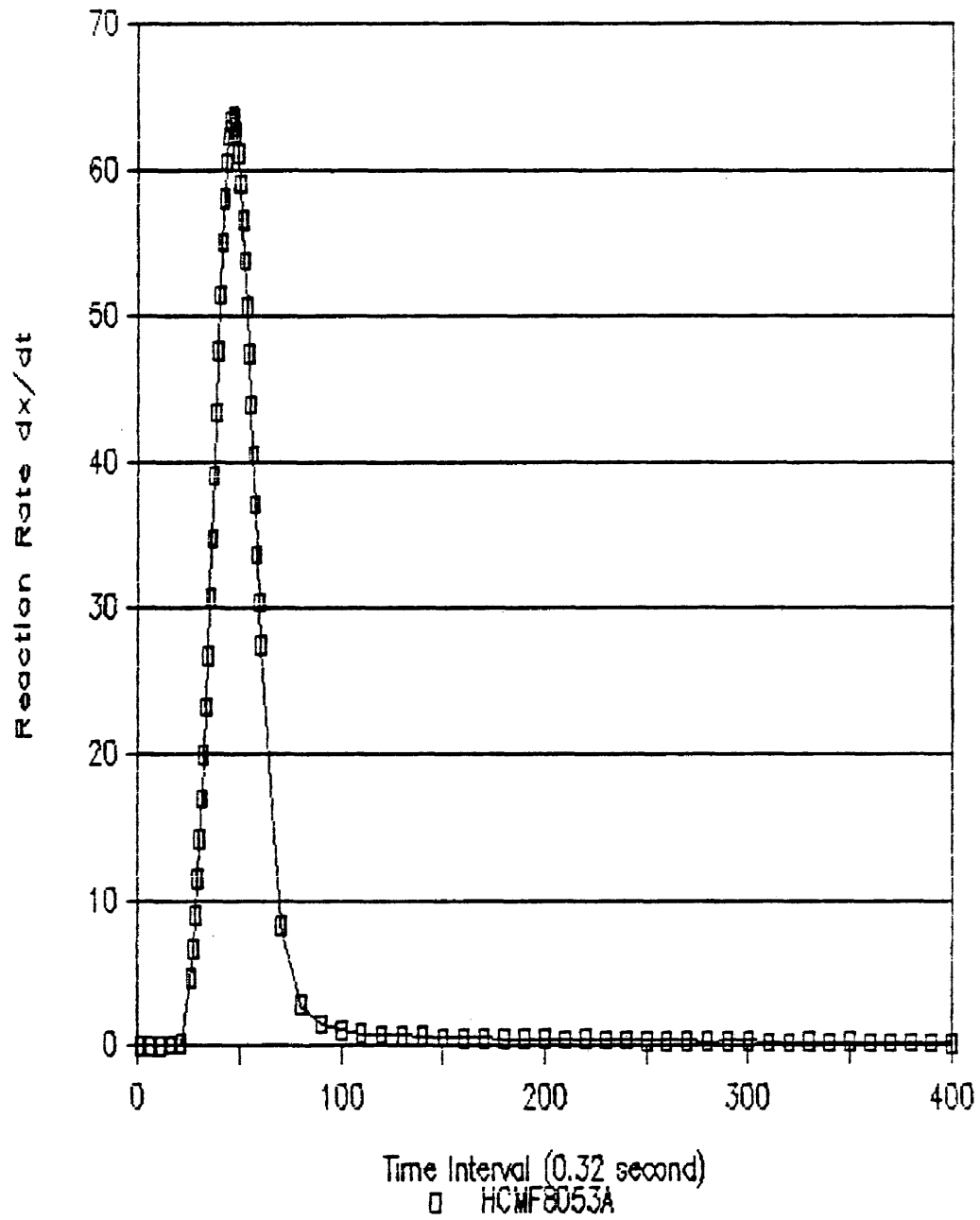
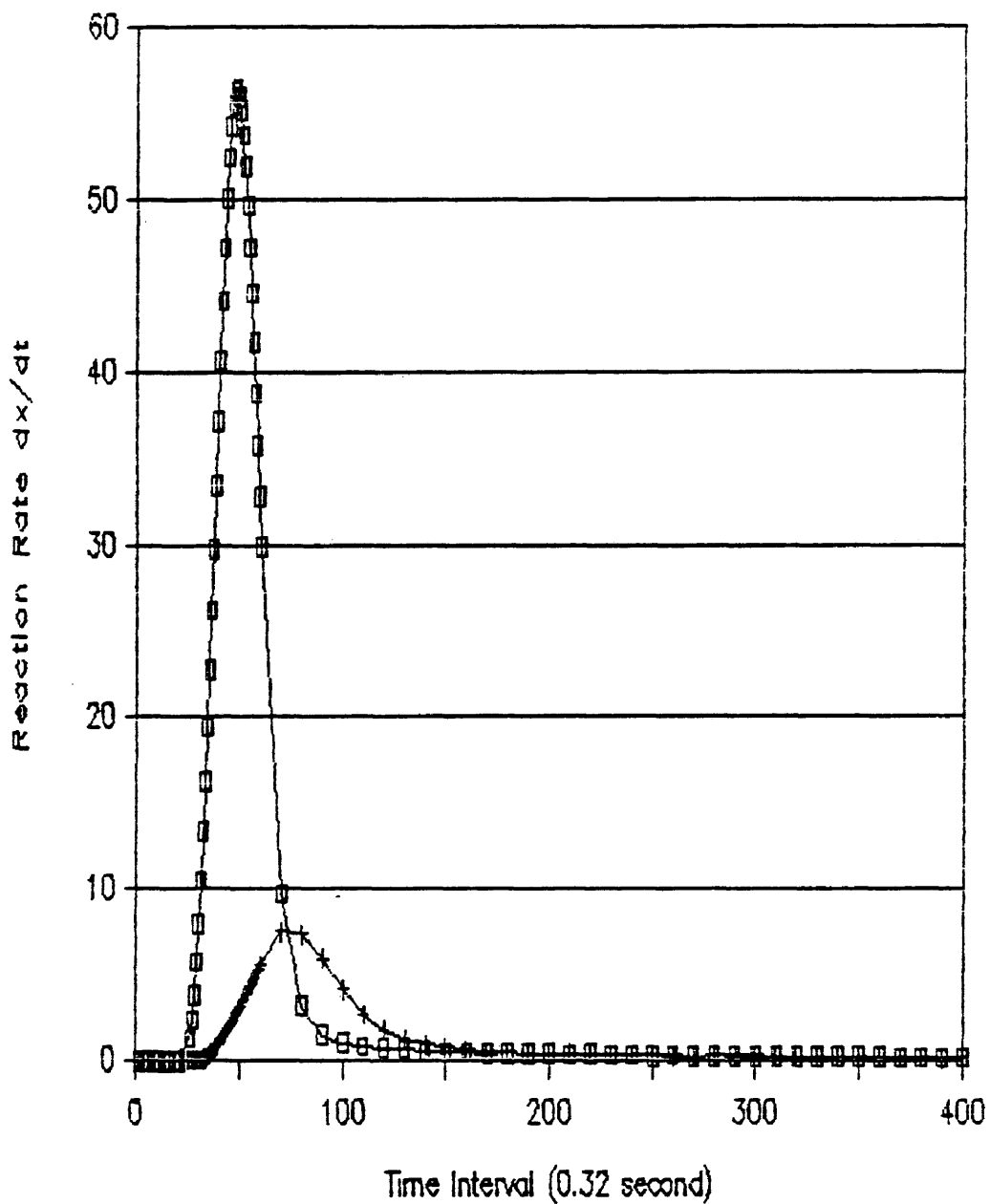


Figure 10

Reaction Rate vs Time for HCMF8053A
(Hydropyrolysis moisture and carbonate
free sample at 805°C)



□ : Reaction at 765°C + : Reaction at 542°C

Figure 11

Effect of Temperature on Reaction Rate
for Same Weight (1 mg), But Different
Temperature (765°C and 542°C)

higher and broader reaction peaks as shown graphically in Figure 12.

The MF sample showed a second peak on the pyrolysis rate curve which was caused by the release of carbon dioxide from the carbonate decomposition reaction. This second peak became more pronounced when the reaction temperature exceeded 550 degree C. A typical curve for a MF (carbonate-containing) sample is shown on Figure 13.

A typical corresponding analog pyrolysis curve from the TCD is shown in Figure 14.

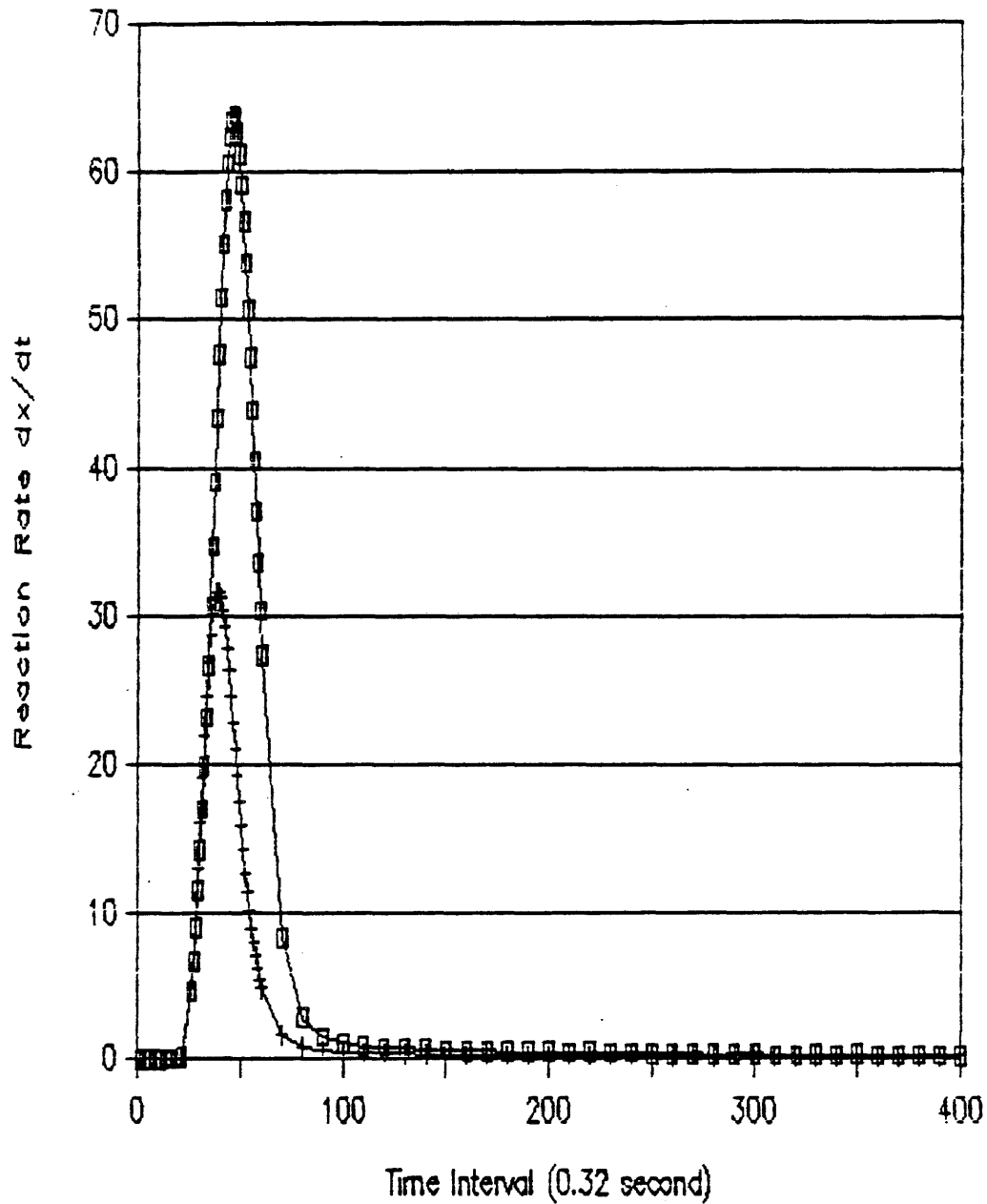
3.3 Cumulative Normalized conversion

The cumulative normalized conversion curves (cumulative conversion vs time) were prepared from the pyrolysis rate curves by the following steps;

- 1) 100 % conversion was assumed for each pyrolysis experiment, and the pyrolysis reaction curve was integrated via Simpson's rule, starting from point zero to the end point.

- 2) The percentage of the cumulative conversion was calculated for each time interval.

- 3) The percentage conversion of each point of the cumulative conversion was corrected by the results of the actual conversion experiments at the same reaction temperature.



□ : Sample Weight was 1 mg
+ : Sample Weight was 0.4 mg

Figure 12

Effect of Sample Weight on Reaction Rate
for Same Temperature (805°C) But Different
Weight (0.4 and 1 mg)

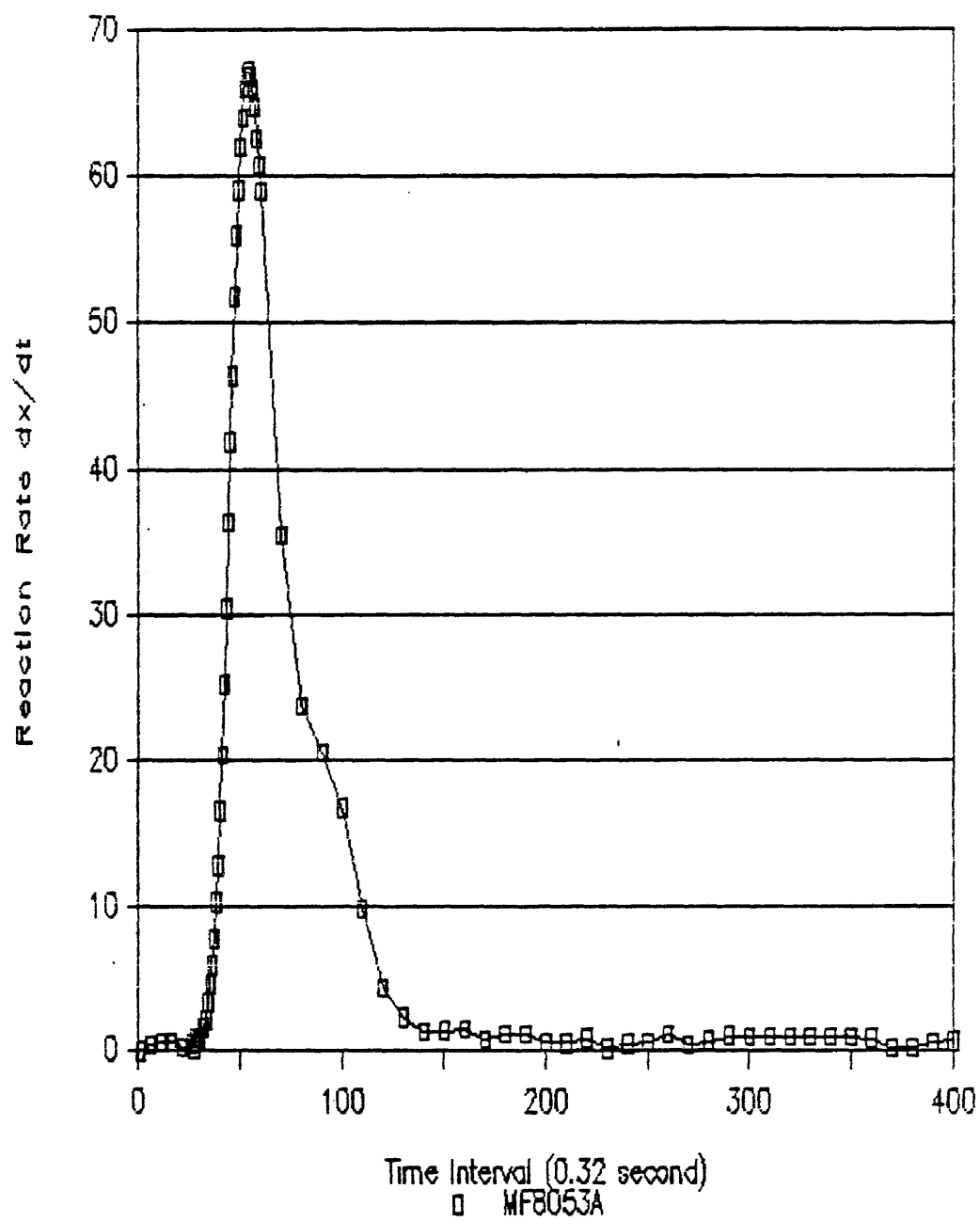


Figure 13
Reaction Rate with Second Peak
MF8053A
(pyrolysis moisture free sample at 805°C)

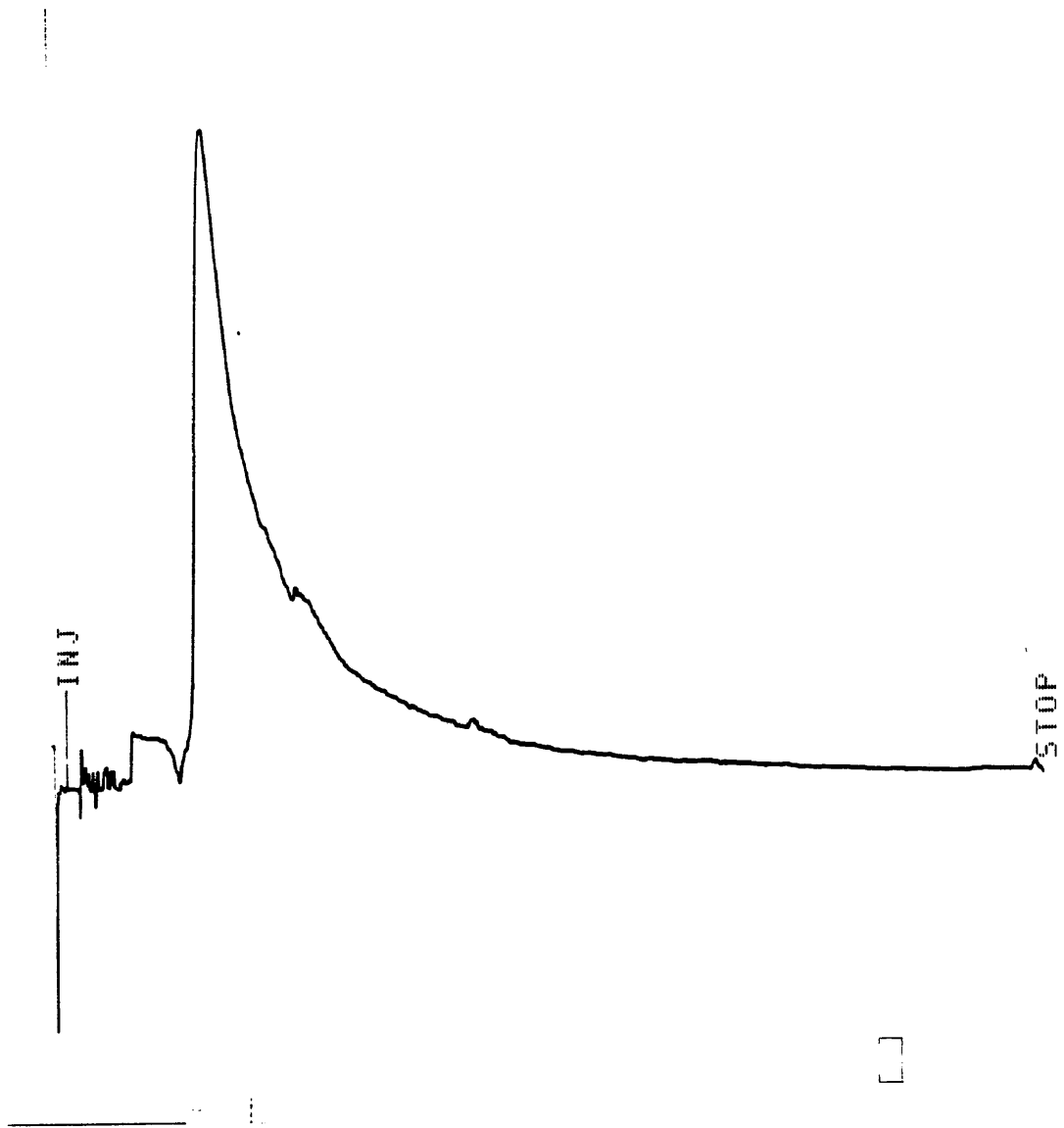


Figure 14
Reaction Rate Curve by GC
MF 4581A
(pyrolysis moisture free sample at 458°C)

A typical normalized cumulative conversion curve is shown in Figure 15. Normalized conversion curves for other samples are shown in Figure 16 through 19.

The expected variation of cumulative conversion with temperature was found in all cases except for the catalyst-impregnated sample reacted at 805 °C. This situation will be discussed more fully in the next section.

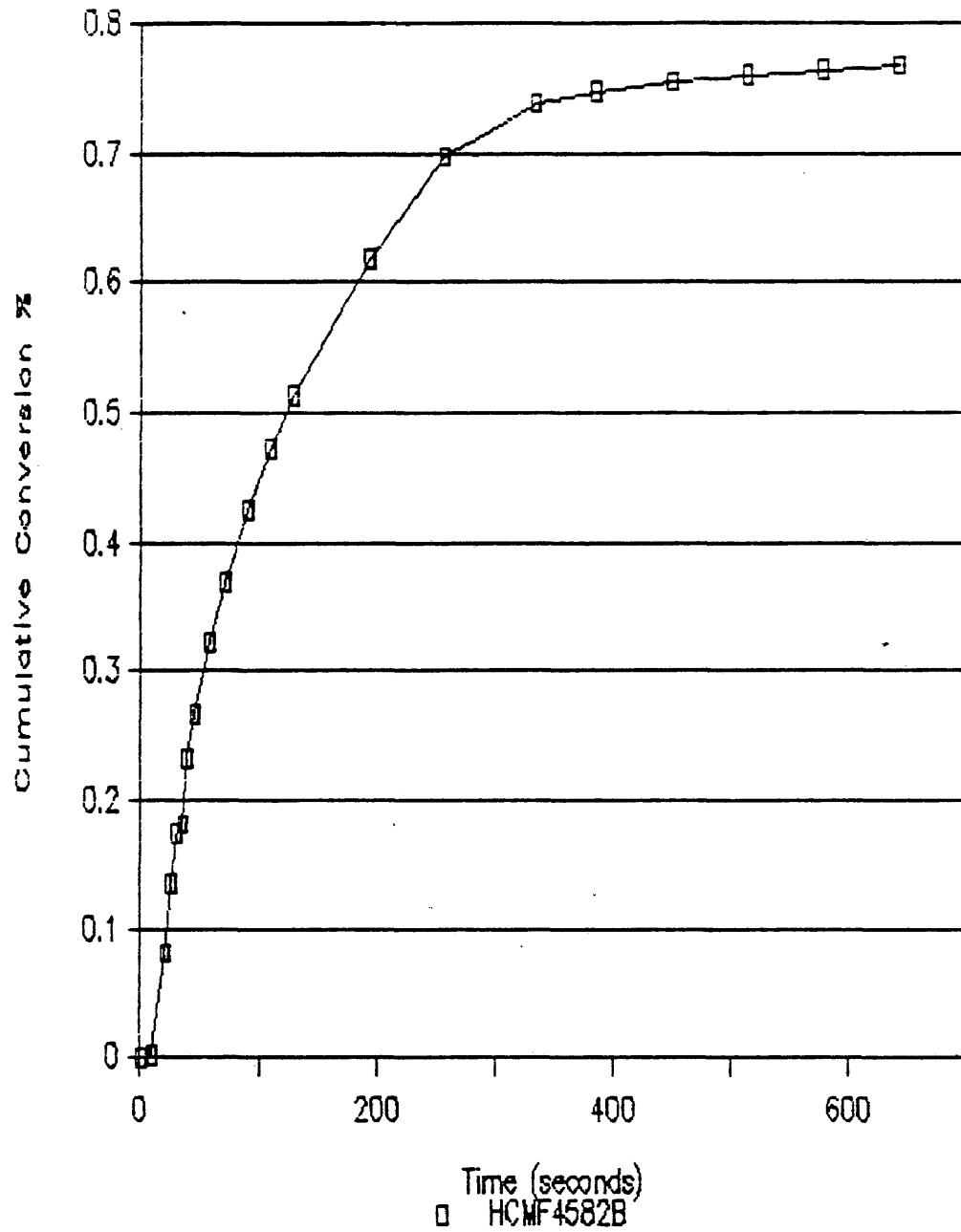


Figure 15

Typical Normalized Cumulative Conversion Curve
HCMF4582B
(hydropyrolysis carbonate and moisture free
sample at 458°C)

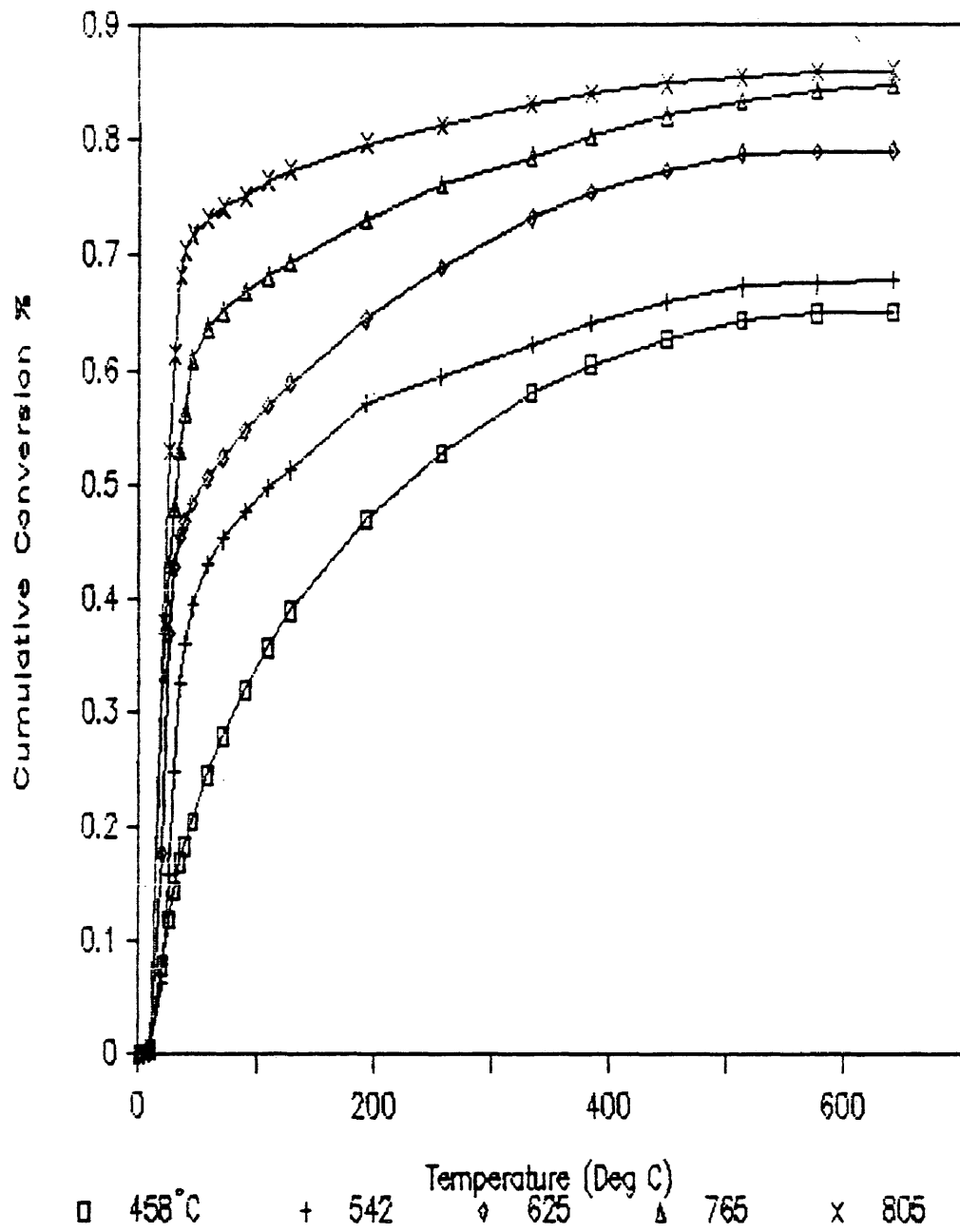


Figure 16
 Cumulative Conversion for MF Sample

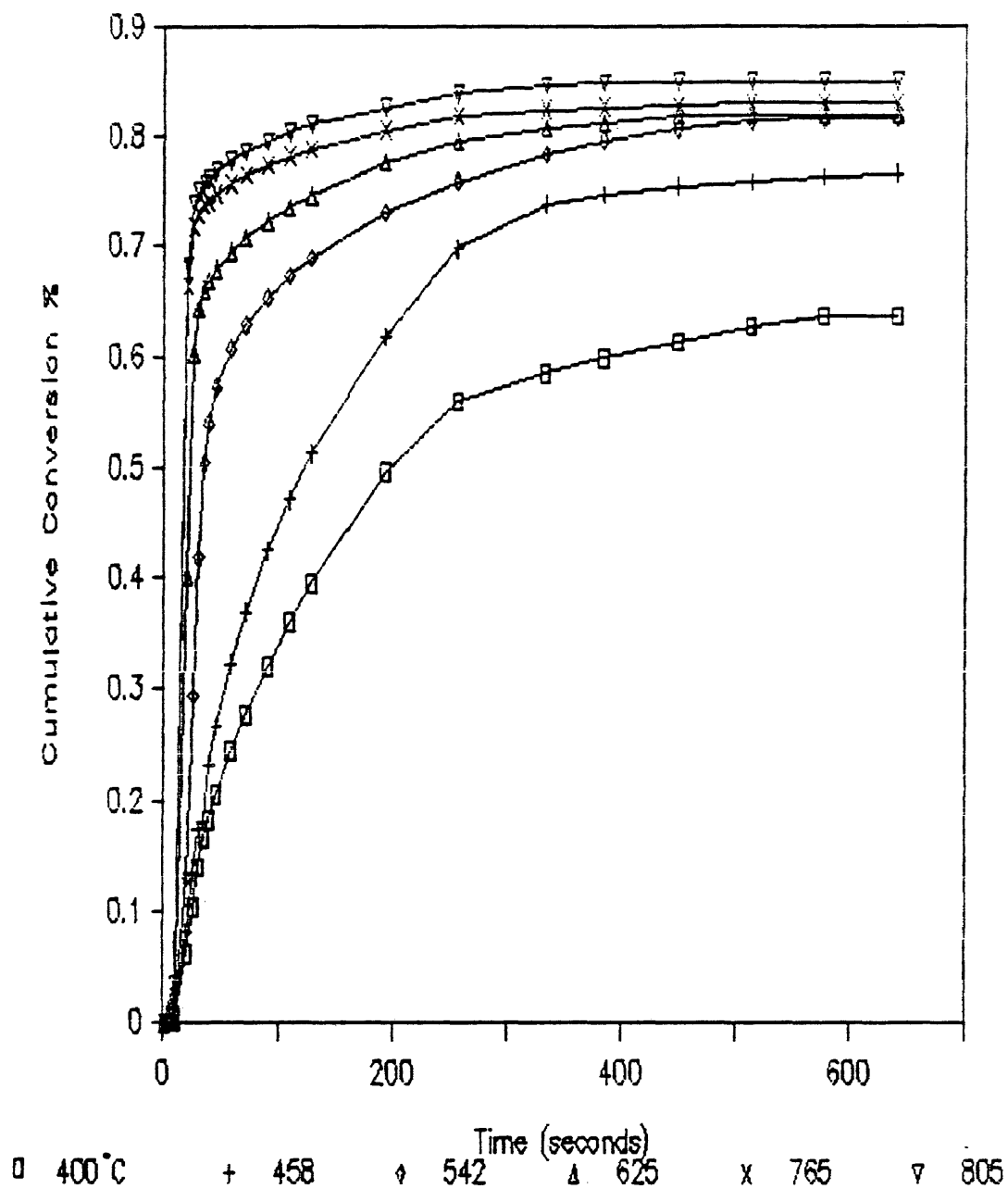


Figure 17
Cumulative Conversion for HCMF Sample

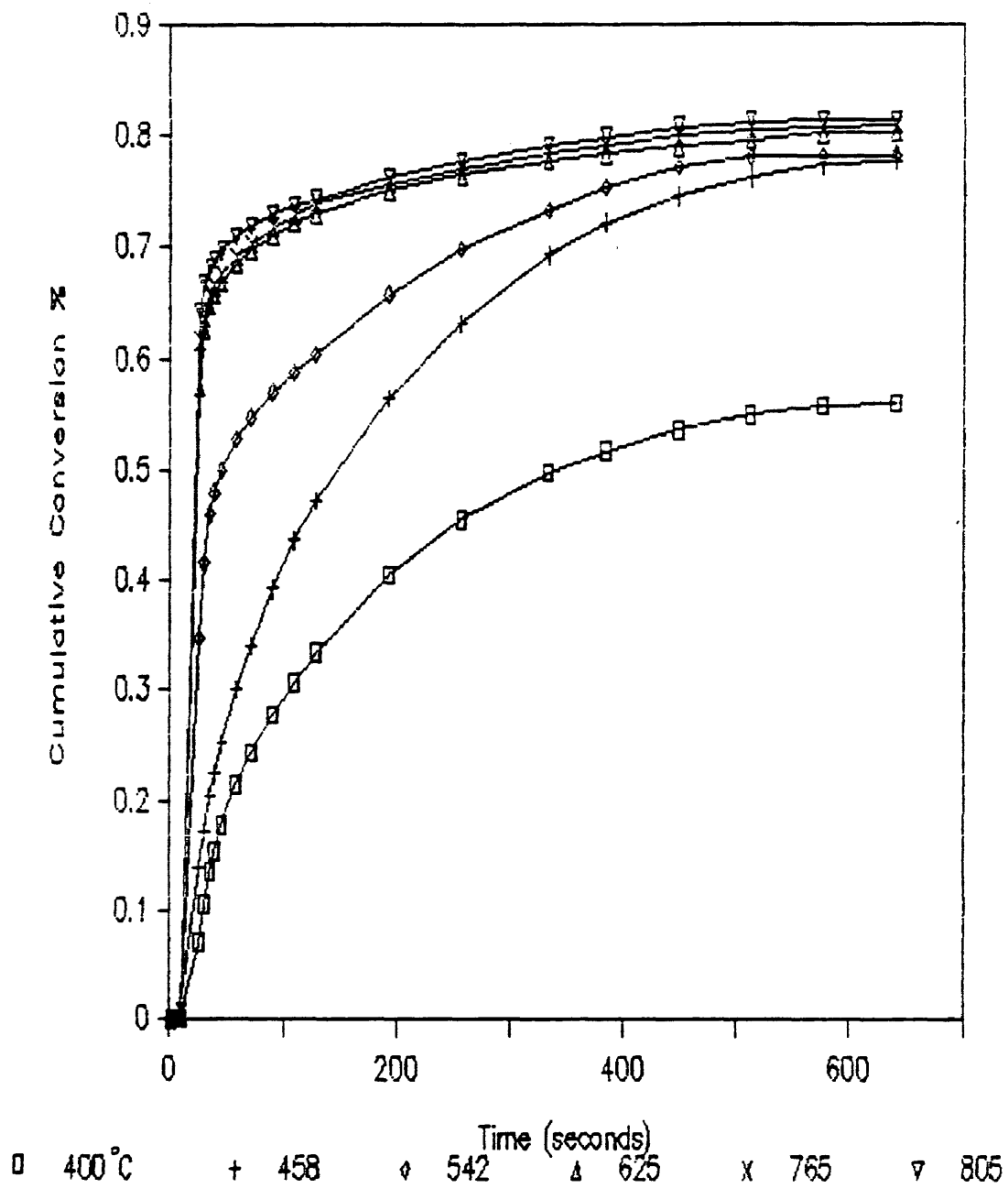


Figure 18

Cumulative Conversion for CMF Sample

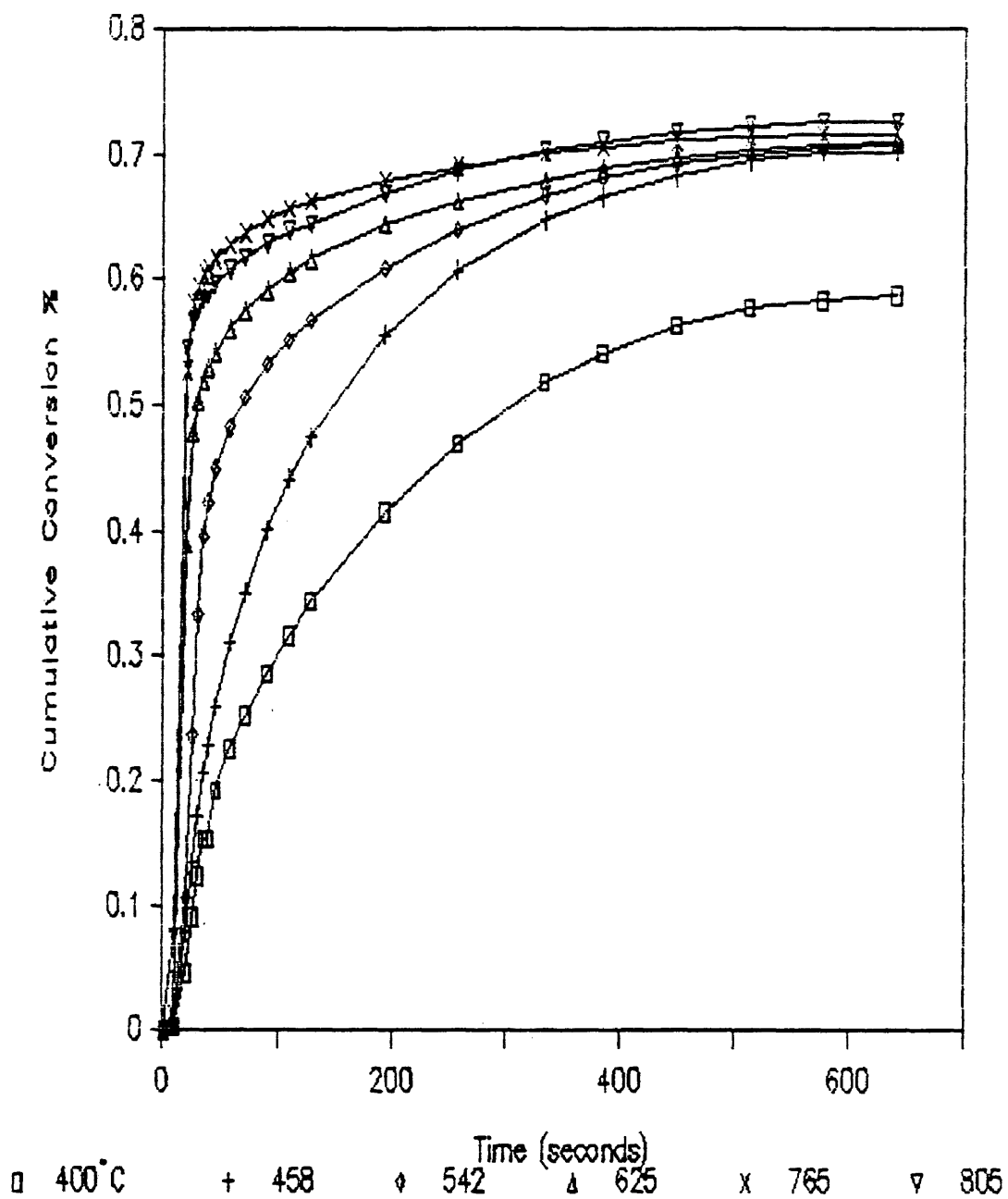


Figure 19
Cumulative Conversion for HCCMF Sample

4. DISCUSSION OF RESULTS

4.1. Introduction

This study contained three separate objectives. The first objective was to design, construct and operate a micro-reactor with a computerized data collection and handling system. Next, this system was used to measure the reaction rate of pyrolysis and hydro-pyrolysis for each oil shale sample (MF, CMF, HCMF, HCCMF). Finally, these were compared to determine the effect of hydrogen and an impregnated catalyst at low hydrogen pressure on the reaction rate of oil shale decomposition.

The basic assumption of oil shale pyrolysis and hydro-pyrolysis for this study was

organic carbon in oil shale-----> products

The study concentrates only on the oil shale decomposition. The kinetic models which were developed were based on essential phenomenological foundations not on the fundamental bond rupture and propagation steps of the actual chemical reactions. The properties of oil shale, the chemical structure of kerogen, the parameters of pyrolysis reaction, and the variation of products distribution were not included in this study.

Basically, this pyrolysis reaction system was designed

to operate at isothermal conditions, short residence times, and atmospheric pressure. For purposes of eliminating the intraparticle and interparticle mass transfer limitations, the particle size of the shale was 100 % -200 mesh (-74 um), and the particle weight selected for each experiment was in the range of 0.4 mg to 1.0 mg. The temperature variations during each pyrolysis experiments were about 1 C to 5 C deviation from the pre-stablized reaction temperature. This deviation would occur when the sample was first injected into the reactor, and the temperature could recover to its original value within about 20 seconds. These temperature fluctuations primarily depended on the actual reaction temperature and sample weight.

Two other unique features of these experiments were the direct temperature measurement and automatic data collection. Other researchers using similar systems have used the furnace temperature as the pyrolysis reaction temperature. This can introduce large variations into the temperature measurement due to convection and radiation effects. The thermocouple was located at the highest temperature zone in the quartz tube, hence there was no inaccuracy associated with temperature measurement. The reaction data were collected through a digital computer system at a frequency of every 0.32 second. The speed of

the automatic data logging system eliminated time lags from the experiment, and minimized any possible errors from operations. This resulted in high quality data that could represent the reaction system more precisely.

4.2. Processing Errors

There were two disadvantages to the furnace temperature control system. The first one was that the reactor's temperature could not stabilize exactly at one point for long periods of time. Furnace temperature fluctuated in the range of $\pm 0.5^{\circ}\text{C}$ even without any adjustment. The second difficulty was that the furnace's temperature control system was coarse, which meant that the adjustment range was very narrow but the response range was very large and also changed very quickly (e.g. a small adjustment in the temperature set point would cause a temperature variation of about $\pm 5^{\circ}\text{C}$). The estimated errors introduced by these problems was about 1 % at low temperatures (400°C) and about 0.5 % at high temperatures (800°C).

4.2.1 Errors from Conversion Experiments

The possible processing errors from the conversion experiments were as follows:

- 1) When the sample cup and oil shale residue were

removed from the quartz tube after the conversion reaction was completed, the temperature of the residue was still very high. If the residue were removed at that time, oxidation could occur rapidly and burn some of the residual carbon. The results of the conversion experiment at that temperature would thus be incorrect.

2) After the conversion experiments, the sample was very dry, and would absorb water very easily. Since the organic and/or inorganic carbon analyses depended on sample weight, errors could come from the sample weight if contaminated by moisture from the atmosphere.

4.2.2. Errors From Pyrolysis Experiments

1) Noise: Because an amplifier with a gain of 100 to 1 was used in boosting the signal from the TCD for input to the A/D card, noise was a problem in all experiments where the rate of pyrolysis was being measured. Source of noise were difficult to control, and came from:

- a. ground loops
- b. electrical wire connections
- c. shielding of electrical wires (RF noise)

The effect of noise on the signal was only in the range of 0.25 to 0.40 % , as shown in Figure 20, but the total effect on the integration curve was very significant. A comparison of normalized curves with and

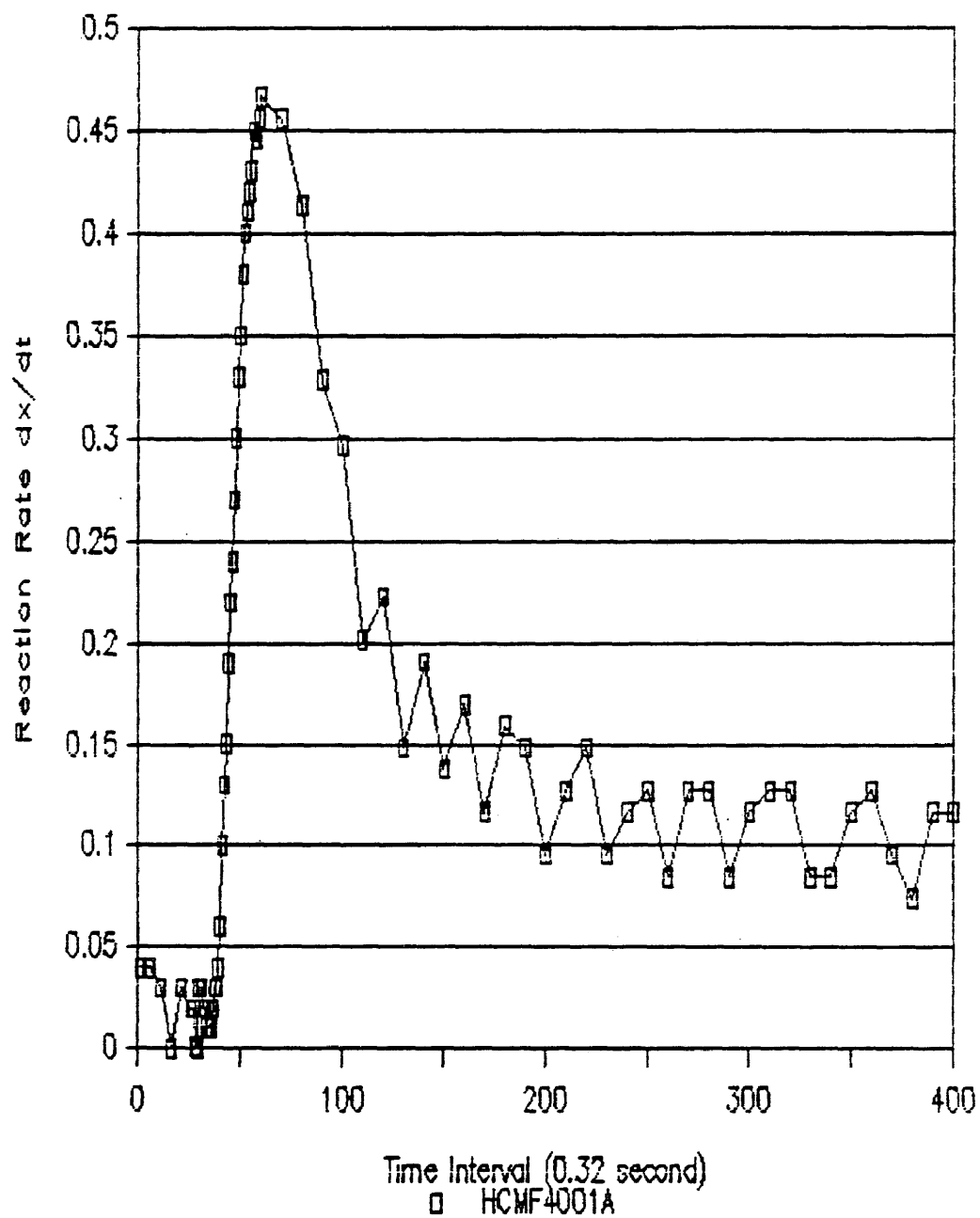


Figure 20

Noise on Reaction Rate Curve's Tail

without noise is shown on Figures 21 and 22.

Noise could be smoothed by use of the following equation:

$$F_n = X_n * (1-f) + F_o * f$$

F_n : the current filtered value

X_n : the current unfiltered value

F_o : the last filtered value

f : filtration factor (0.25 to 0.75)

Otherwise, a special consideration would be taken in the normalization step, as discussed in the next section.

2) Heavy end condensation and cracking

Carbonaceous residue from shale was produced by a series reaction pathway as follows;

Kerogen----> Bitumen -----> Oil + Gas + carbon residue
or simplified:

Aliphatic kerogen-----> Bitumen -----> Oil + Gas

Aromatic kerogen -----> Carbon residue

It is possible that a portion of the volatiles which were produced during the pyrolysis experiments condensed before passing to the detector. Thus, these products would be undetectable during the experiments. Reasons for heavy end condensation could be as follows:

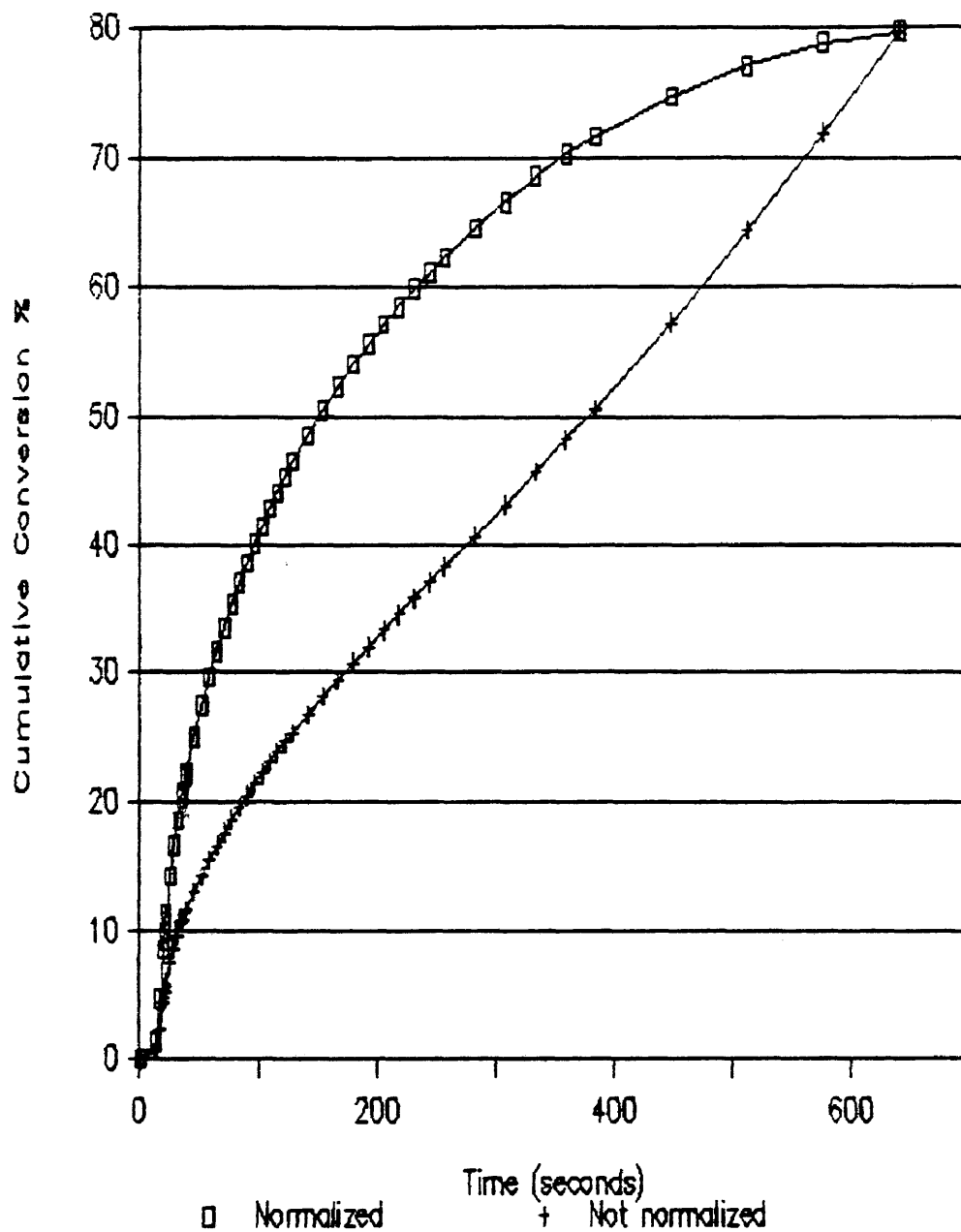


Figure 21

Comparison of Noise on Normalized Cumulative Conversion Curve for Low Reaction Temperature (400°C) (HCMF400)

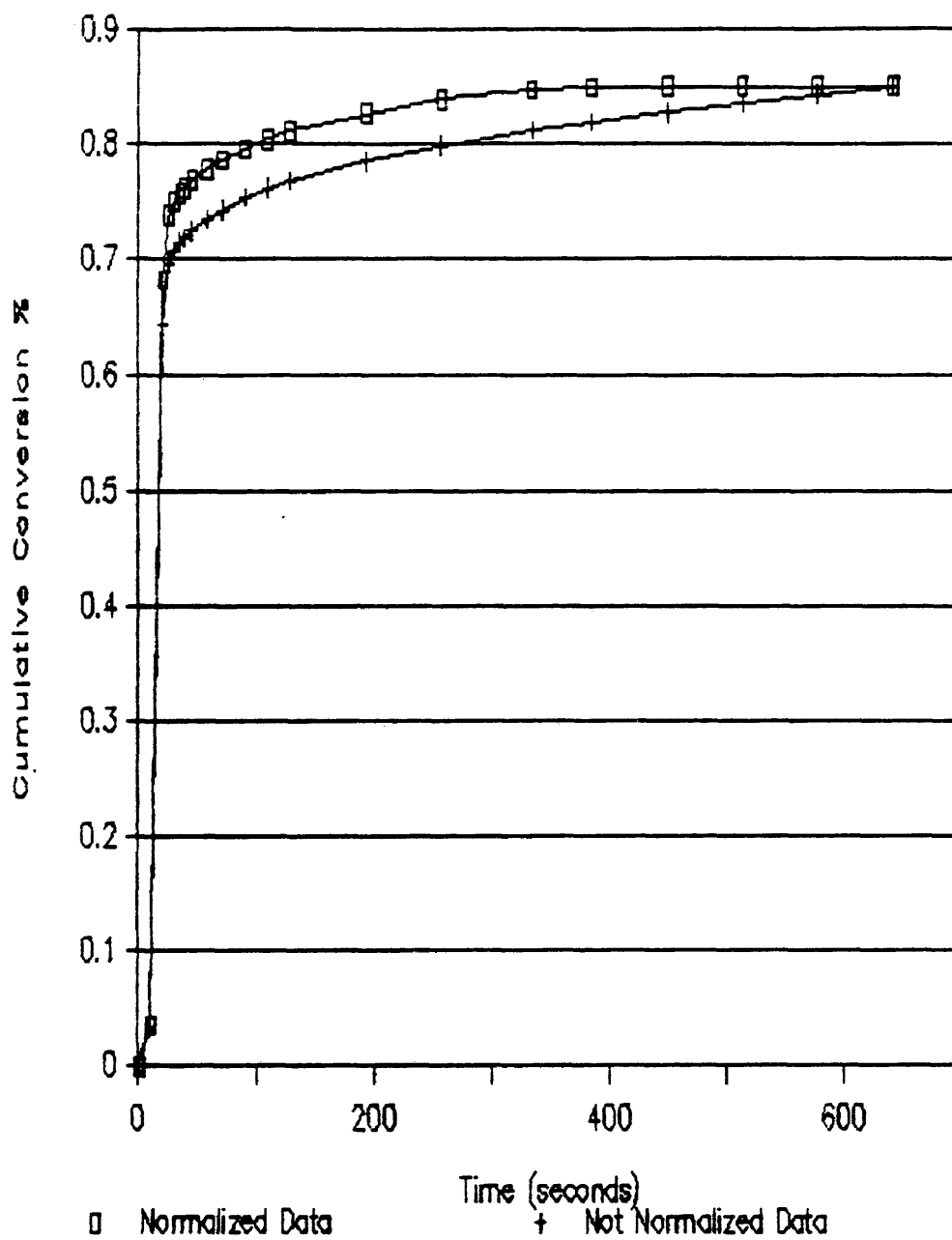


Figure 22

Comparison of Noise on Normalized Cumulative Conversion Curve for High Reaction Temperature (805°C) (HCMF805)

1) The transfer line distance between the reaction zone and the detector was long enough to provide an additional 0.6 seconds average residence time. Secondary reactions such as cracking and coking could thus have been completed in that area.

2) The temperature in the bottom of the reactor tube (8-3/16 inch long) was lower than the pyrolysis temperature of the sample, but still high enough to cause some coking. The connection line between the reactor and the detector was insulated and heat traced with an electrical tape, but heavier components could have condensed between the reactor and the detector.

The quartz reactor tube was removed and visually inspected after every run. During the pyrolysis experiments, no deposit of carbon residue or condensed heavy oil could be found in the tube after an experimental run. For the conversion experiments, some coke and/or condensed heavy components were noted inside the reactor. This difference could be caused by the fact that the sample weight for the pyrolysis experiments (0.4 to 1.0 mg) was much smaller than the sample weight for the conversion experiments (50-100 mg).

This kind of processing error was very hard to avoid. The reaction system was designed to minimize the distance

between reaction zone and the detector. During normalization, this was somewhat compensated for by multiplication of the integrated cumulative conversion data by the total absolute conversion measured at the same reaction temperature.

4.3. Normalization

The reaction rate data (dx/dt vs t) was integrated to generate data on conversion vs time (x vs t). Simpson's method numerical integration was used in this study. Some noise was always present on the tail of the signal from the TCD. Figure 23 shows a characteristic pyrolysis curve and indicates the magnitude of the noise present. Additionally, the signal normally did not return to the original baseline value at the end of the experiment. Accordingly, a procedure was used to compensate for these problems as follows:

- 1) Calculate the average value of the last 250 or 500 points of the tail of the signal.

- 2) A straight line connecting the origin (0,0) and the average value of the last data points of the rate curve was then drawn as shown in Figure 23. The intersect of this line with the final average defined the baseline for purposes of integration.

A typical normalized curve with the noise compensated for is shown in Figure 15. The program, TEXT14B, used for this normalization procedure, is provided in Appendix A.

4.4. Conversion Experiment Results

The conversion results for the MF, CMF, HCMF, and HCCMF samples at eight different temperatures (370°C, 400°C, 430°C, 458°C, 542°C, 625°C, 765°C, and 805°C) are provided in Table 4 and Figure 7.

Tables 5 through 8 and Figures 24 through 27 contain the result of calculations regarding the 95% confidence interval and 95% tolerance limits. The 95% tolerance limits contain 90% of the experimental results for each sample at eight different temperatures.

The 95% confidence interval confirms that the conversion data used to correct the normalized accumulative results of each sample were within a small and reasonable range. As shown in Tables 5 through 8, 100% of the results of conversion experiments are located within the appropriate tolerance limits.

From a theoretical standpoint, the conversion data obtained do not represent the ultimate conversion data. Since the pyrolysis reaction is normally thought to be irreversible, if we prolonged the reaction time, some

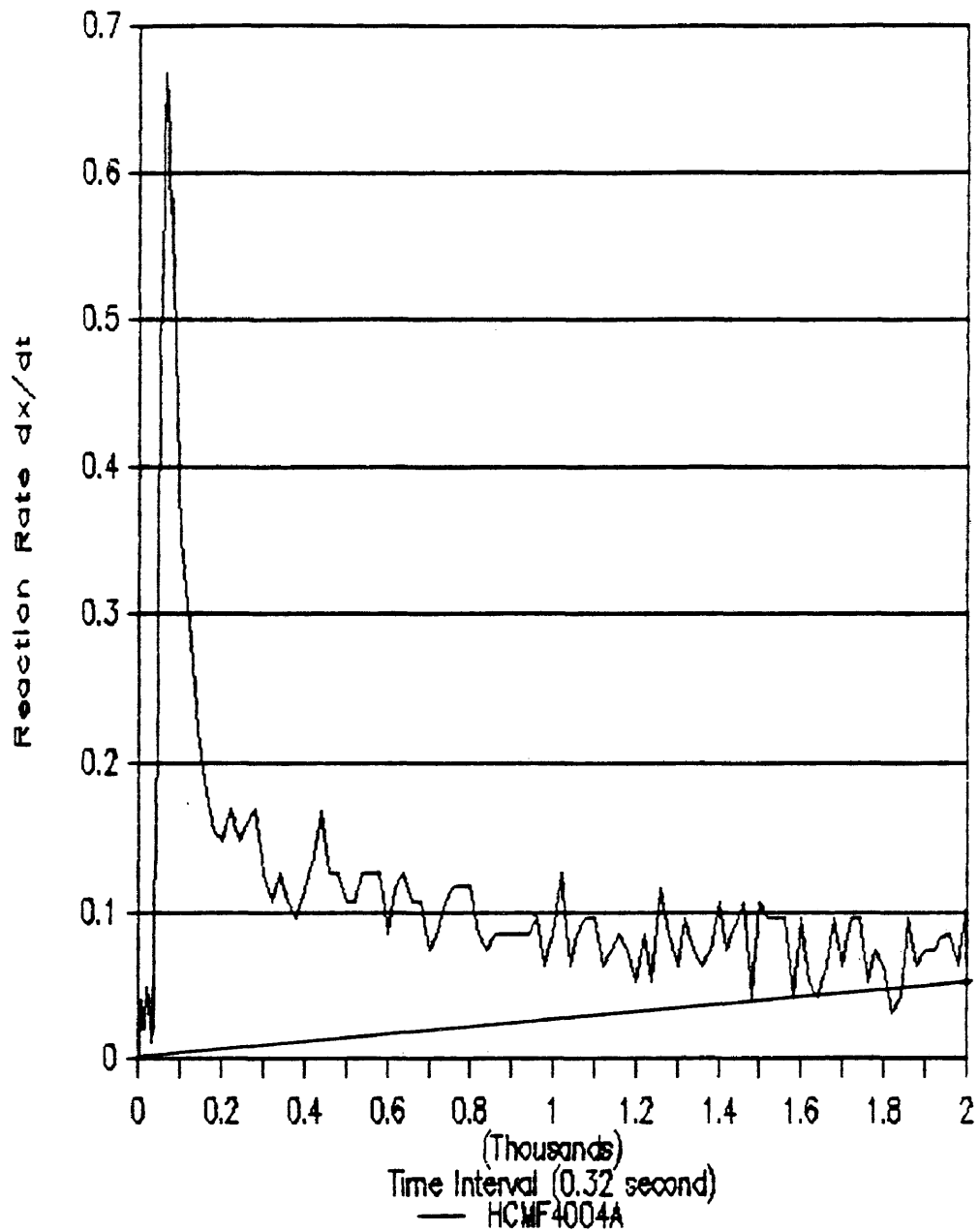


Figure 23

Normalized with Tilt Straight Line
(Average of Last 500 Points is 0.0636948)

Table 4
Carbon Conversion Results Summary

Temperature (°C)	Carbon Conversion (%)				
-----	MF (TOT.)	MF (ORG.)	CMF (ORG.)	HCMF (ORG.)	HCCMF (ORG.)
-----	-----	-----	-----	-----	-----
805	85.8987	84.2552	81.3851	85.0019	72.5918
765	84.6651	83.3084	80.9736	83.0282	71.6229
625	79.0056	81.9949	80.3139	81.9917	71.0385
542	67.8383	80.6408	78.2794	81.7038	70.6827
458	64.9195	79.9639	77.8128	79.6890	79.6130
425	59.3327	73.1705	74.9511	76.6634	69.3735
400	50.7099	61.7811	56.3416	63.6225	58.7296
372	18.7596	22.4492	24.4015	39.0280	22.6662

Note: The samples of CMF, HCMF, HCCMF are all carbonate free.

The carbon content in the feed shales for the CMF, HCMF, and HCCMF was 33.23% (organic carbon only), and 26.96% for the MF shale sample (organic plus inorganic carbon)

additional volatiles might continue to evolve, however, the rate would be extremely slow involving many hours or days. From a practical standpoint, oil shale retorting must be fairly rapid, therefore, these data can be assumed to represent a ultimate conversion of pyrolysis reaction, and a kinetic model can be developed from these data.

The conversion of all the samples increased consistently with increasing temperature. This was as expected since the rate of reaction increases with increasing temperature, which will lead to high conversion, if the reaction is irreversible as assumed.

About 70 % of the conversion was completed at 450°C, with the remaining 10 to 15 % completed from 450°C to 800°C. These results showed that the bulk of the reaction took place between 350°C to 450°C. Above this temperature, the reaction was rather insensitive to the temperature variation. This conclusion was consistent with all four different samples. The order of carbon conversion between the four shale samples was as follows:

HCMF > MF > CMF > HCCMF

The differences between these samples were not very large except for the impregnated (HCCMF) sample, which had a significantly lower carbon conversion over the entire temperature range studied.

Table 5

95% Confidence Interval, and 95% Tolerance limits That
Will Contain 90% Measurements for MF Sample

Temperature °C	805	765	625	542	458	430	400	370
1	84.16	85.85	77.12	71.00	67.19	58.89	49.85	20.14
2	85.13	82.81	77.29	66.66	67.65	59.57	49.21	16.64
3	87.26	85.61	77.35	65.89	61.80	60.10	51.74	16.47
4	87.04		80.55		63.04	58.77	52.04	21.79
5			82.73					
Average	85.90	84.67	79.01	67.84	64.92	59.33	50.71	18.76
SSD	1.503	1.603	2.525	2.763	2.933	0.621	1.393	2.634
ASSD	2.002	2.002	2.002	2.002	2.002	2.002	2.002	2.002
$t(\alpha/2)$	3.182	4.303	2.776	4.303	3.182	3.182	3.182	3.182
$n^{0.5}$	2.000	1.736	2.236	1.732	2.000	2.000	2.000	2.000
Range	3.184	4.962	2.485	4.973	3.185	3.185	3.185	3.185
COF-U	89.08	89.63	81.49	72.81	68.10	62.52	53.90	21.94
COF-L	82.71	79.70	76.52	62.87	61.73	56.15	47.53	15.58
K	5.369	8.380	4.275	8.380	5.369	5.369	5.369	5.369
Interval	10.75	16.77	8.557	16.77	10.75	10.74	10.75	10.75
TOR-U	96.65	100	87.56	84.61	75.67	70.08	61.46	29.51
TOR-L	75.15	67.89	70.45	51.06	54.17	48.58	39.96	8.013

Note: Average is the mean value of total runs.
 $t(\alpha/2)$ is the "t" value in the range of $\alpha/2$ and 95% confidence interval.
 "n" is the sample number.
 SSD means sample standard deviation.
 ASSD means average of SSD
 $\text{Range} = t(\alpha/2) * \text{ASSD}/n^{0.5}$
 $\text{COF-U} = \text{Average} + \text{Range}$
 $\text{COF-L} = \text{Average} - \text{Range}$
 K is the value of 95% tolerance limits with 90% populations
 $\text{Interval} = K * \text{ASSD}$
 $\text{TOR-U} = \text{Average} + \text{Interval}$
 $\text{TOR-L} = \text{Average} - \text{Interval}$

Based on total carbon content (26.96% in MF sample).
 All experimental results are inside the tolerance limits.

Table 6

95% Confidence Interval, and 95% Tolerance Limits That Will Contain 90% Measurements for CMF Sample

Temperature °C	805	765	625	542	458	430	400	370
1	82.16	81.20	79.36	77.31	76.93	73.81	54.38	24.39
2	81.50	81.38	80.10	77.91	77.57	75.69	40.84	24.41
3	81.50	79.99	80.28	78.65	77.59	73.34	58.30	24.56
4	79.58	81.14	81.27	78.95	78.87	76.96	43.06	24.24
5	82.13	81.27	80.57	78.59	78.10			
Average	81.39	80.97	80.31	78.28	77.81	74.95	56.34	24.40
SSD	1.053	0.619	0.696	0.666	0.723	1.081	8.510	0.129
ASSD	1.558	1.558	1.558	1.558	1.558	1.558	1.558	1.558
$t(\alpha/2)$	2.776	2.776	2.776	2.776	2.776	3.182	3.182	3.182
$n^{0.5}$	2.236	2.236	2.236	2.236	2.236	2.000	2.000	2.000
Range	1.935	1.935	1.935	1.935	1.935	2.479	2.479	2.479
COF-U	83.32	82.91	82.25	80.21	79.75	77.43	58.82	26.88
COF-L	79.45	79.04	78.38	76.35	75.88	72.47	53.86	21.92
K	4.275	4.275	4.275	4.275	4.275	5.369	5.369	5.369
Interval	6.662	6.662	6.662	6.662	6.662	8.367	8.367	8.367
TOR-U	88.05	87.64	86.98	84.94	84.48	83.32	64.71	32.77
TOR-L	74.72	74.31	73.65	71.62	71.15	66.58	47.95	16.03

Note: Average is the mean value of total runs.
 $t(\alpha/2)$ is the "t" value in the range of $\alpha/2$ and 95% confidence interval.
 "n" is the sample number.
 SSD means sample standard deviation.
 ASSD means the average of SSD
 $\text{Range} = t(\alpha/2) * \text{ASSD}/n^{0.5}$
 $\text{COF-U} = \text{Average} + \text{Range}$
 $\text{COF-L} = \text{Average} - \text{Range}$
 K is the value of 95% tolerance limits with 90% populations
 $\text{INTERVAL} = K * \text{ASSD}$
 $\text{TOR-U} = \text{Average} + \text{Interval}$
 $\text{TOR-L} = \text{Average} - \text{Interval}$

Based on organic carbon content (33.23% in CMF sample).
 All experimental results are inside the tolerance limits

Table 7

95% Confidence Interval, and 95% Tolerance Limits That Will Contain 90% Measurements for HCMF Sample

Temperature °C	805	765	625	542	458	430	400	370
1	85.33	84.06	81.78	81.23	79.00	75.68	64.08	40.89
2	85.33	83.61	81.92	82.53	79.88	76.42	63.00	41.26
3	84.55	82.65	82.00	81.87	80.14	77.02	64.71	41.26
4	84.80	81.79	82.28	81.35	79.74	77.54	62.69	32.69
Average	85.00	83.03	81.99	81.70	79.69	76.66	63.63	39.03
SSD	0.391	1.013	0.259	0.719	0.492	0.802	0.942	4.227
ASSD	1.105	1.105	1.105	1.105	1.105	1.105	1.105	1.105
$t(\alpha/2)$	3.182	3.182	3.182	3.182	3.182	3.182	3.182	3.182
$n^{0.5}$	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Range	1.759	1.759	1.759	1.759	1.759	1.759	1.759	1.759
COF-U	86.76	84.79	83.75	83.46	81.45	78.42	65.38	40.79
COF-L	83.24	81.27	80.23	79.95	77.93	74.91	61.86	37.27
K	5.369	5.369	5.369	5.369	5.369	5.369	5.369	5.369
Interval	5.935	5.935	5.935	5.935	5.935	5.935	5.935	5.935
TOR-U	90.94	88.96	87.93	87.64	85.62	82.60	69.56	44.96
TOR-L	79.07	77.09	76.06	75.77	73.75	70.73	57.69	33.09

Note : Average is the mean value of total runs.
 $t(\alpha/2)$ is the "t" value in the range of $\alpha/2$ and 95% confidence interval.
 "n" is the sample number.
 SSD means sample standard deviation.
 ASSD means the average of SSD
 $\text{Range} = t(\alpha/2) * \text{ASSD}/n^{0.5}$
 $\text{COF-U} = \text{Average} + \text{Range}$
 $\text{COF-L} = \text{Average} - \text{Range}$
 K is the value of 95% tolerance limits with 90% populations
 $\text{Interval} = K * \text{ASSD}$
 $\text{TOR-U} = \text{Average} + \text{Interval}$
 $\text{TOR-L} = \text{Average} - \text{Interval}$

Based on organic carbon content (33.23% in HCMF sample).

All experimental results are inside the tolerance limits.

Table 8

95% Confidence Interval, and 95% Tolerance Limits That Will Contain 90% Measurements for HCCMF Sample

Temperature °C	805	765	625	542	458	425	400	372
1	71.88	71.69	71.03	71.10	70.04	69.73	57.77	21.36
2	71.98	71.54	71.34	70.62	70.38	69.47	58.63	21.04
3	73.29	71.78	71.04	70.34	70.31	69.28	58.72	25.43
4	73.22	71.48	71.04	71.34	70.31	69.28	59.80	22.83
Average	72.59	71.62	71.04	70.69	70.16	69.37	58.73	22.67
SSD	0.763	0.137	0.123	0.381	0.218	0.297	0.834	2.001
ASSD	0.559	0.559	0.559	0.559	0.559	0.559	0.559	0.559
$t(\alpha/2)$	3.182	3.182	3.182	3.182	3.182	3.182	3.182	3.182
$n^{0.5}$	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Range	0.890	0.890	0.890	0.890	0.890	0.890	0.890	0.890
COF-U	73.48	72.51	71.93	71.58	71.05	70.26	59.62	23.56
COF-L	71.70	70.73	70.15	69.80	69.27	68.48	57.84	21.78
K	5.369	5.369	5.369	5.369	5.369	5.369	5.369	5.369
Interval	3.003	3.003	3.003	3.003	3.003	3.003	3.003	3.003
TOR-U	75.60	74.63	74.05	73.69	73.17	72.38	61.73	25.67
TOR-L	69.59	68.62	68.04	67.68	67.16	66.37	55.73	19.66

Note : Average is the mean value of total runs.
 $t(\alpha/2)$ is the t value in the range of $\alpha/2$ and 95% confidence interval.
 "n" is the sample number.
 SSD means sample standard deviation.
 ASSD means the average of SSD
 $\text{Range} = t(\alpha/2) * \text{ASSD}/n^{0.5}$
 $\text{COF-U} = \text{Average} + \text{Range}$
 $\text{COF-L} = \text{Average} - \text{Range}$
 K is the value of 95% tolerance limits with 90% populations
 $\text{Interval} = K * \text{ASSD}$
 $\text{TOR-U} = \text{Average} + \text{Interval}$
 $\text{TOR-L} = \text{Average} - \text{Interval}$

Based on organic carbon content (33.23% in HCCMF sample).
 All experimental results are inside the tolerance limits.

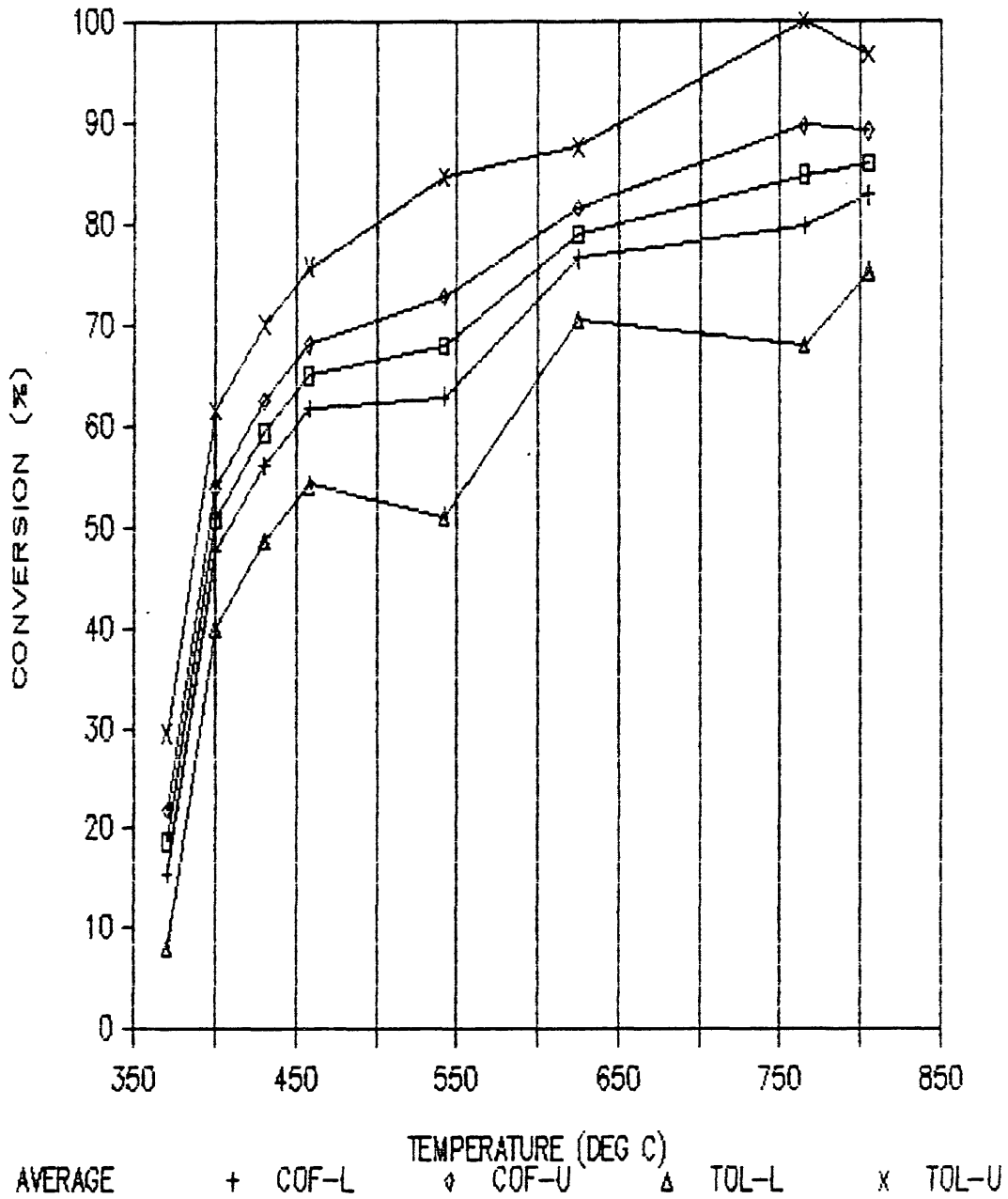


Figure 24

95% Confidence Interval, and 95% Tolerance Limits That Will Contain 90% Measurements for MF Sample

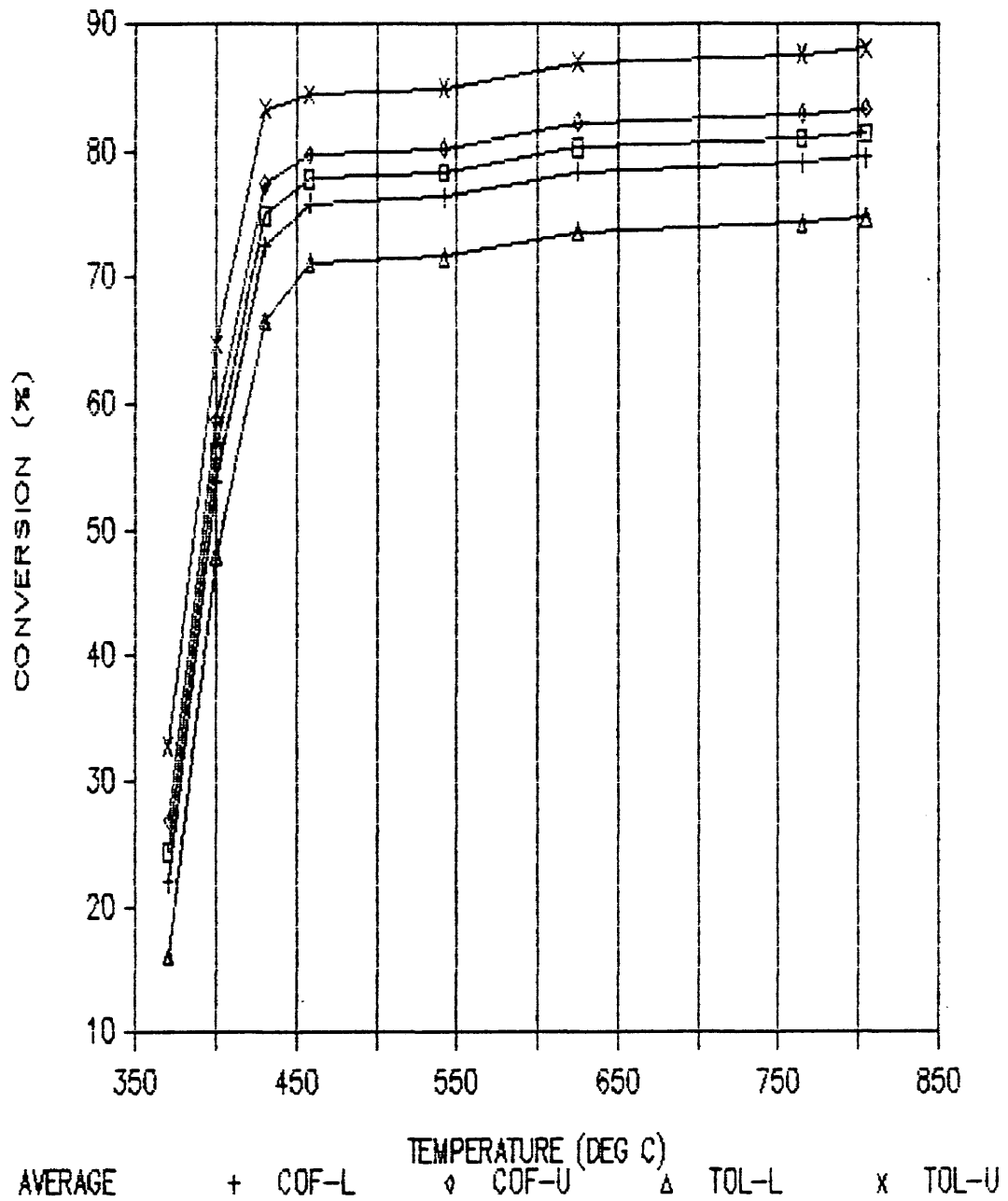


Figure 25

95% Confidence Interval, and 95% Tolerance Limits That Will Contain 90% Measurements for CMF Sample

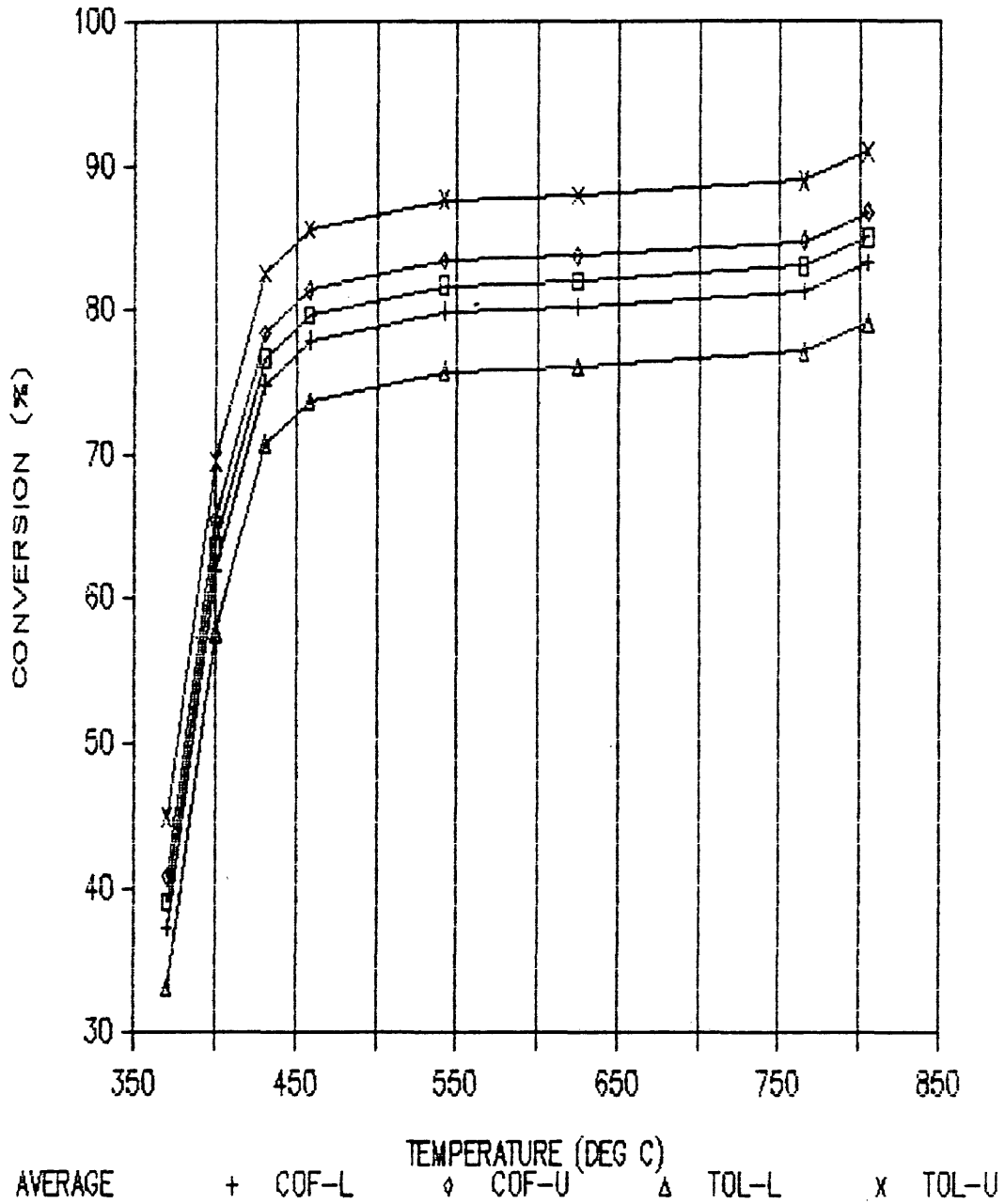


Figure 26

95% Confidence Interval, and 95% Tolerance Limits That Will Contain 90% Measurements for HCMF Sample

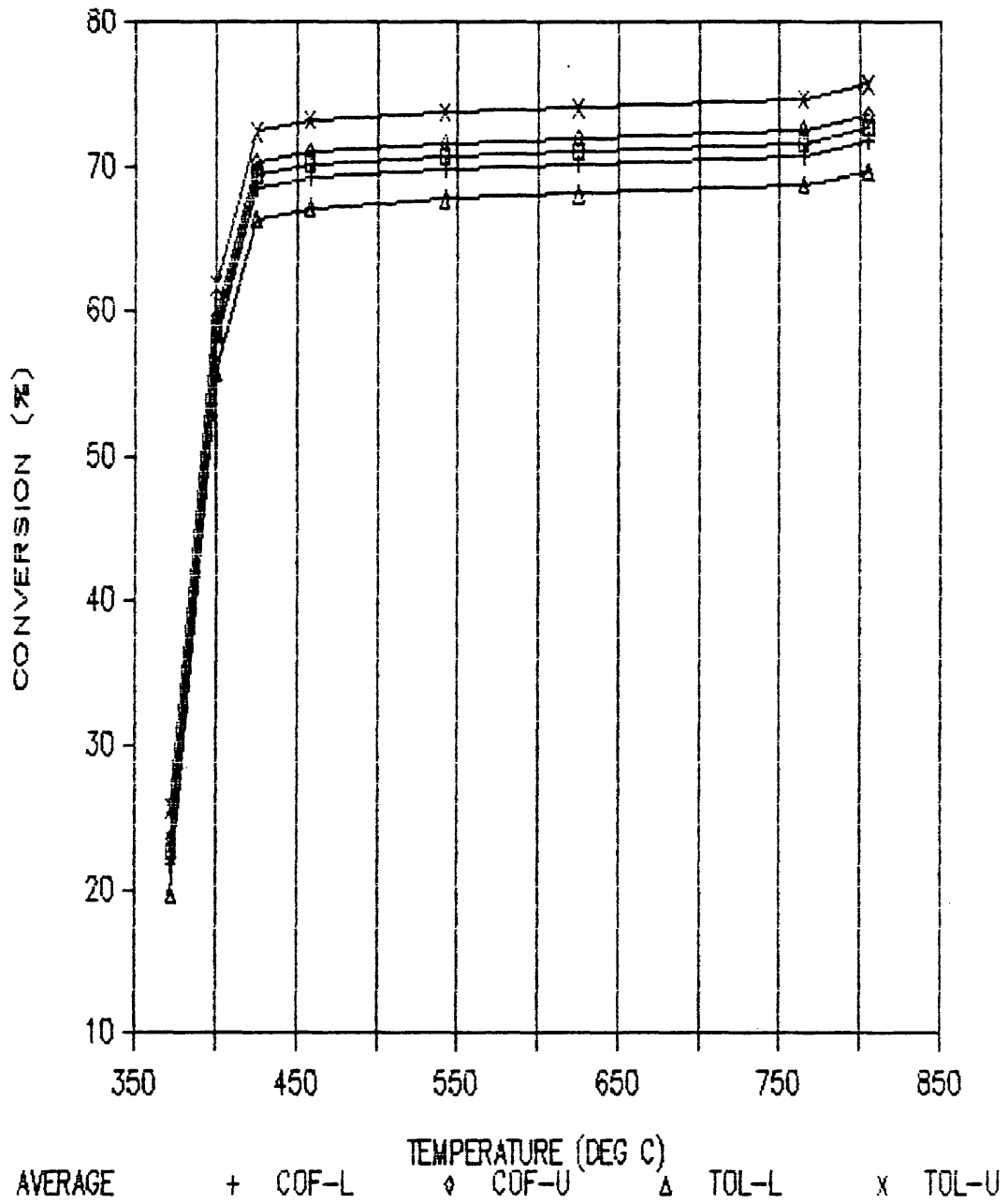


Figure 27

95% confidence Interval, and 95% Tolerance Limits That Will Contain 90% Measurements for HCCMF Sample

The carbon conversions from the hydropyrolysis experiments were only slightly higher than the conversion from the pyrolysis reactions carried out in helium gas on the same carbonate, and moisture-free shale samples. This can be explained by the fact that the hydrogen effect on the conversion should not be significant at pressures near ambient. The effect of hydrogen pressure on the conversion of oil shale by hydropyrolysis has been studied by Baldwin and Chen (14), who reported the following data:

Hydrogen pressure	Organic carbon conversion
-----	-----
0.1 MPa	28.5 %
1.0 MPa	48.0 %
2.5 MPa	55.5 %

The hydropyrolysis conversions of the impregnated sample (HCCMF) were about 10 to 15 % lower than the conversions of the non-impregnated (CMF and HCMF) samples. The HCCMF sample was comprised of approximately 1 % Molybdate (Mo) metal impregnated on the CMF sample. This sample was then pyrolysed in hydrogen ambient pressure. The 1% Mo loading on the oil shale could function as a hydrogen dissociation catalyst. The adsorbed and activated hydrogen atoms could diffuse on the surface and spill over to the oil shale surface to react with organic matter, saturating and/or cracking large hydrocarbon molecules. However, the results found from this experiment were that

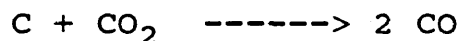
at low hydrogen pressure, the carbon conversion was actually decreased by the presence of the catalyst. This finding is in opposition to results recently present by Toreis et al.(3), who reported significant rate enhancement by impregnated catalysts based on TGA data. The reduction in conversion found from these experiments could be due to pore mouth blockage by the catalyst species, hindering diffusion of volatiles.

Figure 9 showed that the inorganic carbon content of the spent shale decreased significantly when the temperature was over 550°C. This is also shown in Figure 7, where the total carbon conversion of the MF sample evidenced a large change at a temperature of 550°C.

Figure 9 suggests that the release of carbon dioxide occurs primarily above 550°C. As proposed by Campbell (15), carbon dioxide (CO₂) is produced during the decomposition and reaction of carbonate minerals.



carbon monoxide (CO) is then produced by the subsequent reaction of CO₂ with carbon.



4.5. Results of Pyrolytic Experiments and Kinetic Modeling

Summaries of the data for conversion vs time, based on different temperatures for each different sample, have been shown previously in Figures 16 through 19. The reaction was essentially instantaneous for temperatures of 625 C and above. This instantaneous reaction was characterized by the cumulative conversion increasing rapidly, reaching 90% of the final value after approximately 64 seconds, then increasing very slowly from that point on. Beyond 200 seconds the reaction rate was essentially zero.

The rate data can be analyzed by either the differential method or the integral method. The methods used in this study were limited to integral analysis procedures.

Three different rate models, first order, 3/2 order, and second order were proposed initially. The appropriate rate expression and the integrated form for each are as follows:

derivative form

first order:

$$\frac{dx}{dt} = k (a - x)$$

integral form

$$\ln \left(1 - \frac{x}{a} \right) = - kt$$

3/2 order:

$$\frac{dx}{dt} = k (a - x)^{1.5} \quad 2 \left(\frac{1}{(a - x)^{0.5}} - \frac{1}{(a)^{0.5}} \right) = kt$$

second order:

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

a : final conversion

k : rate constant

t : time (second)

x : conversion (%)

In each of these expressions, conversion (X) is defined as:

$$x = \frac{\text{original organic carbon} - \text{residue organic carbon}}{\text{original organic carbon}}$$

Organic carbon was used as the basis for calculation of carbon conversion for all samples except the MF sample, which used total carbon as the basis.

The general formula for the model can be expressed as follows (for n = 1):

derivative form:

$$\frac{dx}{dt} = k (a - x)^n$$

integral form :

$$\frac{1}{n-1} \left(\frac{1}{(a-x)^{n-1}} - \frac{1}{(a)^{n-1}} \right) = kt$$

4.6. Induction Time

Approximately 6 to 13 seconds of induction time was present at the beginning of each pyrolysis rate curve (Figure 28). This induction period gave rise to the characteristic "S-shaped" curve for cumulative conversion vs time, and also affected the rate modeling of the kinetic data. This induction time at the beginning of each pyrolysis experiment could be caused by the following reasons:

1. Time lag by operation and computer program:

In order to make sure that the computer program, A/D-18, functioned properly and did not lose any data from the pyrolysis reaction, the injection step was always carried out about 1.6 to 3.2 seconds behind the step of starting the A/D-18 program.

2. Time lag by heat transfer resistance:

The sample and sample cup stored in the autosampler were initially at ambient temperature. Two observations suggest that significant time was required to heat the sample to the pyrolysis temperature. First, every time a

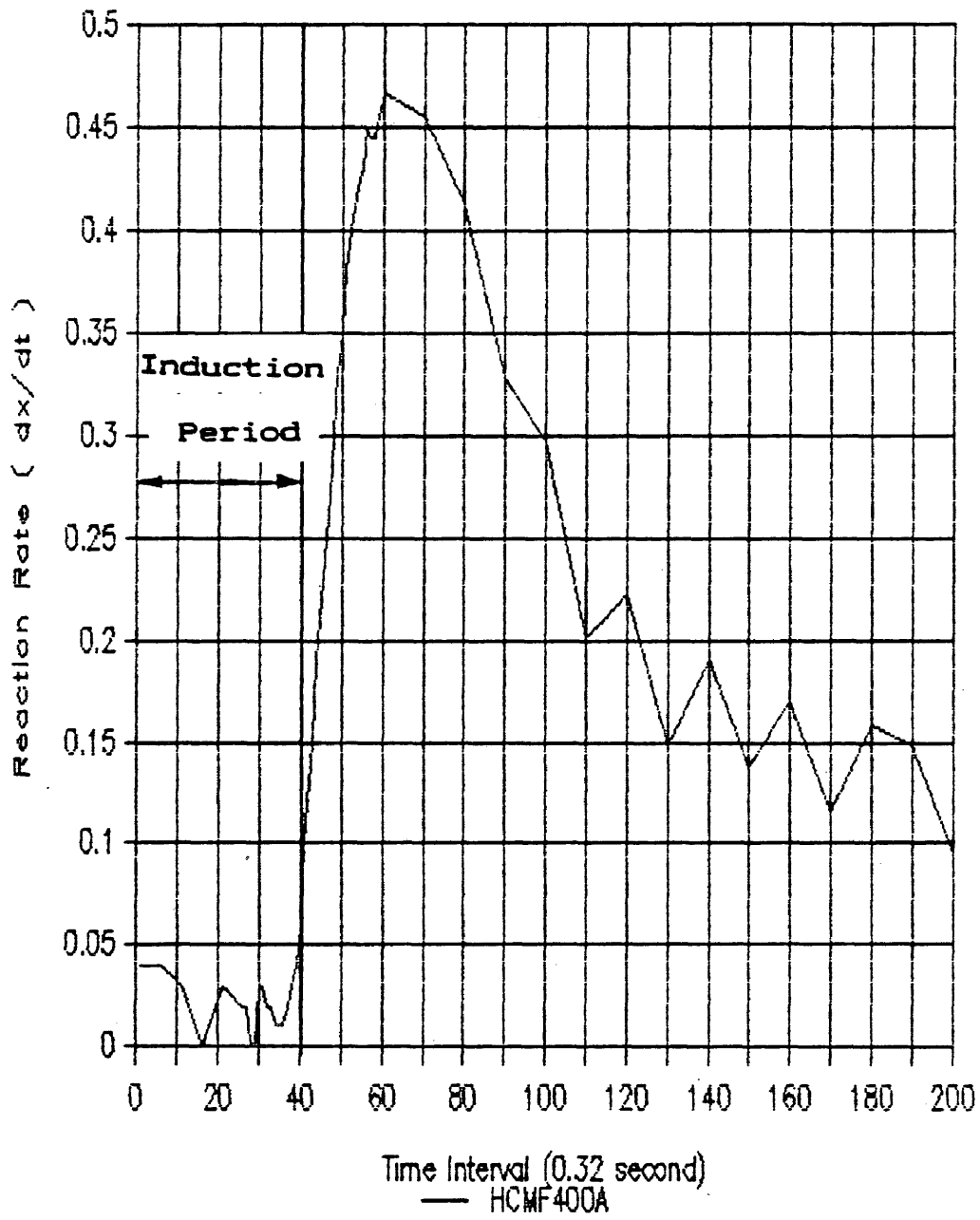


Figure 28

Induction Period at the Beginning of Pyrolysis Curve

sample was injected. The magnitude of this temperature decrease was a function of both pyrolysis temperature and sample weight, but generally was in the range from 0.5 to 5°C. Next, according to the analysis of Table 9 and Figures 29 through 31, the time required for the reaction rate, dx/dt , to exceed 0.1% was not affected by sample weight but decreased consistently with increasing reaction temperature. This is also shown by the position of the maximum point in dx/dt (the pyrolysis rate curve), which moved steadily toward lower value of time as the pyrolysis temperature increased.

3. Retention time of products inside the reactor:

A 0.64 second of average residence time normally retained in this experimental apparatus for each pyrolysis run. The stagnant gas product around the sample cup caused a resistance of mass transfer when gas products passed through this stagnant layer which could also make an another additional retention time.

It is quite difficult to separate and quantify the induction time period on each step. However, comparison of the estimated induction time to the time where 90% of the reaction is completed is small (about 1/10 for high reaction temperature and 1/20 for low reaction temperature). This fact indicates that the influence of

Table 9

The Induction Time Required (seconds) for HCCMF
Sample When Reaction Rate, dx/dt , Exceed 0.1%

HCCMF Sample Weight	Reaction Temperature °C					
	400	458	542	625	765	805
0.4 mg	12.48	11.84	9.92	8.00	7.68	8.32
0.6	12.48	11.52	10.56	8.64	7.68	7.36
0.8	11.84	10.88	11.20	9.92	7.36	6.72
1.0	12.80	11.20	11.20	8.96	7.04	7.34

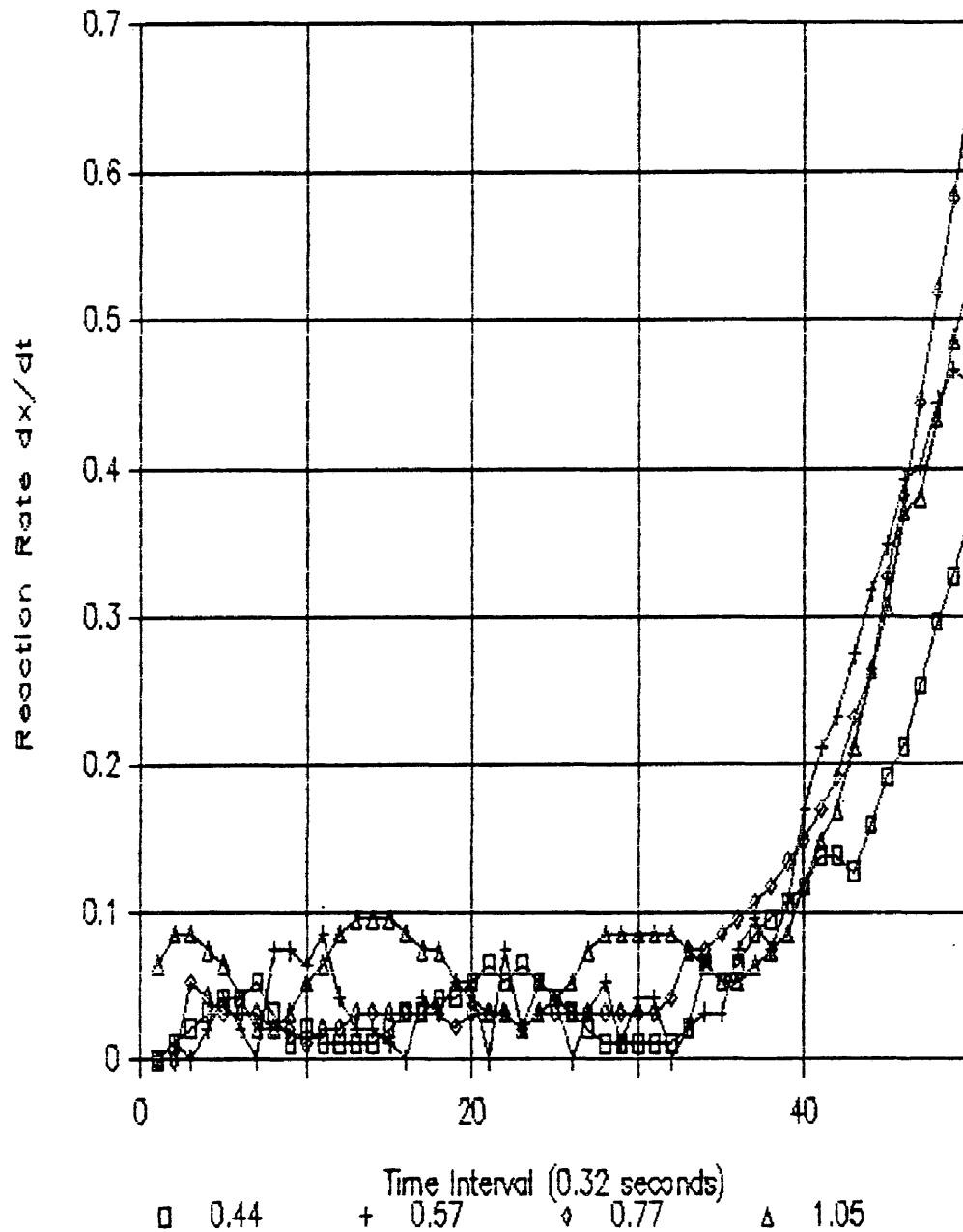


Figure 29

Comparison of Induction Time Required for Same Reaction Temperature (400°C) But Different Sample Weight (0.4 to 1.0 mg) for HCCMF Sample

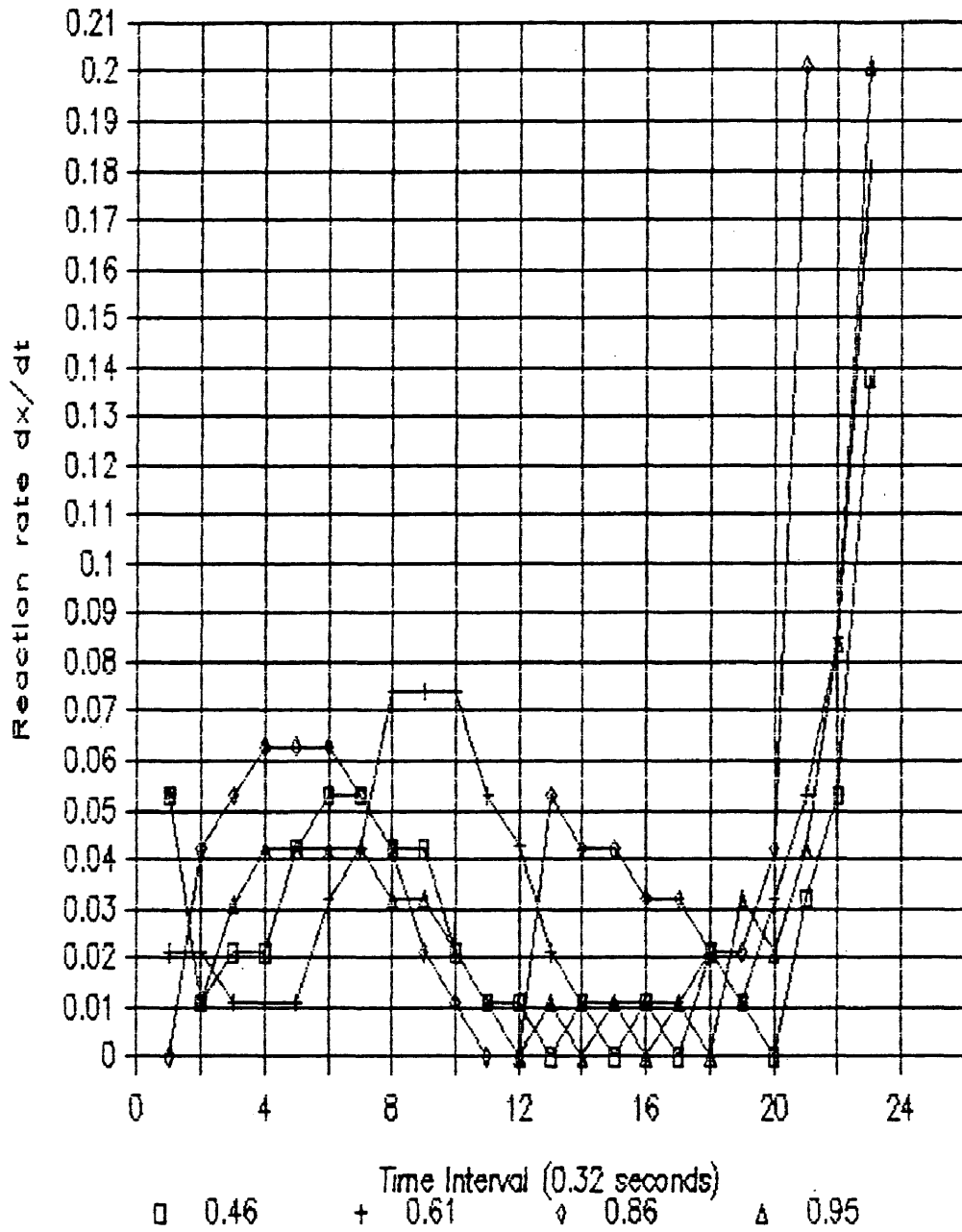


Figure 30

Comparison of Induction Time Required for Same Reaction Temperature (805°C) But Different Sample Weight (0.4 to 1.0 mg) For HCCMF Sample

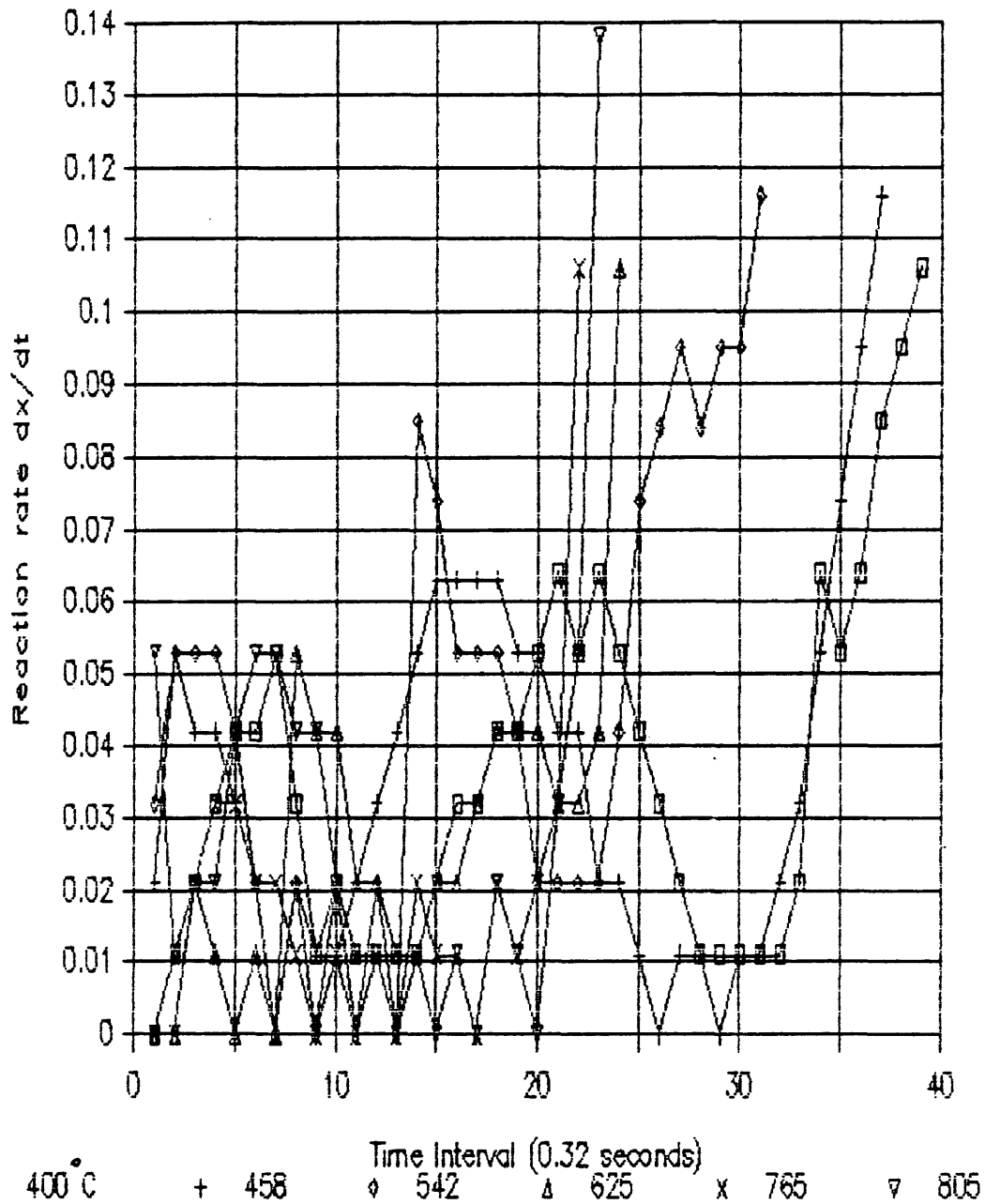


Figure 31

Comparison of Induction Time Required for Same Sample weight (0.4 mg) But Different Reaction Temperature (400 to 805 °C) For HCCMF Sample

induction time on the rate data is not significant, hence this effect is ignoral in the following analysis.

4.7. Model Discrimination

The integral expressions shown above can be analysed by regression procedures in order to find the rate constant " k ". The statistical program "Minitab" from the CSM computer library was used for these purposes. The validity of a given model can then be evaluated by the statistical value " R^2 ".

The results of regression analysis to find the " k " value and the corresponding R-square data are shown in Appendix B. For the purposes of finding the best model for the data, kinetic modeling was done via the following matrix;

order	sample	temperature	time (second)
-----	-----	-----	-----
1	MF	400 °C	64
3/2	CMF	458	128
2	HCMF	542	192
	HCCMF	625	256
		765	384
		805	640

All combinations of the 4 shale samples at the 6 temperatures and 6 times were investigated. Hence, $3 \times 4 \times 6 \times 6 = 432$ runs were altogether tested using Minitab. Detailed results for each run are provided

in Appendix B. Results of data fitting for the rate model of a second order reaction on different samples (MF,CMF,HCMF,HCCMF) are provided in Figures 32 through 35. A comparison of the "Goodness of Fit" statistics for kinetic modeling of the MF,CMF,HCMF,HCCMF samples for each of the different rate models (first order,3/2 order,second order) is provided in Tables 10 through 13. From these Tables and Figures, The following observations can be made:

1) First order kinetics fit the data very well ($R^2 > 90\%$) in the lower temperature range (400°C, 458°C, 542°C) over the entire time span. First order kinetics also fit the data well for temperatures of 625°C and 765°C, as the R squared values were in the range of 80% to 90%, however, this model did not fit the data at 805°C,where the R squared value was less than 80%.

2) The results for 3/2 order kinetics were better than for 1'st order, but problems still existed at the temperatures of 765°C and 805°C. A further problem was encountered in that this model could not cover the range when reaction time was over 384 seconds.

3) Second order kinetics fit the data very well at all temperatures, but was not able to cover the range of time over 384 seconds.

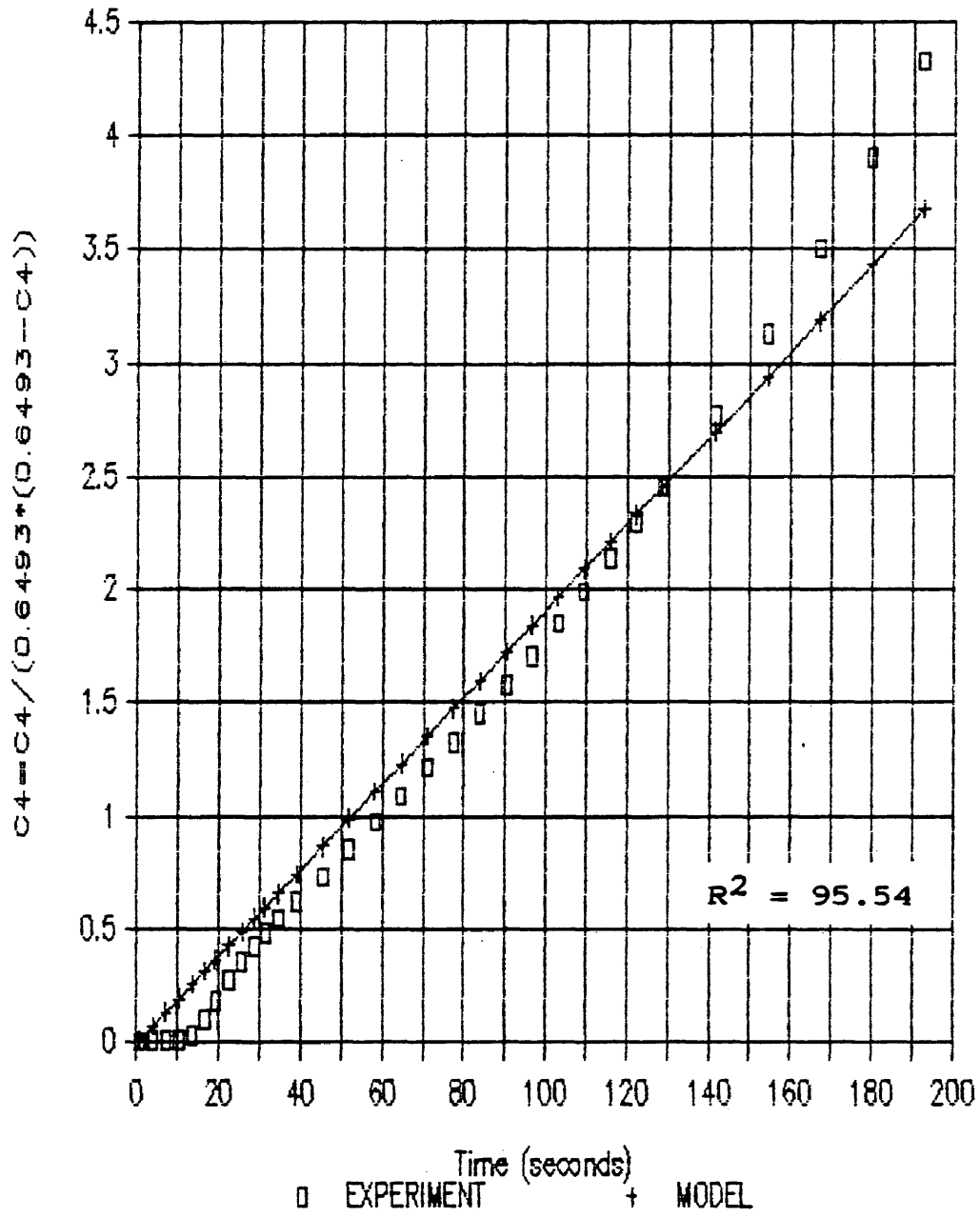


Figure 32

Second Order Kinetics Model for MF Sample
at 458°C and 192 Seconds

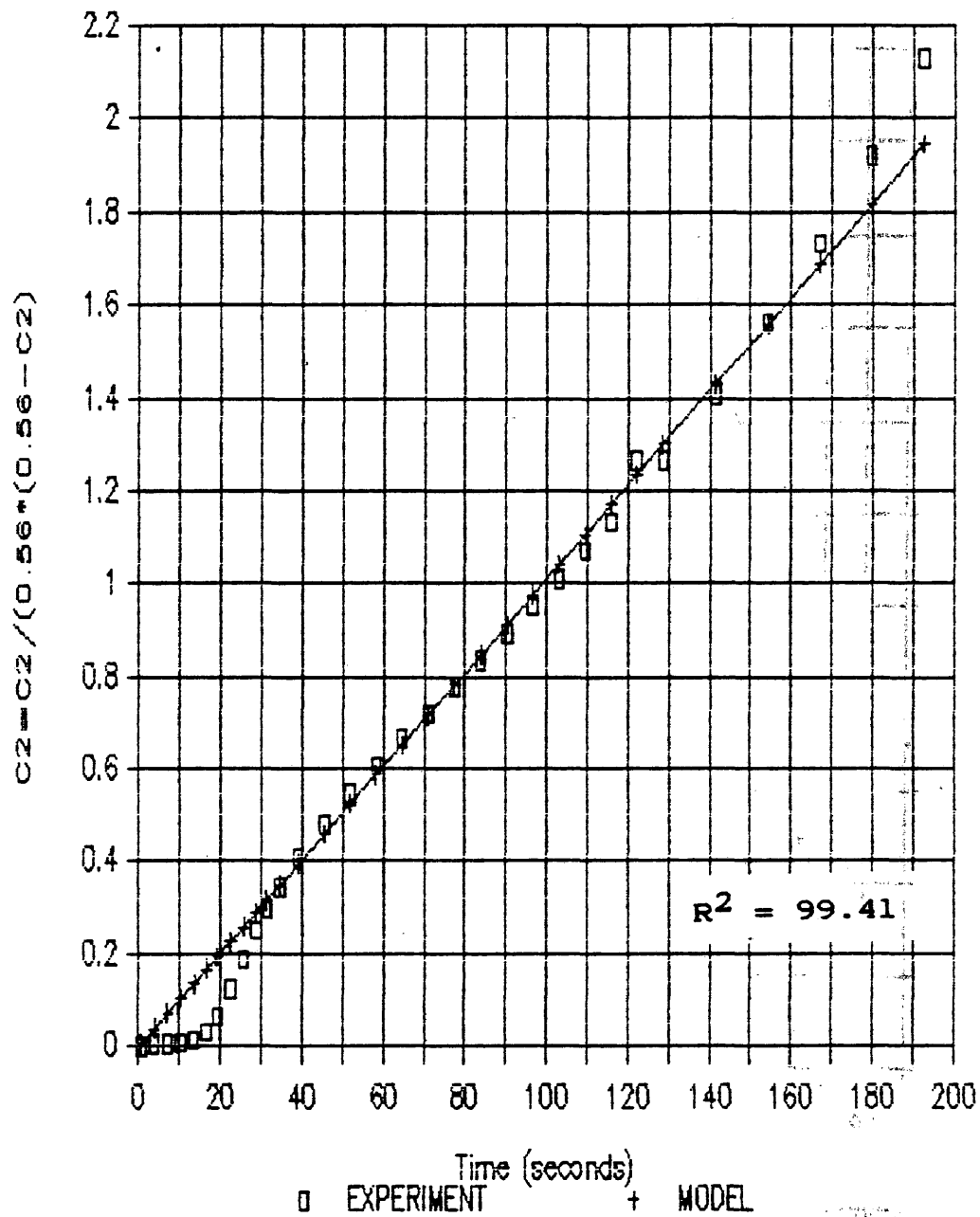


Figure 33

Second Order Kinetics Model for CMF Sample
at 400°C and 192 Seconds

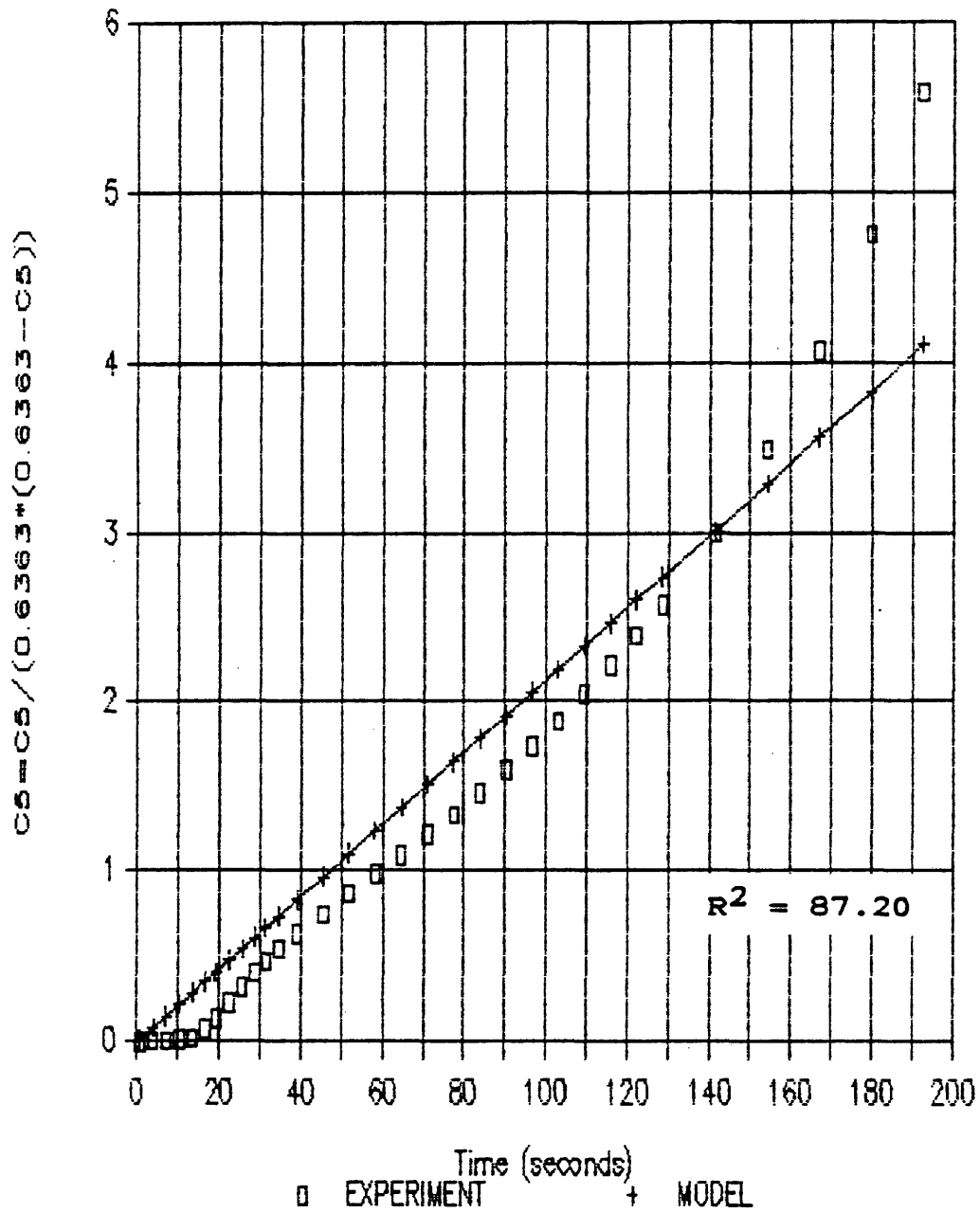


Figure 34

Second Order Kinetics Model for HCMF Sample
at 400°C and 192 Seconds

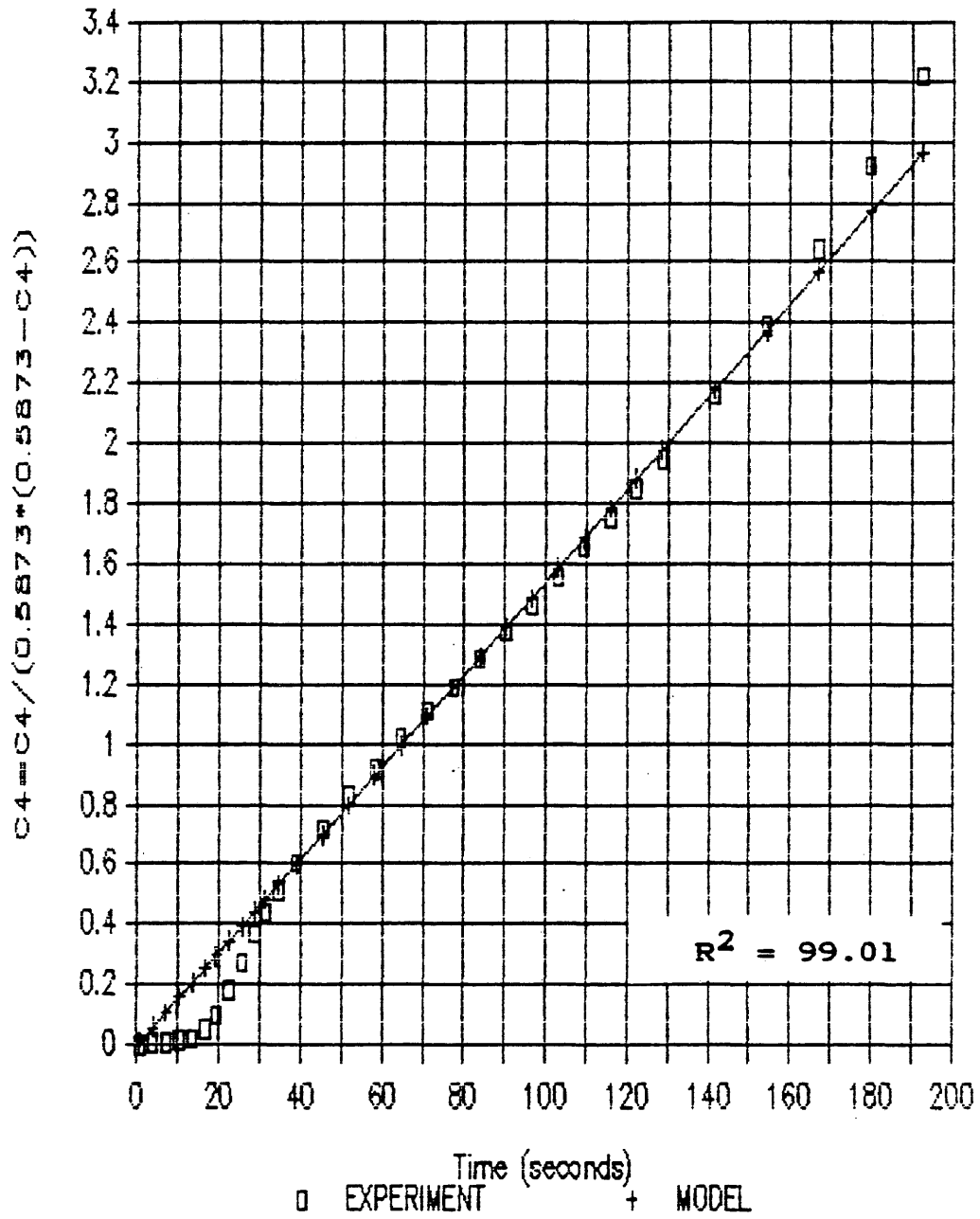


Figure 35

Second Order Kinetics Model for HCCMF Sample at 400°C and 192 Seconds

Summarizing the goodness-of fit statistical data, the following comparisons can be made.

	MF	CMF	HCMF	HCCMF
	-----	-----	-----	-----
1'st order	94.7%	89.0%	85.5%	87.6%
3/2 order	82.9%	88.2%	90.0%	93.1%
2'nd order	97.8%	94.1%	92.1%	95.0%

As shown, the second order models were uniformly superior for all shale samples.

Table 10

Summary of Goodness-of-Fit Statistics for MF Sample

A: First order :

805	B	B	C	C	B
765	B	B	B	B	B
625	B	B	B	A	A
542	A	A	A	A	A
458	A	A	A	A	A
400					

B: 3/2 order

805	B	B	B	A	X
765	A	B	B	B	X
625	A	A	A	A	X
542	A	A	A	A	X
458	A	A	A	A	X
400					

C: Second order:

805	A	A	A	A	X
765	A	A	A	A	X
625	A	A	A	A	X
542	A	A	A	A	X
458	A	A	A	A	X
400					

0 64 128 192 256 384 640

R SQUARE: 100 > A > 90 > B > 80 > C > 70 >> X

Table 11

Summary of Goodness-of-Fit Statistics for CMF Sample

A: First order :

805	A	B	C	C	C	B
765	A	B	C	C	C	B
625	A	B	B	B	B	B
542	A	A	A	A	A	A
458	A	A	A	A	A	A
400	A	A	A	A	A	A

B: 3/2 order:

805	B	B	B	B	B	X
765	B	B	B	B	B	X
625	A	A	A	A	A	X
542	A	A	A	A	A	X
458	A	A	A	A	A	X
400	A	A	A	A	A	X

C: Second order:

805	A	A	A	A	A	X
765	A	A	A	A	A	X
625	A	A	A	A	A	X
542	A	A	A	A	C	X
458	A	A	A	A	B	X
400	A	A	A	A	B	X

0 64 128 192 256 384 640

R SQUARE: 100 > A > 90 > B > 80 > C > 70 >> X

Table 12

Summary of Goodness-of-Fit Statistics for HCMF Sample

A: First order :

805	A	B	C	C	C	B
765	A	B	B	B	B	B
625	A	B	B	B	B	B
542	A	A	A	A	A	A
458	A	A	A	A	A	A
400	A	A	A	A	A	A

B: 3/2 order:

805	A	B	A	A	A	X
765	A	A	A	A	A	X
625	A	A	A	A	A	X
542	A	A	A	A	A	X
458	A	A	A	A	A	X
400	A	A	A	A	A	X

C: Second order:

805	A	A	A	A	A	X
765	A	A	A	A	B	X
625	A	A	A	A	B	X
542	A	A	A	A	A	X
458	A	A	A	A	B	X
400	A	A	A	A	A	X

0 64 128 192 256 384 640

R SQUARE: 100 > A > 90 > B > 80 > C > 70 >> X

Table 13

Summary of GOODNESS-of-Fit Statistics for HCCMF Sample
 A: First order :

805	A	B	C	C	C	B
765	A	B	C	C	C	B
625	A	B	B	B	B	B
542	A	A	A	A	A	A
458	A	A	A	A	A	A
400	A	A	A	A	A	A

B: 3/2 order:

805	A	B	B	B	A	X
765	A	B	B	B	A	X
625	A	A	A	A	A	X
542	A	A	A	A	A	X
458	A	A	A	A	A	X
400	A	A	A	A	A	X

C: Second order:

805	A	A	A	A	B	X
765	A	A	A	A	B	X
625	A	A	A	A	A	X
542	A	A	A	A	A	X
458	A	A	A	A	A	X
400	A	A	A	A	A	X

0 64 128 192 256 384 640

R SQUARE: 100 > A > 90 > B > 80 > C > 70 >> X

4.8. Arrhenius Plot

The next step in the development of a suitable kinetic expression was the preparation of an Arrhenius plot to determine the activation energy and frequency factor. The "k" values which were used for in this determination and for the pre-exponential (k_0) and activation energy (E_A) are summarized in Tables 14, 15, and 16. The reaction rate constants (k) at 805°C was characteristic of instantaneous reaction, and was often inconsistent with other data; therefore, the 805°C CMF and HCCMF data sets were not used in this analysis. Thus, the activation energy is not applicable to temperature over 800°C.

Arrhenius plots for different reaction orders, for all of the different shale samples are shown in Figures 36 through 47. The results of these calculations for the frequency factor k_0 , and activation energy E_A can be summarized as Table 17.

Although the results for the activation energy are lower than expected (100 to 150 KJ/mole), they were still in the range of 200 to 240 KJ/mole, as suggested by Rajeshwar et al (16). One possible problem that in these data is a shift from chemical reaction to mass transfer control as temperature is increased. This is indicated by an apparent change in the slope of Arrhenius plot at a

Table 14
Kinetic Modeling of Rate Constant (k)
for First Order Reaction

Temperature (K)	MF	CMF	HCMF	HCCMF
673		0.00653		0.00899
673		0.00540		0.00653
673		0.00443		0.00653
673		0.00671		0.00665
731		0.00591	0.00618	0.00727
731	0.00609	0.00591	0.00599	0.00942
731	0.00642	0.00669	0.00871	0.00801
731	0.00683	0.00682	0.00930	0.00830
815	0.00895	0.01480	0.00921	0.00870
815	0.00876	0.00973	0.01050	0.01010
815	0.00906	0.00795	0.00737	0.01160
815	0.01160	0.01510	0.01150	0.01120
898	0.01110	0.02430	0.06020	0.03670
898	0.01080	0.03540	0.04280	0.03850
898	0.01021	0.03980	0.05080	0.03630
898	0.01080	0.03760	0.04820	0.03900
1038	0.02030	0.04280	0.07440	0.05680
1038	0.02250	0.04940	0.06850	0.05150
1038	0.01940	0.05620	0.06430	0.05370
1038	0.01870	0.05400	0.06150	0.05570
1078	0.02240		0.05580	
1078	0.02390		0.06500	
1078	0.02600		0.06400	
1078			0.06640	
LN(k ₀)	-1.100	1.490	2.560	1.240
k ₀	3.004	4.437	12.936	3.456
SD	1.215	1.576	1.832	1.613
E/R	2921	4631	5507	4341
E	24.285	38.504	45.785	36.092
R ²	94.7	89.9	85.5	87.6

SD : Standard Deviation

k₀ : Pre-Exponential (1/second)

E : Activation Energy (KJ/mole)

Table 15
Kinetic Modeling of Rate Constant (k)
for 3/2 Order Reaction

Temperature (K)	MF	CMF	HCMF	HCCMF
673		0.00951		0.0125
673		0.00684		0.0116
673				0.0097
673				0.0122
731		0.00859	0.00986	0.0130
731	0.0118	0.00806	0.00946	0.0192
731	0.0129	0.01130	0.01440	0.0147
731	0.0192	0.01510	0.02260	0.0294
815	0.0187	0.01950	0.01830	0.0229
815	0.0192	0.01510	0.02260	0.0294
815			0.02660	
815			0.02560	
898	0.0193	0.03940	0.04680	0.0329
898	0.0151	0.03405	0.06430	0.0372
898	0.0182	0.03360		0.0428
898	0.0158			
1038	0.0325	0.03620	0.06880	0.0524
1038	0.0366	0.03400	0.06310	0.0393
1038	0.0308			0.0448
1038	0.0293			0.0471
1078	0.0366	0.03700	0.06170	
1078	0.0469	0.03920	0.15900	
1078	0.0406		0.09000	
1078			0.07990	
LN(k ₀)	-1.06	-0.141	1.82	-0.322
k ₀	0.347	0.868	6.172	0.725
SD	1.397	1.483	1.592	1.257
E/R	2471	3189	4528	2775
E	20.544	26.515	37.648	23.072
SD	2.493	2.691	3.350	1.516
R ²	82.9	88.2	90.0	93.5

SD : Standard Deviation
k₀ : Pre-Exponential (1/second)
E : Activation Energy (KJ/mole)

Table 16
Kinetic Modeling of Rate Constant (k)
for Second Order Reaction

Temperature (K)	MF	CMF	HCMF	HCCMF
673		0.01500		0.0202
673		0.01130		0.0214
673		0.00968		0.0169
673				0.0227
731		0.01920	0.0133	0.0235
731	0.0121	0.01770	0.0120	0.0278
731	0.0128		0.0173	0.0305
731	0.0163			
815	0.0178	0.0375	0.0348	0.0342
815		0.0277	0.0472	0.0475
815		0.0264	0.0279	0.0663
815			0.0515	0.0603
898	0.0265	0.0902	0.1060	0.0821
898	0.0286	0.1100	0.1640	0.0913
898	0.0281	0.0989	0.1320	0.0994
898				0.1130
1038	0.0463	0.2450	0.2020	0.1590
1038	0.0476	0.0261	0.1820	0.1320
1038	0.0502			0.1560
1038	0.0451			0.1760
1078	0.0569		0.2310	
1078	0.0520		0.2030	
1078			0.2110	
LN(k ₀)	-0.043	4.14	4.52	2.09
k ₀	0.958	62.803	91.836	8.085
SD	1.171	1.745	1.803	1.323
E/R	3133	5910	6304	4082
E	26.048	49.138	52.414	33.939
SD	1.178	3.690	4.264	1.879
R ²	97.8	94.1	92.1	95.0

SD : Standard Deviation
k₀ : Pre-Exponential (1/second)
E : Activation Energy (KJ/mole)

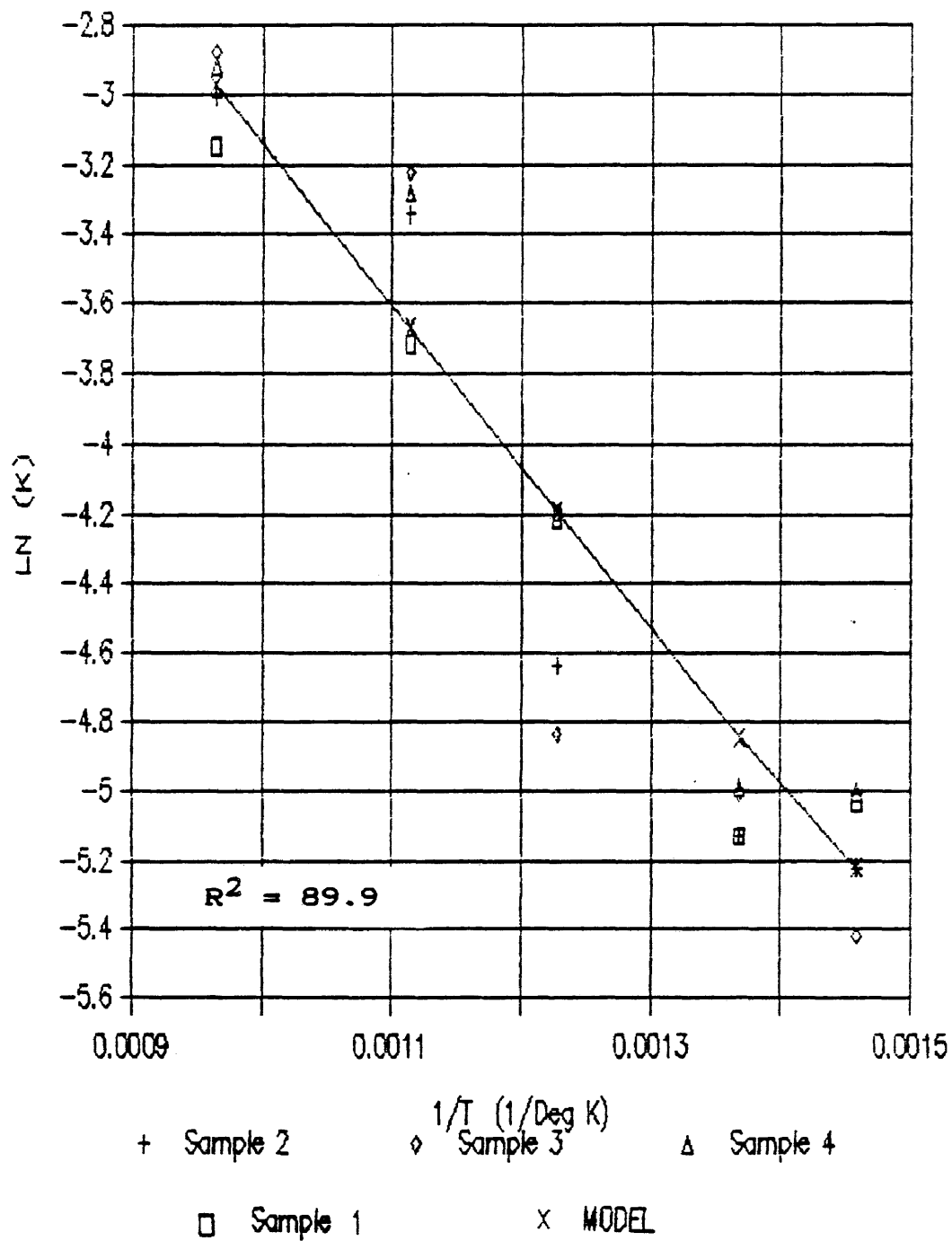


Figure 36

Arrhenius Plot for First Order Reaction and CMF Sample

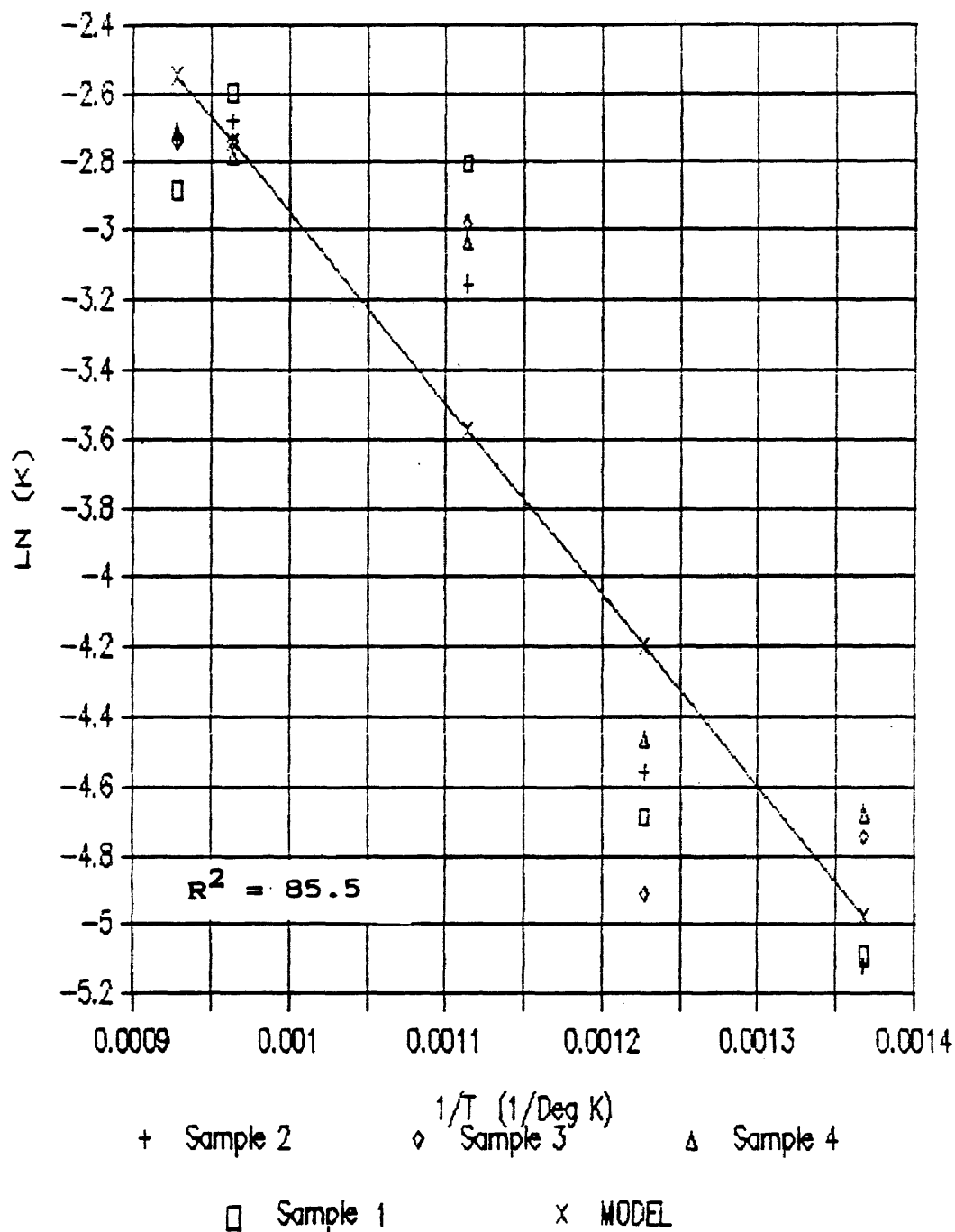


Figure 37

Arrhenius Plot for First Order Reaction and HCMF Sample

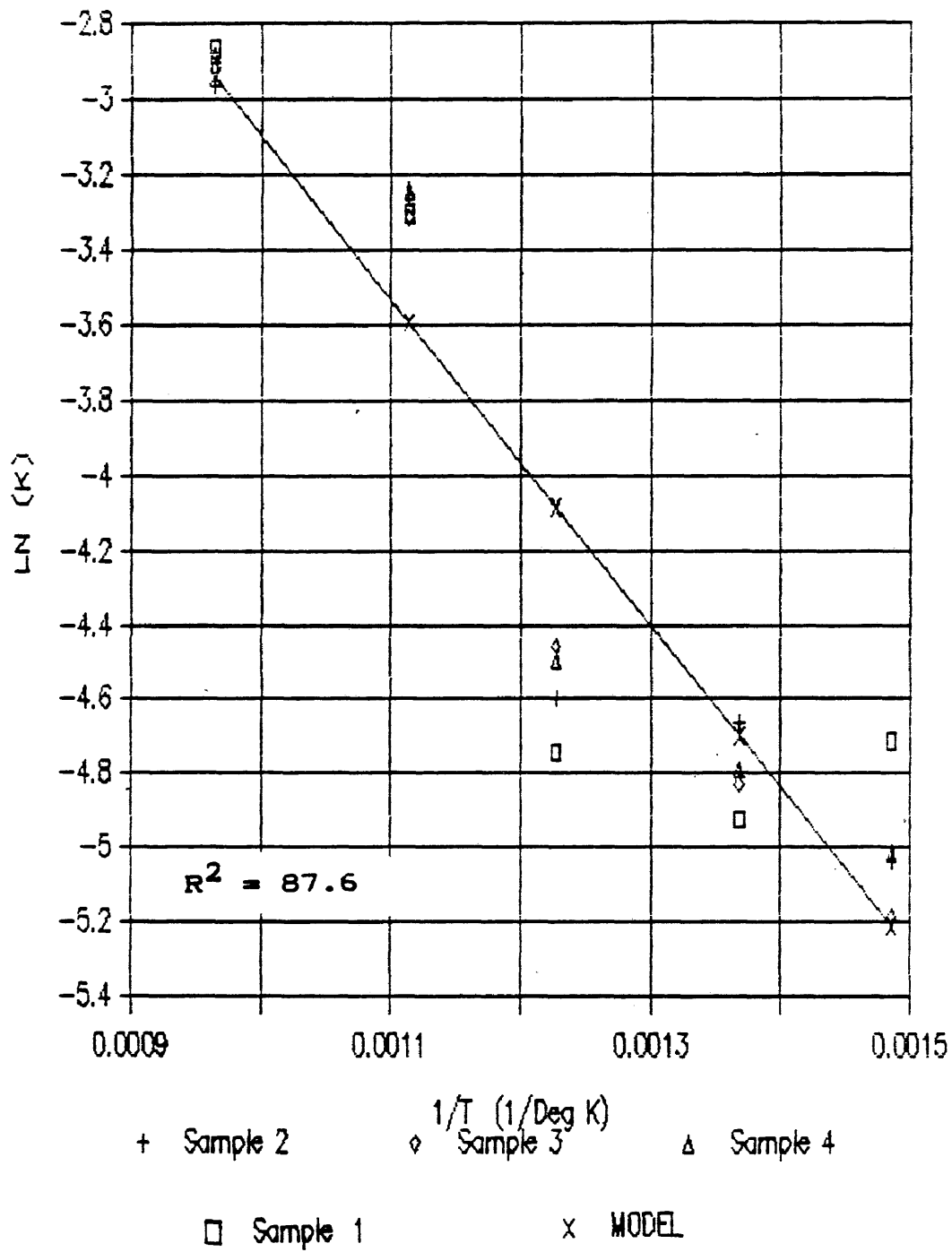


Figure 38

Arrhenius Plot for First Order Reaction and HCCMF Sample

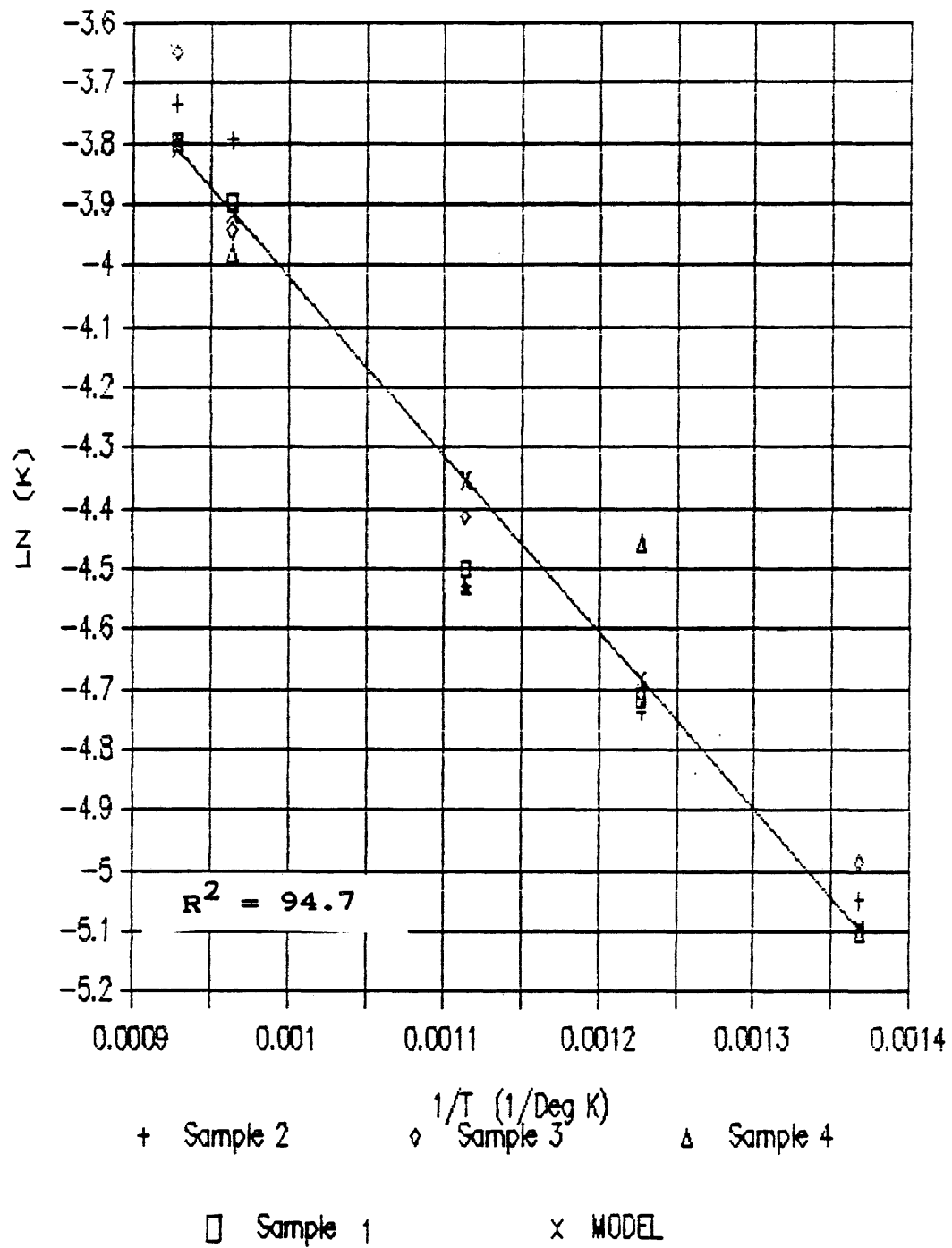


Figure 39

Arrhenius Plot for First Order Reaction and MF Sample

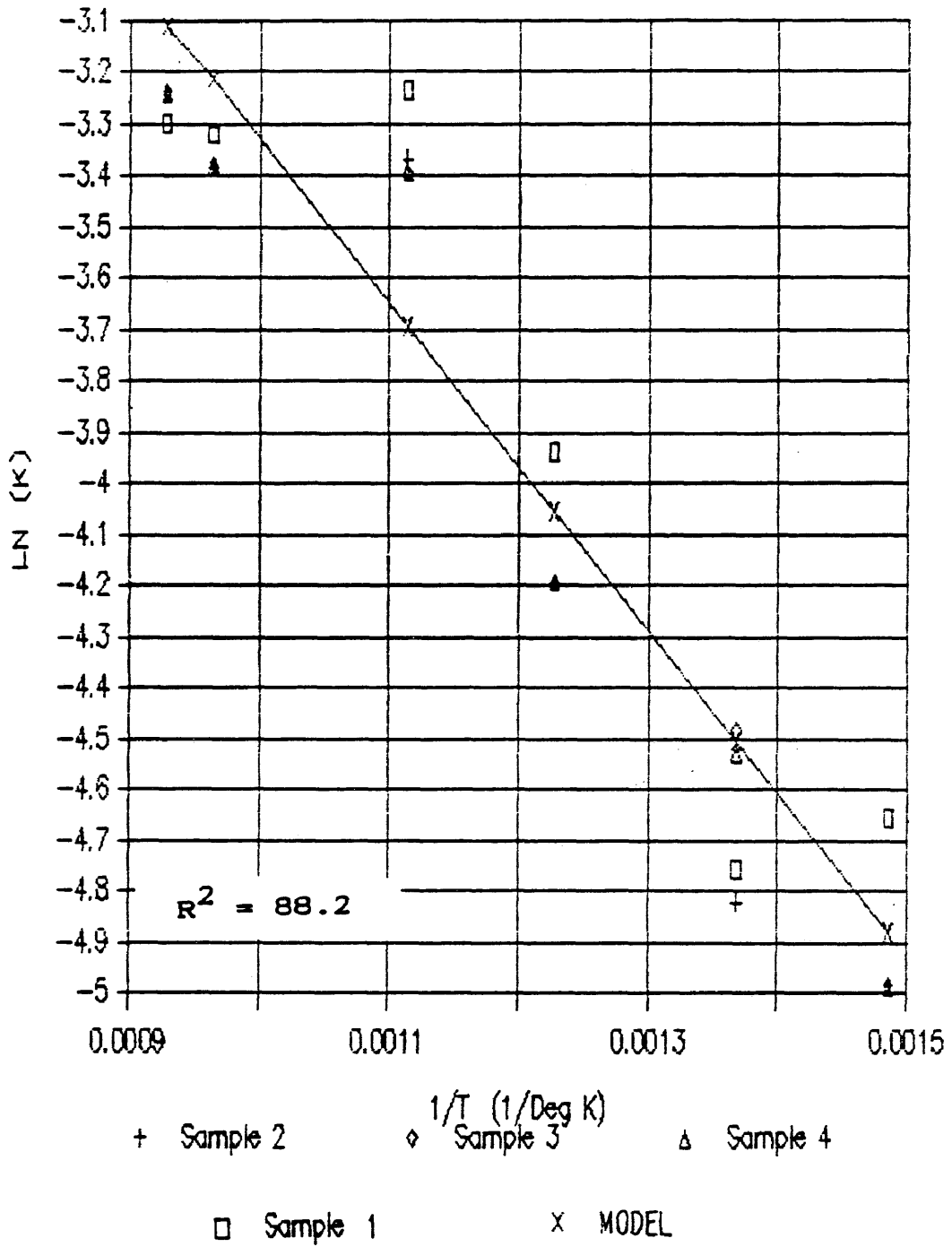


Figure 40

Arrhenius Plot for 3/2 Order Reaction and CMF Sample

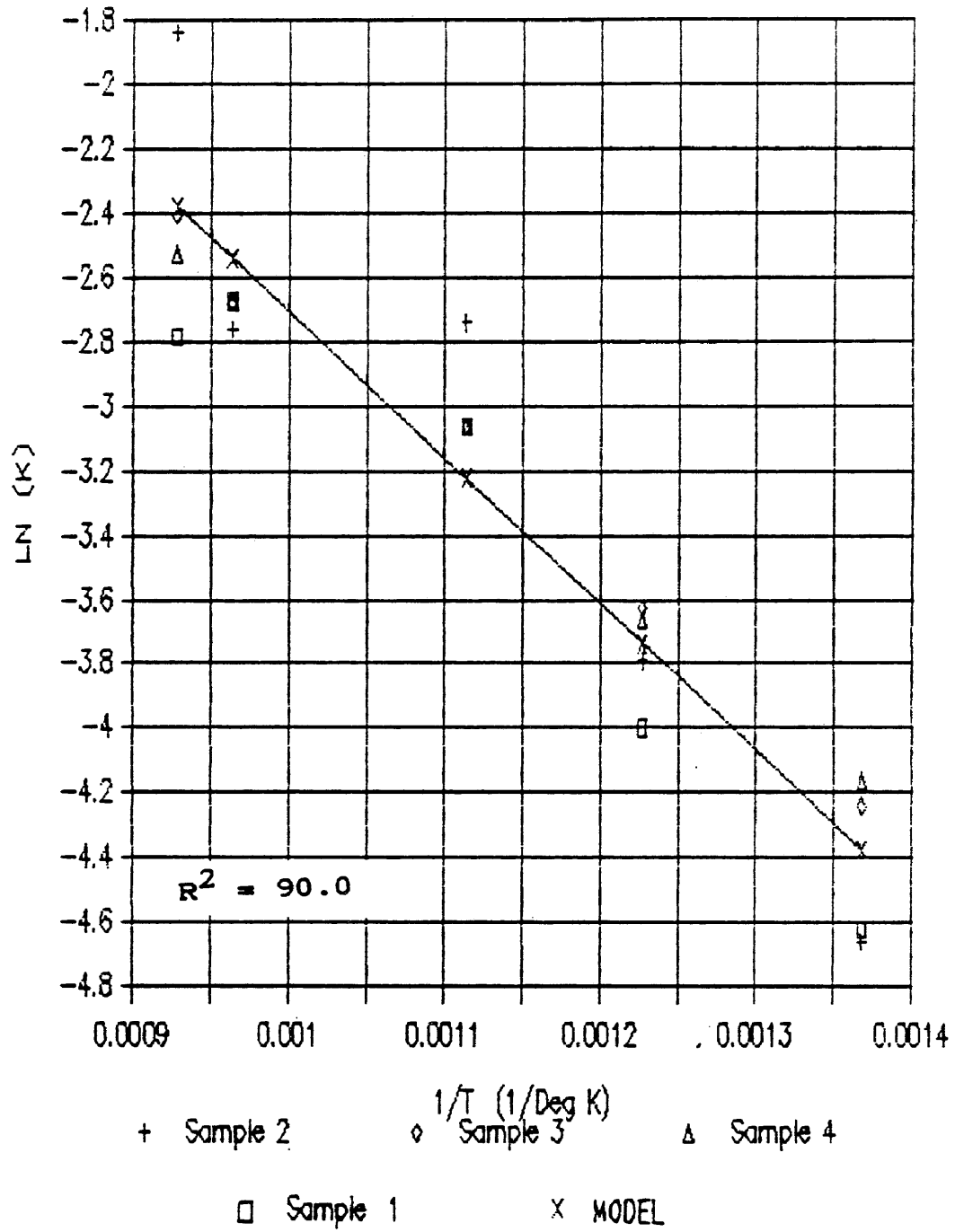


Figure 41

Arrhenius Plot for 3/2 Order Reaction and HCMF Sample

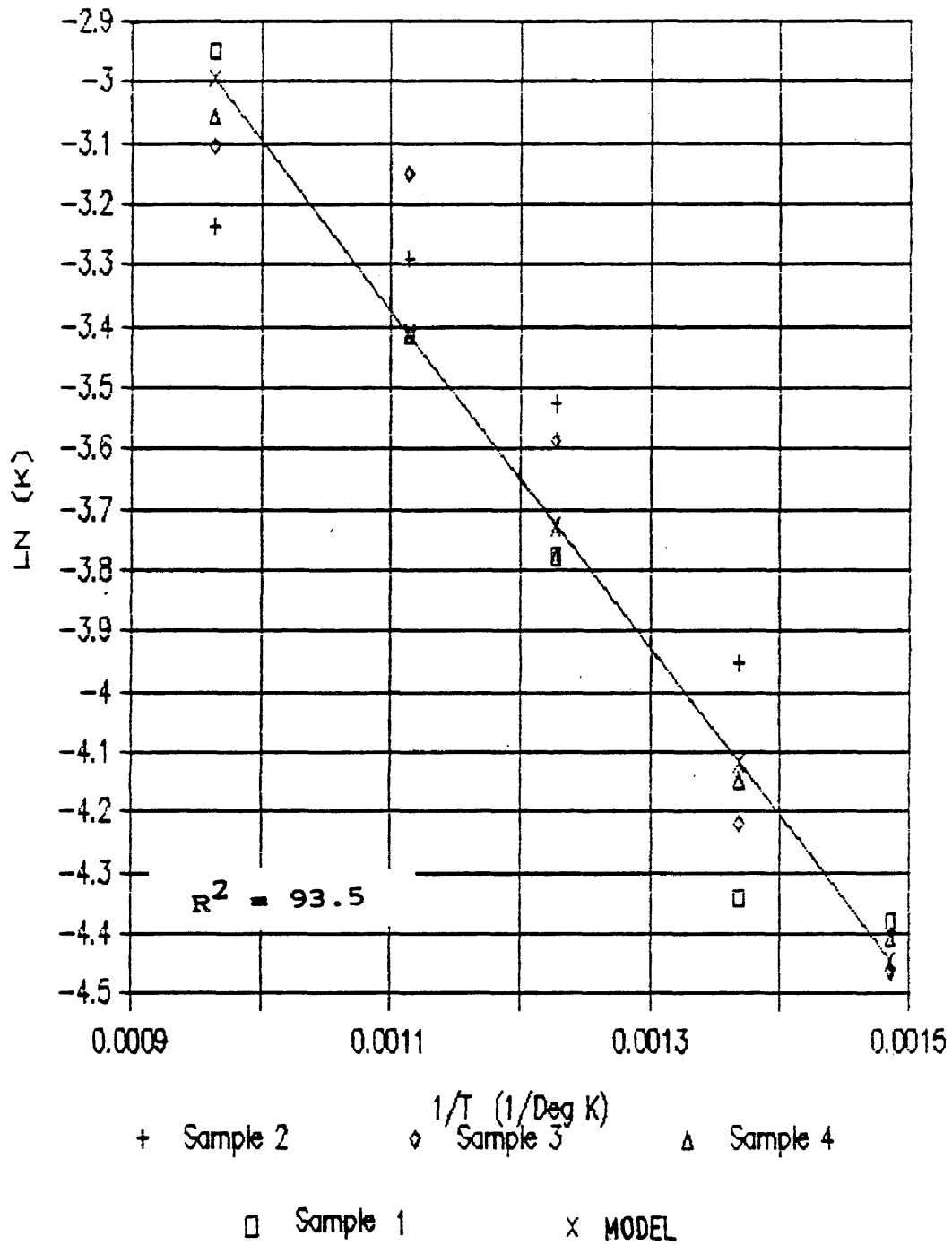


Figure 42

Arrhenius Plot for 3/2 Order Reaction and HCCMF Sample

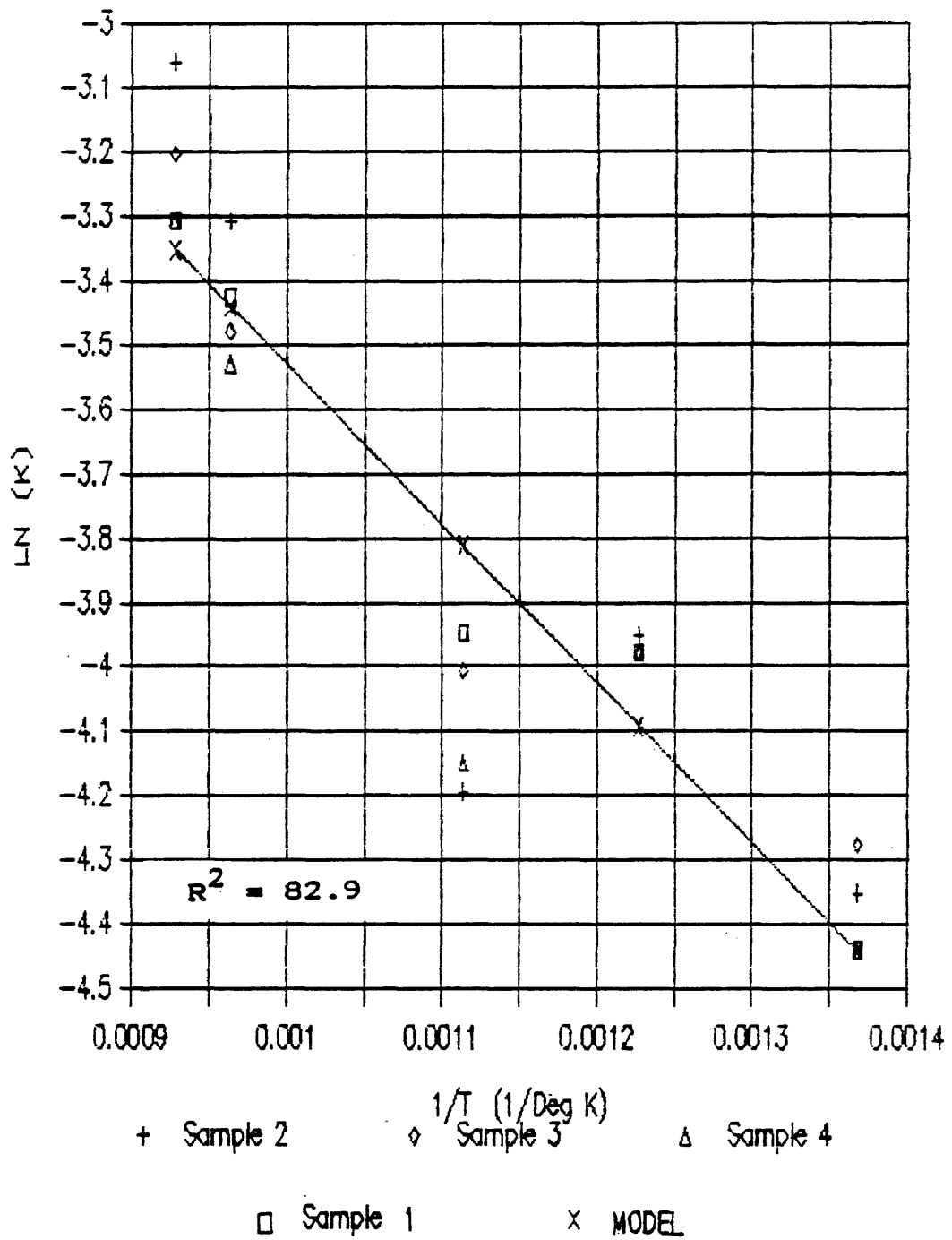


Figure 43

Arrhenius Plot for 3/2 Order Reaction and MF Sample

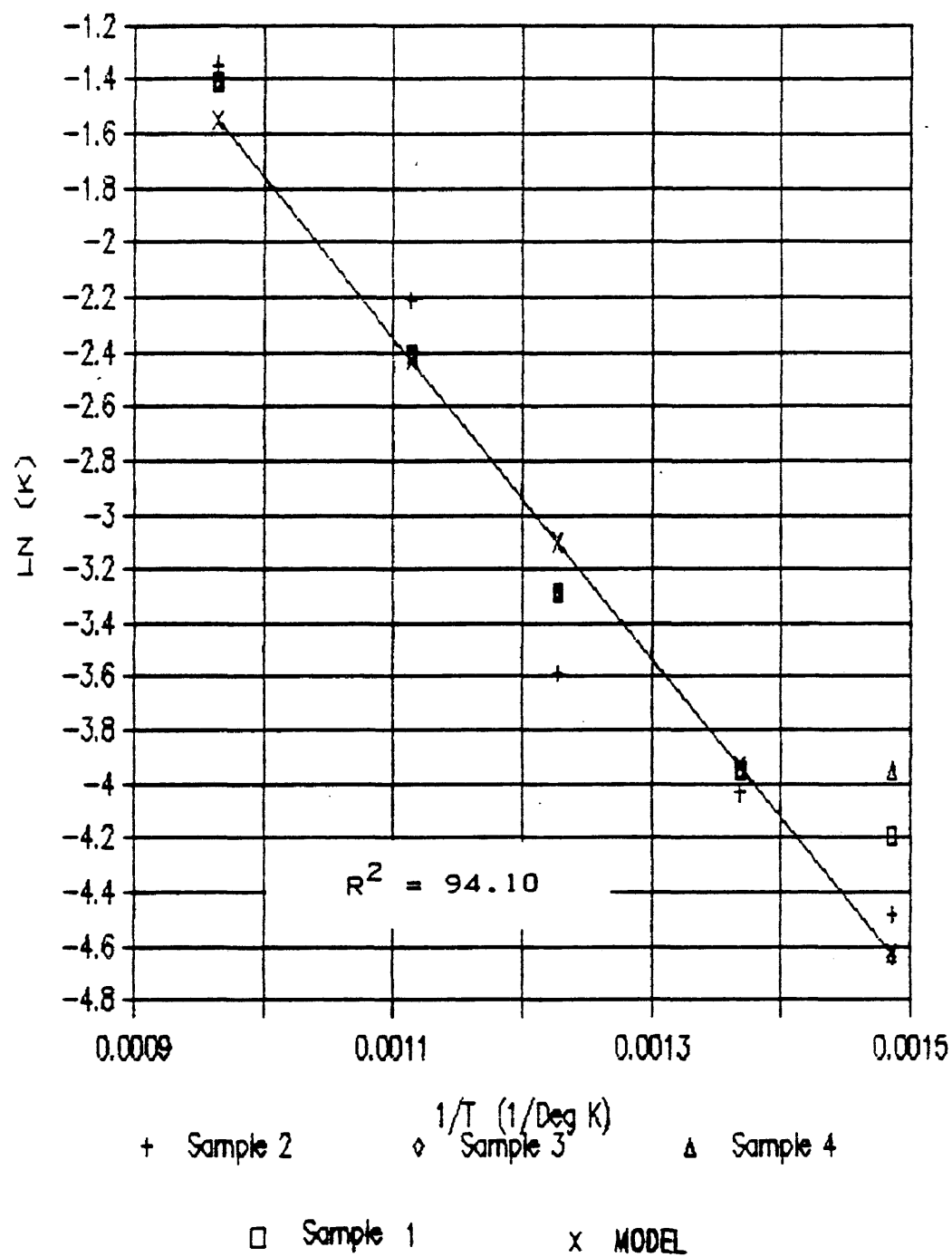


Figure 44

Arrhenius Plot for Second Order Reaction and CMF Sample

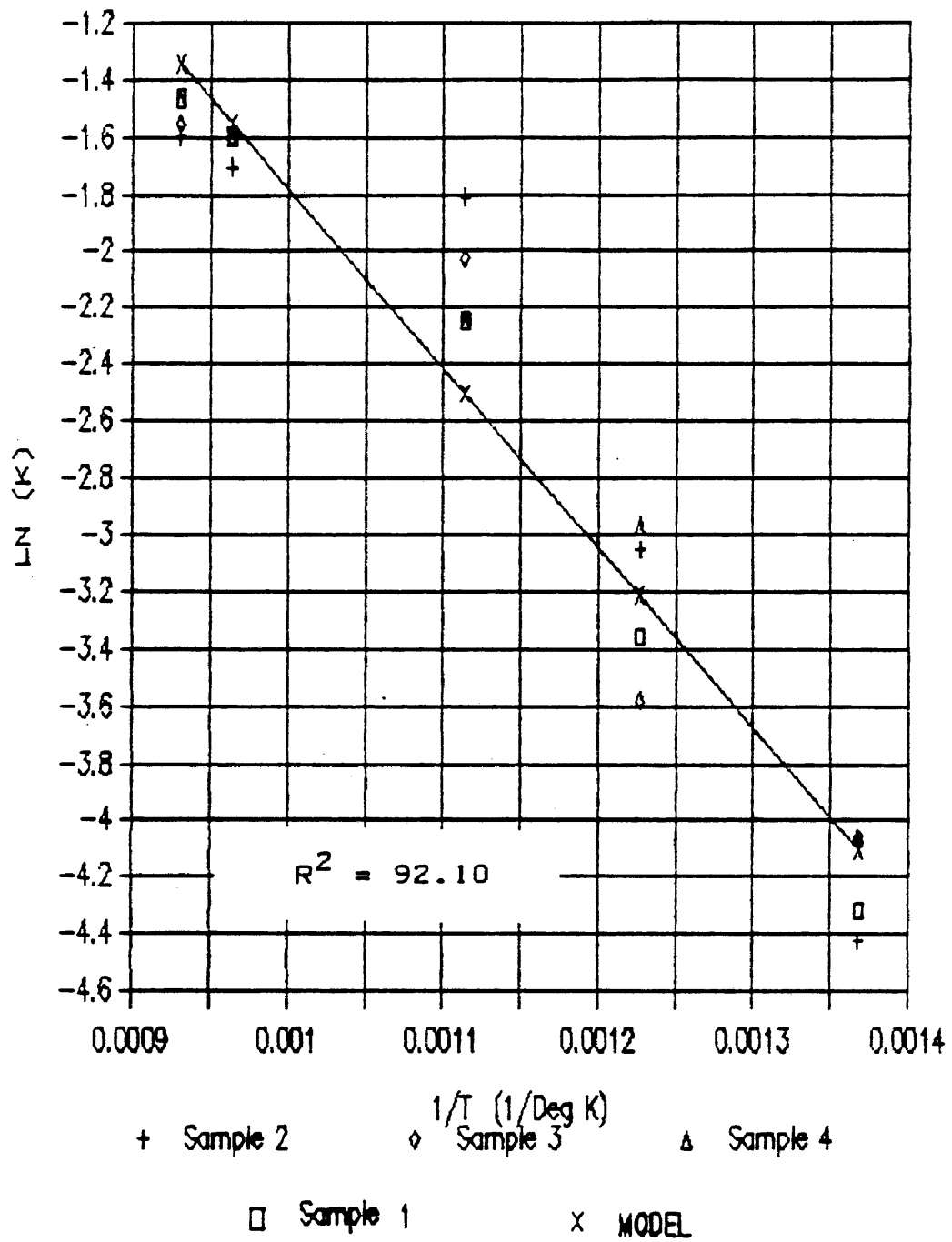


Figure 45

Arrhenius Plot for Second Order Reaction and HCMF Sample

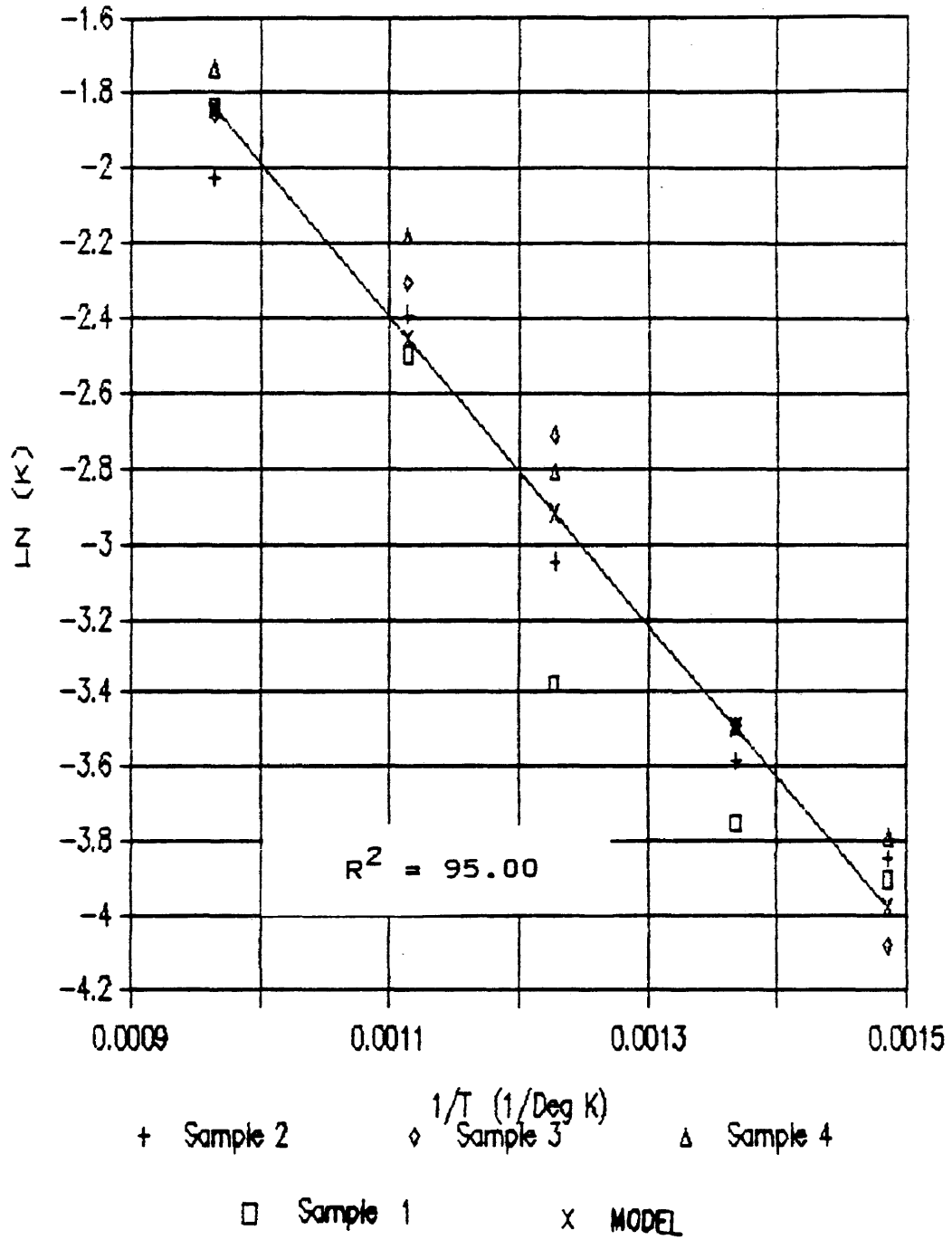


Figure 46

Arrhenius Plot for Second Order Reaction and HCCMF Sample

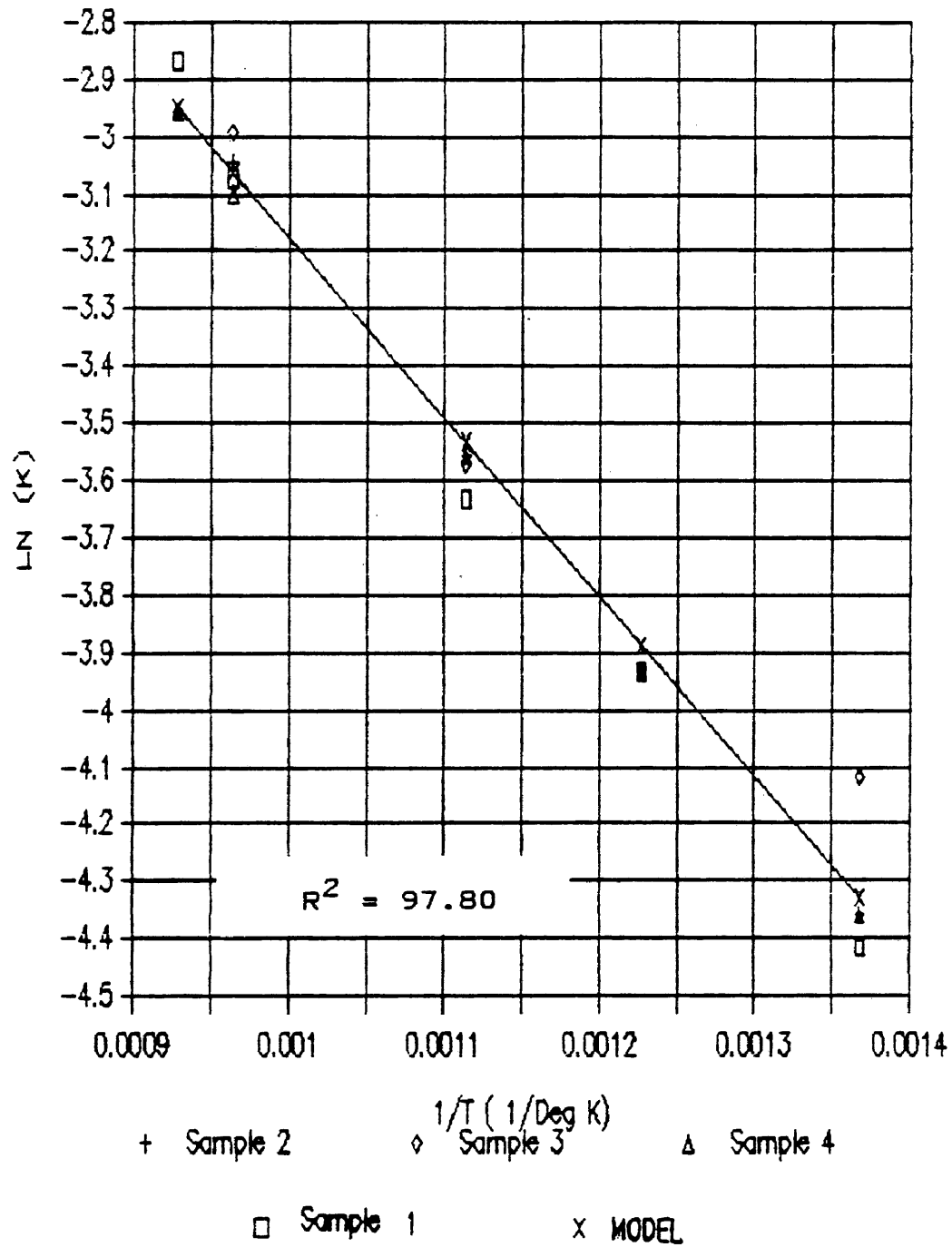


Figure 47

Arrhenius Plot for Second Order Reaction and MF Sample

temperature of approximately 625 °C, as shown in Figure 45. If the data for reaction at temperature above 625 °C are ignored, a new activation energy for temperature range of 400 to 625 °C can be computed for each of these samples. These result are shown in Table 18, and are compared to the overall results for 400 to 805 °C in Table 17. As can be seen, in all cases the activation energy increase if only the data below 625 °C are used, indicating that a shift in the mechanism to mass transfer control may be occurring. The activation energy for the HCCMF sample was lower than for the other samples, indicating that the catalyst on the sample may accelerate the reaction rate. As noted previously however, this was not successful in terms of bringing about increased shale conversion.

Table 17

Summary of Overall Second Order Rate Data
(From 400 to 800°C)

	k_0 (1/second)	E_A (KJ/mole)
	-----	-----
MF	0.96 ± 1.17	26.05 ± 1.18
CMF	62.80 ± 1.75	49.14 ± 3.69
HCMF	91.84 ± 1.80	52.41 ± 4.26
HCCMF	8.09 ± 1.32	33.94 ± 1.88

Table 18

Summary of Second Order Rate Data
(From 400 to 625 °C)

	k_0 (1/second)	E_A (KJ/mole)
	-----	-----
MF	13.46 ± 1.69	42.90 ± 3.45
CMF	139.77 ± 1.62	52.81 ± 3.17
HCMF	2018.28 ± 2.74	72.63 ± 6.76
HCCMF	15.65 ± 1.73	37.65 ± 3.31

5. CONCLUSIONS

The following conclusions can be drawn from the present study:

1) An irreversible second order model adequately describes the reaction kinetics and predicts an apparent activation energy as follows;

MF	sample	26.049	KJ/MOLE
CMF	sample	49.138	
HCMF	sample	52.414	
HCCMF	sample	33.939	

2) This second order kinetic model does not apply very well to the pyrolysis reaction at temperatures greater than 805 C, where the reaction becomes essentially instantaneous.

3) The oil shale conversion reaction starts at about 350°C, and about 70% of the ultimate conversion reaction is completed between 350°C and 450°C.

4) Contrary to the results for hydrolysis at high hydrogen pressures, the oil shale conversion and reaction rate is not increased when the hydrolysis reaction is carried out at low hydrogen pressure.

5) The presence of an impregnated metal (1% Mo loading) on the oil shale coupled with hydrogen at atmospheric pressure did lower the apparent activation energy for the

reaction however, the carbon conversion decreased by about 10-15%.

6. RECOMMENDATIONS

The following are as recommendations for future work.

1) The micro-reactor system should be re-designed to minimize the residence time for pyrolysis products inside the reactor and the connecting line to the detector. This must be done in order to minimize further cracking of shale oil to coke and to be sure that all the products from the pyrolysis reaction are measured by the detector.

2) Noise should be more effectively reduced by re-design of the data collection system (lower gain on amplifier, better shielding).

3) In order to describe the pyrolysis kinetic model more precisely and appropriately, more data should be obtained in the following ranges:

temperature: from 400°C to 600°C

sample weight: from 1 mg to 4 mg

4) The furnace temperature control system should be improved in order to reduce the operation errors and also to save on the time required for each experimental run.

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APPENDIX A. COMPUTER PROGRAMS

Program 1. A/D-18

```
1  DIM AAA(2000)
2  L=0
3  CALL 49664
4  S=(44-PEEK(1146))*(PEEK(1274)*256+PEEK(1402))
6  REM :THIS PROGRAM IS TO STORE GC'S OUTPUT INTO DISK
8  REM :BY S. H. CHU, AUG 1987 CSM
9  INPUT "FILE NAME=";F$
11 INPUT "MAX SAMPLE NO.=";M
20 REM :CLK SET
25 CLK=50177
27 MTH=1148:DAY=1276:YEAR=1404:HOUR=1532:MIN=1660:SEC=1788
   HS=1915:TH=2044
30 DEF FN DEC(X)=PEEK(HOUR)*3600+PEEK(MIN)*60+PEEK(SEC)+
   PEEK(HS)/1000+PEEK(YH)/1000
40 CALL CLK+7
45 STT=FN DEC(X)
50 DEF FN VOLTS(N)=(44-PEEK(1146))*(PEEK(1274)*256+PEEK
   (1402))
60 CALL 49664
70 IF FN VOLTS(N) < S THEN S=FN VOLTS(N)
85 Y=(-1.*FN VOLTS(N)/ABS(S))*159
90 L=L+1
91 IF L > M THEN 190
96 AAA(L)=Y
100 PRINT "AAA(L)      FN VOLTS(N) "
127 GOTO 60
190 CALL CLK+7
195 OVR=FN DEC(X)
200 REM :OPEN AND CLOSE DATA FILE FOR GC DATA
210 D$=CHR$(4)
220 PRINT D$;"OPEN";F$
230 PRINT D$;"WRITE";F$
240 FOR J=1 TO M
243 L$=STR$(J)
245 B$=STR$(AAA(J))
250 PRINT L$
252 PRINT B$
260 NEXT J
270 PRINT D$;"CLOSE";F$
272 TTT=OVR-STT:FRQ=TTT/L
275 PRINT "TOTAL REACTION TIME=";TTT"      "SEC
276 PRINT "FREQUENCY=";FRQ
280 PRINT "TOTAL=";L
290 PRINT "PROGRAM END"
295 PRINT "S=";S
300 END
```

Program 2. TEXT66

```
1  REM :THIS PROGRAM IS TO PLOT GC'S DATA IN ONE
    CONCENTRATED SCREEN
3  REM :BY S. H. CHU  AUG 1987  CSM
4  PRINT CHR$(4);"BRUN LOMEM:";& LOMEM: 4096
6  PRINT CHR$(4);"BLOAD EZEPSON":POKE 1014,0:POKE 1015,08
10 INPUT "FILE NAME=";F$
20 INPUT "SAMPLE NUMBER=";N
22 INPUT "REACTION TEMP=";T
24 INPUT "FREQUENCY=";FRQ
25 INPUT "SAMPLE WEIGHT=";Z
50 INPUT "K=";K
70 HGR
80 HPLOT 0,0 TO 0,159 TO 259,159
82 HPLOT 0,40 TO 259,40
84 HPLOT 0,80 TO 259,80
86 HPLOT 0,120 TO 259,120
88 HPLOT 0,0 TO 259,0 TO 259,159
100 D$=CHR$(4)
110 PRINT D$;"OPEN";F$
120 PRINT D$;"READ";F$
130 FOR I=1 TO N
140 INPUT L$,B$
145 L=VAL(L$)
150 Y=VAL(B$)
155 YY=(1.-K*(1.-Y/159.))*159
160 X=I/N*260.
165 W=(1.-Y/159.)*100
175 HPLOT X,Y
176 HPLOT X,YY
180 PRINT "L=";L,'W=';W
190 NEXT I
200 PRINT D$;"CLOSE";F$
205 &"*RL"
210 PR#1
220 PRINT "GAS FLOW=H2 OR HE"
225 PRINT "REACTION TEMPERATURE=";T
230 PRINT "SAMPLE WEIGHT";Z
235 PRINT "SAMPLE FREQUENCY="FRQ
240 PRINT "FILE NAME=";F$
245 CLK=50177:AD=49357
250 CALL CLK
255 PR#0
260 END
```

Program 3. TEXT11

```
1  REM :THIS PROGRAM IS TO TRANSFER EXPERIMENTAL DATA
    INTO % AND SHOW ON SCREEN
3  REM :HY S. H. CHU AUG 1987 CSM
10  INPUT "FILE NAME=";F$
60  INPUT "SAMPLE NUMBER=";N
100 D$=CHR$(4)
110 PRINT D$;OPEN";F$
120 PRINT D$;"READ" F$
130 FOR I=1 TO N
140 INPUT L$,B$
160 B=(1.-VAL(B$)/159)*100
170 PRINT I,B
190 NEXT I
200 PRINT D$;"CLOSE";F$
290 REM
300 END
```

Program 4. TEXT12

```
1  REM : THIS PROGRAM IS TO SHOW GC'S DATA ON SCREEN
3  BY S. H. CHU AUG 1987 CSM
10  INPUT "FILE NAME=";F$
60  INPUT "SAMPLE NUMBER=";N
100 D$=CHR$(4)
110 PRINT D$;"OPEN";F$
120 PRINT D$;"READ";F$
130 FOR I=1 TO N
140 INPUT L$,B$
150 B=VAL(B$)
170 PRINT I,B
180 NEXT I
200 PRINT D$;"CLOSE";F$
290 REM
300 END
```

Program 5. AVERAGE

```
10 REM: THIS PROGRAM IS TO CALCULATE THE AVERAGE VALUE
20 REM: BY S. H. CHU OCT. 1987 CSM
30 INPUT "FILE NAME=";F$
40 INPUT "START POINT=";M
50 INPUT "END POINT=";N
60 D$=CHR$(4)
70 PRINT D$;"OPEN";F$
80 PRINT D$;"READ";F$
85 S=0:T=0
90 FOR I=1 TO 2000
100 INPUT L$,B$
110 B=(1.-VAL(B$)/159)*100
120 IF I < N THEN 200
150 IF I > M THEN 300
160 NEXT I
170 PRINT D$;"CLOSE";F$
184 AVG1=S/N
185 AVG2=T/2000-M
188 PRINT "AVG1=";AVG1
190 PRINT "AVG2=";AVG2
195 GOTO 400
200 S=S+B
220 GOTO 160
300 T=T+B
305 GOTO 160
400 REM: CHECK STARTING POINT
410 D$=CHR$(4)
420 PRINT D$;"OPEN";F$
430 PRINT D$;"READ";F$
440 FOR I=1 TO 2000
450 INPUT L$,B$
460 B=(1.-VAL(B$)/159)*100
470 P=ABS(B-AVG2)
480 IF P <= 0.01 THEN 500
490 NEXT I
500 IF I >100 THEN 510
505 GOTO 490
510 PRINT "STARTING POINT=";I
520 END
```

Program 6. TEXT14

```
1  REM : THIS PROGRAM IS TO INTEGRATE THE RAW DATA BUT
    WITHOUT NORMALIZATION
3  REM : BY S. H. CHU  AUG. 1987  CSM
8  DIM S(2000),SA(2000),B(2000)
10 INPUT "FILE NAME=";F$
50 INPUT "FREQUENCY=";H
60 INPUT "SAMPLE NUMBER=";N
100 D$=CHR$(4)
110 PRINT D$;"OPEN";F$
120 PRINT D$;"READ";F$
130 FOR I=1 TO N
140 INPUT L$,B$
160 B(I)=(1.-VAL(B$)/159.)*100.
190 NEXT I
200 PRINT D$;"CLOSE";F$
310 REM: INTEGRATION
320 S(0)=0:SA(0)=0
330 FOR I=1 TO N STEP 2
335 J=(I+1)/2
340 S(J)=(H/3)*((B(I-1)-B(1))+4*(B(I)-B(1))+(B(I+1)-B(1)))
350 SA(J)=SA(J-1)+S(J)
360 NEXT I
370 N1=J
380 REM: OPEN A FILE
385 INPUT "FILE NAME=";F$
387 D$=CHR$(4)
388 PRINT D$;"OPEN";F$
389 PRINT D$;"WRITE";F$
410 FOR I=1 TO N STEP 2
415 J=(I+1)/2
420 SK=(S(J)/SA(N1))*100
445 ST=(SA(J)/SA(N1))*100
475 C$=STR$(SK)
476 E$=STR$(ST)
477 PRINT C$
478 PRINT E$
480 NEXT I
485 PRINT D$;"CLOSE";F$
488 PRINT "N1=";N1
490 PRINT "PROGRAM STOP"
510 END
```

Program 7. TEXT14A

```
1  REM: THIS PROGRAM IS TO INTEGRATE THE RAW DATA AND WITH
    STRAIGHT LINE NORMALIZED
3  REM: BY S. H. CHU  AUG 1987  CSM
8  DIM S(20000,SA(20000),B(20000))
10 INPUT "FILE NAME=";F$
50 INPUT "FREQUENCY=";H
60 INPUT "AVG1=";A
70 INPUT "AVG2=";D
80 INPUT "STARTING POINT=";P
90 INPUT "N=";N
100 D$=CHR$(4)
110 PRINT D$;"OPEN";F$
120 PRINT D$;"READ";F$
130 FOR I=1 TO N
140 INPUT L$,B$
160 B(I)=(1-VAL(B$)/159)*100
190 NEXT I
200 PRINT D$;"CLOSE";F$
310 REM: INTEGRATION AND NORMALIZATION
320 S(0)=0:SA(0)=0
330 FOR I=1 TO N STEP 2
335 J=(I+1)/2
336 IF I > P THEN 600
340 S(J)=(H/3.)*((B(I-1)-A)+4*(B(I)-A)+(B(I+1)-A))
350 SA(J)=SA(J-1)+S(J)
360 NEXT I
370 N1=J
380 REM: OPEN A FILE
385 INPUT "FILE NAME=";F$
387 D$=CHR$(4)
388 PRINT D$;"OPEN";F$
389 PRINT D$;"WRITE";F$
410 FOR I=1 TO N STEP 2
415 J=(I+1)/2
420 SK=(S(J)/SA(N1))*100
445 ST=(SA(J)/SA(N1))*100
475 C$=STR$(SK)
476 E$=STR$(ST)
477 PRINT C$
478 PRINT E$
480 NEXT I
485 PRINT D$;"CLOSE";F$
510 END
600 S(J)=(H/3)*((B(I-1)-D)+4*(B(I)-D)+(B(I+1)-D))
610 GOTO 350
```

Program 8. TEXT14B

```
1  REM:THIS PROGRAM IS TO INTEGRATE THE RAW DATA AND
   NORMALIZED WITH SLOP LINE
3  REM:BY S. H. CHU AUG 1987 CSM
8  DIM S(2000),SA(2000),B(2000)
10 INPUT "FILE NAME=";F$
50 INPUT "FREQUENCY=";H
70 INPUT "N=";N
100 D$=CHR$(4)
110 PRINT D$;"OPEN";F$
120 PRINT D$;"READ";F$
130 FOR I=1 TO N
140 INPUT L$,B$
160 B(I)=(1-VAL(B$)/159)*100
190 NEXT I
200 PRINT D$;"CLOSE";F$
310 REM: INTEGRATION AND NORMALIZATION
320 S(0)=0:SA(0)=0
330 FOR I =1 TO N STEP 2
335 J=(I+1)/2
336 A=E*I/2000
340 S(J)=(H/3)*((B(I-1)-A)+4*(B(I)-A)+(B(I+1)-A))
350 SA(J)=SA(J-1)+S(J)
360 NEXT I
370 N1=J
380 REM: OPEN A FILE
385 INPUT "FILE NAME=";F$
387 D$=CHR$(4)
388 PRINT D$;"OPEN";F$
389 PRINT D$;"WRITE";F$
410 FOR I=1 TO N STEP 2
415 J=(I+1)/2
420 SK=(S(J)/SA(N1))*100
445 ST=(SA(J)/SA(N1)0*100
475 C$=STR$(SK)
476 E$=STR$(ST)
477 PRINT C$
478 PRINT E$
480 NEXT I
485 PRINT D$;"CLOSE";F$
490 PRINT "PROGRAM STOP"
510 END
```

Program 9. TEXT100A

```
1  REM:THIS PROGRAM IS TO PLOT THE NORMALIZED CURVE IN
    ONE CONCENTRATED SCREEN
3  REM:BY S. H. CHU  AUG 1987  CSM
10 PRINT CHR$(4);'BRUN LOMEM:":&LOMEM:4096
15 PRINT CHR$(4);"BLOAD EZEPSON":POKE 1014,0:POKE 1015,08
16 INPUT "REACTION TEMP=";T
17 INPUT "SAMPLE WEIGHT=";W
18 INPUT "SAMP FREQ=";Q
20 INPUT "FILE NAME =" ;F$
32 INPUT "FINAL CONVERSION=";A
33 INPUT "N=";N
35 HGR
36 HPLOT 0,0 TO 0,159 TO 259,159
37 HPLOT 0,40 TO 259,40
38 HPLOT 0,80 TO 259,80
39 HPLOT 0,120 TO 259,120
40 HPLOT 0,0 TO 259,0 TO 259,159
48 D$=CHR$(4)
50 PRINT D$;"OPEN";F$
60 PRINT D$;"READ";F$
70 FOR J=1 TO N
80 INPUT C$,E$
91 ST=(1-(VAL(E$)*A)/100)*159
92 X=J/1000*259
95 HPLOT X,ST
96 PRINT J,ST
100 NEXT J
150 PRINT D$;"CLOSE";F$
153 &"*RL"
160 PR#1
164 PRINT "GAS FLOW=H2 OR HE"
165 PRINT "REACTION TEMP=";T
166 PRINT "SAMPLE WEIGHT=";W
167 PRINT "FINAL CONVERSION=";A
168 PRINT "SAMPLE FREQUENCY=";Q
169 PRINT "FILE NAME=";F$
170 CLK=50177:AD=49357
171 CALL CLK
180 PR#0
200 END
```

Program 10. TEXT13A

```
1  REM:THIS PROGRAM IS TO PRINT OUT THE SELECTED
    NORMALIZED POINT
3  REM:BY S. H. CHU AUG 1987 CSM
5  DIM B(1001)
10 INPUT "FILE NAME=";F$
20 INPUT "CONVERSION=";P
100 D$=CHR$(4)
110 PRINT D$;"OPEN";F$
120 PRINT D$;"READ";F$
130 FOR I=1 TO 1000 STEP 1
140 INPUT C$,E$
160 B(I)=VAL(E$)
190 NEXT I
200 PRINT D$;"CLOSE";F$
250 FOR K=1 TO 25 STEP 5
260 PRINT K*0.64,B(K)*P
270 NEXT K
300 FOR K=26 TO 60 STEP 1
310 PRINT K*0.64,B(K)*P
320 NEXT K
400 FOR K=61 TO 200 STEP 10
410 PRINT K*0.64,B(K)*P
420 NEXT K
430 FOR K=201 TO 400 STEP 20
440 PRINT K*0.64,B(K)*P
450 NEXT K
460 FOR K=401 TO 600 STEP 40
470 PRINT K*0.64,B(K)*P
480 NEXT K
500 FOR K=600 TO 1000 STEP 100
510 PRINT K*0.64,B(K)*P
520 NEXT K
530 END
```

APPENDIX B. K VALUE AND R SQUARED DATA

K VALUE AND R SQUARE FOR 1ST ORDER AND "MF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384 S)		640(S)	
		K	R	K	R	K	R	K	R	K	R
400	C2										
	C3										
	C4										
	C5										
458	C2										
	C3	0.00586	98.47	0.00597	99.21	0.00605	99.51	0.00609	99.78	0.0074	88.38
	C4	0.00608	97.97	0.00622	98.95	0.00627	99.38	0.00642	99.67	0.00836	90.65
	C5	0.0075	99.19	0.00716	99.31	0.00691	99.36	0.00683	99.68	0.00869	92.25
542	C2	0.00895	96.46	0.00788	95.83	0.007	95.62	0.00915	95.32	0.00762	86.07
	C3	0.0133	94.9	0.0114	93.92	0.00995	93.69	0.00876	94.19	0.00968	93.99
	C4	0.015	94.11	0.0126	92.42	0.0107	91.54	0.00906	90.97	0.00993	92.77
	C5	0.0173	95.12	0.0151	94.7	0.0133	94.67	0.0116	94.32	0.0109	93.74
625	C2	0.0125	93.85	0.0111	94.88	0.0102	95.6	0.00923	96.36	0.0106	95.16
	C3	0.0132	88.01	0.0108	87.51	0.00922	88.26	0.00827	91.28	0.0102	92.37
	C4	0.0149	88.67	0.0121	86.58	0.0102	87.26	0.00908	90.26	0.0108	92.69
	C5	0.0134	88.01	0.0108	86.03	0.00914	86.58	0.00809	89.63	0.00959	91.44
765	C2	0.0203	83.85	0.016	83.85	0.0129	82.27	0.0104	81.78	0.0103	87.1
	C3	0.0225	74.25	0.0167	74.25	0.0131	72.63	0.0106	74.4	0.0105	83.38
	C4	0.0194	89.76	0.0157	89.76	0.013	87.91	0.0106	86.55	0.0105	90.13
	C5	0.0187	88.43	0.015	88.43	0.0123	86.73	0.0101	86.25	0.0102	89.82
805	C2	0.017	82.82	0.0134	82.82	0.0108	81.9	0.00908	83.8	0.01	89.37
	C3	0.0224	79.59	0.0171	79.59	0.0134	76.95	0.0108	76.43	0.0107	85.63
	C4	0.0239	80.27	0.0181	80.27	0.0141	76.95	0.0108	78.17	0.0112	85.79
	C5	0.026	85.22	0.0205	85.22	0.0164	82.94	0.0133	82.59	0.0125	88.59

C3 = -1.10 - 2921 * C1
R-SQRE = 94.7%

K VALUE AND R SQUARE FOR 1ST ORDER AND "CMF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384(S)		640(S)	
		K	R	K	R	K	R	K	R	K	R
400	C2	0.00621	97.74	0.00624	98.85	0.00632	99.4	0.00653	99.59	0.00862	91.59
	C3	0.00666	97.72	0.00602	97.26	0.00558	97.68	0.0054	98.63	0.00756	85.92
	C4	0.00444	98.4	0.00426	98.93	0.00421	99.42	0.00443	99.41	0.00685	80.98
	C5	0.00725	97.82	0.00703	98.7	0.00681	99.17	0.00671	99.55	0.00848	91.81
458	C2	0.00565	98.44	0.00571	99.21	0.00575	99.55	0.00591	99.7	0.00799	87.88
	C3	0.00521	98.75	0.00532	99.34	0.00545	99.58	0.00591	99.13	0.00836	88.09
	C4	0.00688	98.33	0.00696	99.15	0.00705	99.51	0.00669	99.45	0.00848	89.98
	C5	0.00772	99.24	0.00731	99.24	0.00698	99.24	0.00682	99.54	0.00857	91.13
542	C2	0.0217	93.55	0.0177	90.62	0.0154	91.13	0.0148	94.91	0.0137	96.1
	C3	0.0158	91.72	0.013	89.53	0.011	89.49	0.00973	91.54	0.0109	94.57
	C4	0.0124	94.54	0.0107	92.44	0.00914	91.91	0.00795	92.56	0.00911	91.27
	C5	0.0216	95	0.0191	94.56	0.0169	94.76	0.0151	95.41	0.0133	94.67
625	C2	0.0167	87.59	0.0133	84.3	0.0109	83.53	0.00919	85.48	0.01	90.43
	C3	0.0258	87.14	0.0209	87.64	0.0173	86.8	0.0143	86.65	0.0132	90.85
	C4	0.0254	89.33	0.0214	83.4	0.0172	81.53	0.0137	80.52	0.0126	86.3
	C5	0.0272	86.86	0.0205	83.97	0.0165	82.44	0.0134	82.22	0.0125	88.08
765	C2	0.0273	84.03	0.0211	79.8	0.0168	78.35	0.0139	80.27	0.0129	86.77
	C3	0.0306	81.92	0.0232	77	0.0181	74.36	0.0139	72.6	0.0129	80.88
	C4	0.0375	86.36	0.0297	83.26	0.0239	81.74	0.019	80.58	0.0161	83.7
	C5	0.0341	82.54	0.026	77.82	0.0204	75.5	0.016	75.1	0.0144	82.16
805	C2	0.0105	84.92	0.00843	83.32	0.00712	84.6	0.0632	88.48	0.00783	84.8
	C3	0.0298	83.76	0.0229	79.15	0.018	76.94	0.0143	76.98	0.0136	85.89
	C4	0.0299	83.73	0.0231	79.53	0.0183	77.79	0.0147	78.18	0.0135	85.3
	C5	0.019	82.05	0.0146	77.79	0.0116	76.98	0.00966	79.46	0.0105	87.53

$$C2 = 1.49 - 4631 * C1$$

$$R \text{ SQUARE} = 89.9\%$$

K VALUE AND R SQUARE FOR 1ST ORDER AND "HCHF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384(S)		640(S)	
		K	R	K	R	K	R	K	R	K	R
400	C2	0.01425	98.67	0.0131	99.26	0.0131	99.26	0.0128	99.49	0.0137	99.15
	C3	0.00851	99.08	0.00887	99.7	0.00887	99.7	0.00944	99.2	0.0114	97
	C4	0.00773	99.07	0.00802	99.6	0.00798	99.64	0.00778	99.71	0.00958	93.23
	C5	0.0113	98.06	0.0114	99.08	0.0114	99.08	0.0109	99.3	0.0117	98.71
458	C2	0.00731	99.11	0.00685	99.01	0.00648	99.03	0.00618	99.27	0.00785	87.88
	C3	0.0067	98.99	0.00647	99.31	0.00623	99.42	0.00599	99.56	0.00774	87.25
	C4	0.00811	98.21	0.00817	99.09	0.00834	99.49	0.00871	99.55	0.00978	95.96
	C5	0.00869	99.06	0.00859	99.5	0.00882	99.66	0.0093	99.51	0.0102	96.87
542	C2	0.0149	93.75	0.0124	91.86	0.0106	91.17	0.00921	92.18	0.0101	93.56
	C3	0.0179	92.6	0.0147	90.16	0.0123	89.34	0.0105	90.09	0.0109	93.32
	C4	0.0126	97.95	0.0109	96.01	0.0091	93.2	0.00737	90.07	0.00851	87.67
	C5	0.0184	90.17	0.0155	89.64	0.0132	89.78	0.0115	91.08	0.0118	94.72
625	C2	0.0455	94.77	0.038	92.45	0.0316	90.43	0.0242	84.23	0.0184	80.11
	C3	0.0272	86.15	0.0218	83.93	0.0183	84.91	0.0155	86.36	0.015	92.29
	C4	0.0324	87.3	0.0268	86.7	0.0232	88.26	0.0195	88.57	0.0165	89.51
	C5	0.03	86.56	0.0243	84.83	0.0208	86.5	0.0177	87.84	0.016	91.51
765	C2	0.0525	93.53	0.0496	95.14	0.0409	93.01	0.0318	87.38	0.0234	80.02
	C3	0.0434	88.24	0.0379	88.24	0.0312	88.84	0.0268	89.85	0.0208	85.26
	C4	0.0366	82.14	0.0298	79.15	0.0217	77.32	0.0188	79.93	0.0165	84.91
	C5	0.0352	82.3	0.0286	79.14	0.0228	78.06	0.0181	80.02	0.0164	86.5
805	C2	0.031	80.75	0.0241	77.56	0.0198	78.61	0.0174	83.66	0.016	89.47
	C3	0.0382	84.27	0.0311	83.46	0.0278	87.41	0.0241	89.41	0.0195	87.59
	C4	0.0368	82.35	0.0287	78.74	0.0232	78.64	0.0197	81.91	0.0174	86.61
	C5	0.0376	82.75	0.0291	78.75	0.0234	78.2	0.0202	82.71	0.0178	86.72

$$C2 = 2.56 - 5507 * C1$$

$$R \text{ SQUARE} = 85.5\%$$

K VALUE AND R SQUARE DATA FOR 1ST ORDER AND "HCCMF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384 S)		640(S)	
		K	R	K	R	K	R	K	R	K	R
400	C2	0.007	98.73	0.00853	98.87	0.00895	99.23	0.00899	99.49	0.00954	95.99
	C3	0.00729	98.33	0.0069	98.7	0.00659	99.03	0.00653	99.49	0.00831	91.23
	C4	0.00646	98.28	0.00604	98.49	0.00574	98.84	0.00559	99.32	0.00767	86.62
	C5	0.00798	97.97	0.00736	98.04	0.00688	98.32	0.00665	98.98	0.00849	91.37
458	C2	0.00812	98.8	0.00793	99.29	0.00761	99.4	0.00727	99.47	0.00889	92.76
	C3	0.00985	98.59	0.00991	99.28	0.00984	99.6	0.00942	99.58	0.0107	96.35
	C4	0.00912	98.99	0.00873	99.23	0.00834	99.32	0.00801	99.46	0.0096	94.54
	C5	0.00991	98.9	0.00936	98.99	0.0088	98.98	0.0083	99.07	0.00986	94.85
542	C2	0.0137	94.12	0.0116	92.48	0.00992	92.01	0.0087	92.96	0.00953	92.93
	C3	0.0158	94.51	0.0134	93.04	0.0115	92.57	0.0101	93.22	0.0105	94.67
	C4	0.0178	95.07	0.0153	93.98	0.0133	88.64	0.0116	90.5	0.0117	94.46
	C5	0.0171	94.73	0.0146	93.64	0.0127	90.02	0.0112	91.67	0.0117	94.94
625	C2	0.0229	87.2	0.0182	83.99	0.0147	82.66	0.012	82.93	0.0114	88.31
	C3	0.0241	86.87	0.0191	83.63	0.0155	82.6	0.0128	83.34	0.0121	89.03
	C4	0.0245	88.51	0.0198	86.17	0.0163	85.34	0.0135	85.74	0.013	91.33
	C5	0.026	88.36	0.021	85.87	0.0173	85.14	0.0144	86	0.0134	90.81
765	C2	0.0319	82.08	0.0247	78.26	0.0198	77.62	0.0162	79.28	0.0143	84.74
	C3	0.0293	82.04	0.0225	77.61	0.0177	75.91	0.0143	76.85	0.0133	84.97
	C4	0.0312	83.32	0.0241	79.07	0.019	77.17	0.0152	77.53	0.0139	84.71
	C5	0.0324	83.42	0.025	79.19	0.0197	77.24	0.0157	77.07	0.0141	84.04
805	C2	0.0264	83.15	0.0209	80.66	0.0173	81.5	0.0151	85.45	0.0141	90.77
	C3	0.0256	81.35	0.0197	77.32	0.0157	76.53	0.013	78.79	0.0124	86.089
	C4	0.0278	80.59	0.0212	75.98	0.0167	74.55	0.0135	76.04	0.0128	84.81
	C5	0.0285	81.71	0.0218	77.24	0.0172	75.72	0.014	77.28	0.0133	85.94

$$C2 = 1.24 - 4341 * C1$$

$$R \text{ SQUARE} = 87.6\%$$

K VALUE AND R SQUARE FOR 3/2'RD ORDER AND "MF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384(S)	
		K	R	K	R	K	R	K	R
400	C2								
	C3								
	C4								
	C5								
458	C2								
	C3	0.00839	97.57	0.00913	98.2	0.0102	98.04	0.0118	97.29
	C4	0.00876	97	0.00962	97.86	0.0106	98.12	0.0129	95.84
	C5	0.011	99.41	0.0112	99.66	0.0117	99.63	0.0139	96.76
542	C2	0.0131	97.36	0.0122	97.74	0.0114	98.27	0.0109	98.85
	C3	0.0215	96.05	0.0197	96.68	0.0185	97.64	0.0187	98.64
	C4	0.025	96.14	0.0224	96.2	0.0204	96.69	0.0192	97.66
	C5	0.031	95.96	0.0297	97.52	0.0294	98.65	0.0301	99.13
625	C2	0.018	96.73	0.0175	98.11	0.0179	98.98	0.0193	98.82
	C3	0.019	91.69	0.0164	90.56	0.015	94.13	0.0158	96.55
	C4	0.0223	91.08	0.0192	91.31	0.0174	93.4	0.0182	96.21
	C5	0.00193	90.81	0.0164	92.01	0.0148	92.64	0.0151	95.99
765	C2	0.0325	91.74	0.0268	89.88	0.0231	90.38	0.0206	92.42
	C3	0.0366	83.42	0.0281	78.9	0.0232	79.9	0.021	85.92
	C4	0.0308	96.35	0.0267	95.14	0.0238	95.37	0.0215	96
	C5	0.0293	95.68	0.0248	93.84	0.0218	93.91	0.02	92.52
805	C2	0.0252	89.68	0.0207	87.91	0.0177	88.92	0.0168	93.06
	C3	0.0366	88.23	0.0291	85.1	0.0239	84.46	0.022	89.29
	C4	0.0406	90.07	0.0319	85.56	0.0259	84.09	0.0235	88.77
	C5	0.0469	93.47	0.0396	92.29	0.0342	92.1	0.0319	94.74

$$C3 = -1.06 - 2471 * C1$$

$$R \text{ SQUARE} = 82.9\%$$

K VALUE AND R SQUARE FOR 3/2'RD ORDER AND "CMF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384 S)	
		K	R	K	R	K	R	K	R
400	C2	0.00963	96.95	0.0104	98.1	0.0115	98.05	0.0143	95.07
	C3	0.0102	98.35	0.00966	98.73	0.00951	99.28	0.0104	98.54
	C4	0.00654	98.51	0.00652	99.22	0.00684	99.33	0.00819	96.43
	C5	0.0115	97.54	0.0119	98.69	0.0125	99.08	0.0145	97.46
458	C2	0.00732	97.72	0.00788	98.44	0.00859	98.37	0.0104	96.16
	C3	0.00668	98.07	0.00725	98.49	0.00806	98.01	0.0107	92.93
	C4	0.00922	97.27	0.0101	98.04	0.0113	97.62	0.0122	98.4
	C5	0.0104	99.31	0.0105	99.64	0.0108	99.67	0.0126	97.38
542	C2	0.0383	96.62	0.0339	96.09	0.0338	97.47	0.0527	85.65
	C3	0.0243	94.82	0.0212	94.48	0.0195	95.88	0.0205	97.35
	C4	0.0183	95.93	0.0165	96.28	0.0151	96.76	0.0147	98.14
	C5	0.0404	95.55	0.0402	97.6	0.0419	98.56	0.0502	96.26
625	C2	0.0257	90.9	0.0213	89.35	0.0185	90.43	0.0178	94.35
	C3	0.0475	94.22	0.0431	95.3	0.0399	96.46	0.0394	97.98
	C4	0.0519	91.94	0.044	91.23	0.0382	91.74	0.0345	93.78
	C5	0.048	91.88	0.0409	91.46	0.0359	93.32	0.0336	94.95
765	C2	0.0506	89.68	0.0417	88.09	0.0361	89.4	0.0362	93.73
	C3	0.0599	87.24	0.0483	85.04	0.0401	85.02	0.034	86.67
	C4	0.0879	93.86	0.0784	94.59	0.0722	95.89	0.0693	97.48
	C5	0.0727	88.27	0.0594	86.58	0.0504	87.32	0.0461	91.27
805	C2	0.0139	87.42	0.0116	87.32	0.0104	90	0.0103	94.54
	C3	0.0579	89.17	0.0473	87.31	0.0402	86.05	0.037	91.74
	C4	0.0582	89.19	0.0481	87.98	0.0416	89.18	0.0392	93.23
	C5	0.0295	85.7	0.0236	83.39	0.02	84.91	0.0188	90.49

$$C2 = -0.141 - 3189 * C1$$

$$R \text{ SQUARE} = 88.2\%$$

K VALUE AND R SQUARE DATA FOR 3/2'RD ORDER AND "HCMF SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384 S)	
		K	R	K	R	K	R	K	R
400	C2	0.0255	95.67	0.028	97.28	0.0315	97.52	0.0446	87.72
	C3	0.013	98.58	0.0151	97.21	0.0174	97.04	0.026	84.5
	C4	0.0115	98.9	0.0126	98.61	0.015	96.78	0.0172	97.08
	C5	0.019	94.88	0.0234	94.84	0.0254	97.01	0.0312	94.61
458	C2	0.00979	99.4	0.00974	99.69	0.00986	99.82	0.0108	98.96
	C3	0.00892	98.53	0.00916	99.22	0.00946	99.51	0.0104	98.76
	C4	0.0113	97.01	0.0125	97.76	0.0144	96.97	0.0198	92.01
	C5	0.012	98.4	0.0132	98.57	0.0156	96.4	0.0224	90.57
542	C2	0.0223	95.99	0.0198	95.82	0.0181	96.49	0.0183	97.98
	C3	0.0283	95.71	0.0249	95.27	0.0227	96.08	0.0226	97.82
	C4	0.0182	99.33	0.0167	98.71	0.0147	96.98	0.0266	98.43
	C5	0.0297	96.19	0.0271	96.79	0.0256	97.71	0.0126	95.41
625	C2	0.144	97.14	0.15	98.44	0.155	99.09	0.143	98.52
	C3	0.0511	91.47	0.0449	92.49	0.044	95.62	0.0468	97.48
	C4	0.068	93.78	0.0665	96.16	0.073	97.46	0.0814	97.92
	C5	0.0593	92.5	0.0542	94.39	0.057	96.95	0.0643	97.27
765	C2	0.193	94.43	0.205	96.94	0.205	98.38	0.218	97.36
	C3	0.116	97	0.13	97.66	0.153	96.01	0.204	92.5
	C4	0.075	88.98	0.0632	88.89	0.0635	92.82	0.0688	96.03
	C5	0.0798	89.09	0.0684	89.75	0.0567	91.26	0.0631	95.05
805	C2	0.0594	86.87	0.0502	87.53	0.048	92.15	0.0617	92.5
	C3	0.0864	92.6	0.0853	95.29	0.116	91.03	0.159	90.89
	C4	0.0805	89.9	0.0689	90.31	0.0658	93.54	0.09	89.52
	C5	0.0826	90.36	0.0704	90.42	0.0655	93.8	0.0799	93.8

$$C2 = 1.82 - 4582 * C1$$

$$R \text{ SQUARE} = 90.0\%$$

K VALUE AND R SQUARE DATA FOR 3/2'RD ORDER AND "HCCMF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384(S)	
		K	R	K	R	K	R	K	R
400	C2	0.0125	97.18	0.0153	95.36	0.0187	94.93	0.0233	94.52
	C3	0.0112	98.48	0.0113	99.23	0.0116	99.47	0.0136	97.33
	C4	0.0097	98.53	0.00955	99.19	0.0097	99.55	0.0107	98.63
	C5	0.0124	98.39	0.0121	99.08	0.0122	99.51	0.0138	98.21
458	C2	0.0117	98.12	0.0124	98.83	0.013	99.2	0.0145	98.37
	C3	0.0149	97.24	0.0168	97.45	0.0192	97.37	0.0224	96.44
	C4	0.0134	98.68	0.0139	99.2	0.0147	99.31	0.0169	97.77
	C5	0.0148	98.83	0.0152	99.36	0.0158	99.53	0.0177	98.27
542	C2	0.0216	96.45	0.0198	96.51	0.0178	97.05	0.0179	98.36
	C3	0.0262	96.53	0.0245	97.03	0.0224	97.68	0.0229	98.58
	C4	0.0313	96.66	0.0303	97.72	0.0278	98.32	0.0294	98.52
	C5	0.0295	96.43	0.0283	97.44	0.0261	98.18	0.0277	98.56
625	C2	0.042	92.19	0.0356	91.49	0.0313	92.32	0.0294	95.05
	C3	0.0452	92.05	0.0384	91.41	0.0341	92.71	0.0329	95.78
	C4	0.0473	93.38	0.0415	93.72	0.0378	95.05	0.0372	97.23
	C5	0.0518	93.5	0.0456	93.85	0.0419	95.38	0.0428	97.44
765	C2	0.0595	87.44	0.0567	88.86	0.0512	91.56	0.0524	95.52
	C3	0.0675	89.18	0.0485	86.14	0.0415	87.4	0.0393	92.17
	C4	0.0661	89.65	0.0548	88.47	0.0473	89.46	0.0448	93.46
	C5	0.0702	89.93	0.0585	88.93	0.0506	89.9	0.0471	93.41
805	C2	0.0504	89.14	0.0432	90.05	0.0408	93.62	0.0484	93.64
	C3	0.0477	86.37	0.0389	85.1	0.0337	87.34	0.0332	92.78
	C4	0.0537	86.16	0.0433	84.27	0.0369	85.86	0.0351	91.29
	C5	0.0564	87.27	0.0458	85.6	0.0393	87.09	0.038	92.33

$$C2 = -0.322 - 2775 * C1$$

$$R \text{ SQUARE} = 93.5\%$$

K VALUE AND R SQUARE FOR 2'ND ORDER AND "MF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384 S)	
		K	R	K	R	K	R	K	R
400	C2								
	C3								
	C4								
	C5								
458	C2								
	C3	0.0121	96.16	0.0143	96.05	0.0178	94.31	0.0249	89.96
	C4	0.0128	95.5	0.0152	95.54	0.0187	94.65	0.0288	85.76
	C5	0.0163	98.86	0.0181	98.49	0.0208	97.31	0.0318	85.99
542	C2	0.0196	97.68	0.0192	98.71	0.0194	99.32	0.0206	99.26
	C3	0.0361	96.17	0.0355	97.92	0.0369	98.76	0.0451	94.94
	C4	0.0431	97.03	0.0417	98.32	0.0417	99.09	0.0454	98.35
	C5	0.0594	94.86	0.0638	97.09	0.0736	96.72	0.0961	92.35
625	C2	0.0265	98.66	0.0289	98.43	0.0344	96.49	0.0474	90.52
	C3	0.0281	94.26	0.0259	95.79	0.026	97.71	0.0343	91.06
	C4	0.0345	92.77	0.0317	94.73	0.0316	97.1	0.0426	90.05
	C5	0.0286	93.48	0.0257	94.6	0.0252	96.9	0.0316	93.07
765	C2	0.0546	95.05	0.0482	95.06	0.0452	96.58	0.0463	98.2
	C3	0.0629	86.55	0.05	89.82	0.0442	87.27	0.0476	92.93
	C4	0.0519	98.36	0.0488	98.64	0.0482	99.23	0.0502	99.47
	C5	0.0483	97.76	0.0439	97.61	0.042	98.42	0.0451	98.32
805	C2	0.0387	92.74	0.0334	92.73	0.031	94.87	0.035	95.12
	C3	0.0635	91.55	0.0533	90.48	0.0467	91.56	0.052	92.89
	C4	0.0742	93.09	0.0608	90.37	0.0524	90.75	0.0569	94.03
	C5	0.093	96.12	0.0857	96.93	0.0821	98.04	0.0953	95.75

$$C3 = -0.043 - 3133 * C1$$

$$R \text{ SQUARE} = 97.8\%$$

K VALUE AND R SQUARE FOR 2ND ORDER AND "CHF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384(S)	
		K	R	K	R	K	R	K	R
400	C2	0.0151	95.66	0.0157	99.41	0.0166	99.32	0.0215	93.24
	C3	0.0158	98.9	0.0101	99.03	0.0163	98.12	0.0161	89.36
	C4	0.00968	98.4	0.0176	96.16	0.0219	94.3	0.0353	83.78
	C5	0.0184	96.58	0.0206	97.31	0.0242	96.56	0.0349	88.63
458	C2	0.00958	96.56	0.0101	96.66	0.0124	94.44	0.0217	80.57
	C3	0.00864	97	0.0111	96.63	0.0133	95.1	0.0203	87.21
	C4	0.0125	95.55	0.015	95.37	0.0192	92.67	0.0245	92.83
	C5	0.0142	98.6	0.0155	98.55	0.0177	97.4	0.0262	87.53
542	C2	0.0732	97.43	0.0714	98.54	0.0883	92.98	0.0319	57.7
	C3	0.0387	97.15	0.0365	97.36	0.0375	98.75	0.0515	89.6
	C4	0.0277	96.47	0.0984	94.43	0.0129	91.59	0.0248	76.81
	C5	0.0836	93.21	0.0268	97.91	0.0264	98.86	0.0303	96.99
625	C2	0.0141	93.89	0.0359	93.91	0.0338	95.91	0.0392	95.41
	C3	0.0977	96.88	0.0915	96.93	0.0902	98.31	0.104	96.39
	C4	0.109	95.74	0.102	98.33	0.11	98.42	0.142	92.78
	C5	0.0974	95.49	0.102	96.96	0.0989	98.22	0.108	98.13
765	C2	0.102	94.79	0.113	92.77	0.102	94.93	0.1	96.93
	C3	0.13	92.42	0.0914	95.32	0.0906	97.48	0.123	86.52
	C4	0.245	97.71	0.158	94.39	0.151	96.91	0.174	95.75
	C5	0.177	93.47	0.261	98.49	0.3	97.82	0.373	93.33
805	C2	0.126	94.09	0.114	95.26	0.111	97.23	0.135	94.58
	C3	0.125	94.03	0.111	94.54	0.104	96.36	0.121	94.97
	C4	0.0188	89.95	0.0164	91.61	0.0156	94.46	0.0181	95.14
	C5	0.0476	89.49	0.04	89.13	0.0367	92.24	0.0416	94.39

C2 = 4.14 - 5901 *C1

R SQUARE = 94.1%

K VALUE AND R SQUARE DATA FOR 2'ND ORDER AND "HCHF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384 S)	
		K	R	K	R	K	R	K	R
400	C2	0.0486	89.85	0.0635	91.2	0.0896	88.94	0.0238	58.66
	C3	0.0202	96.92	0.0274	91.69	0.0374	90.11	0.0985	56.39
	C4	0.0175	87.88	0.0213	95.32	0.0303	89.67	0.0436	88.48
	C5	0.0333	89.27	0.0504	87.2	0.0645	90.98	0.0116	76.66
458	C2	0.0133	99.02	0.0142	99.11	0.0157	98.56	0.0205	93.08
	C3	0.012	97.48	0.0133	98.02	0.015	97.76	0.0195	92.94
	C4	0.016	94.9	0.0198	94.29	0.0171	90.2	0.0555	76.02
	C5	0.0173	96.67	0.0212	95.13	0.0306	87.56	0.069	73.41
542	C2	0.0348	97.21	0.0333	98.25	0.0334	99.03	0.0416	94.05
	C3	0.0472	97.56	0.0451	98.41	0.0459	99.11	0.0573	94.26
	C4	0.0279	99.03	0.0269	99.45	0.0249	98.89	0.023	98.56
	C5	0.0515	96.59	0.0521	98.25	0.0558	98.63	0.077	89.66
625	C2	0.661	82.58	0.936	86.98	1.3	88.57	1.44	94.14
	C3	0.106	95.66	0.106	97.58	0.13	94.14	0.199	85.9
	C4	0.164	97.36	0.21	91.1	0.333	84.85	0.562	82.38
	C5	0.132	96.73	0.144	97.12	0.209	88.86	0.367	80.05
765	C2	1.26	66.73	7.04	55.1	8.83	75.96	8.4	84.73
	C3	0.408	92.46	0.719	81.55	1.38	73.16	4.38	65.37
	C4	0.202	95.59	0.199	98.82	0.231	94.9	0.395	81.76
	C5	0.182	94.89	0.175	96.82	0.187	97.24	0.343	79.54
805	C2	0.126	93.03	0.12	95.69	0.146	96.34	0.3693	69.22
	C3	0.231	98	0.317	86.59	0.882	64.31	2.31	69.14
	C4	0.203	96.2	0.208	98.05	0.245	94.36	0.57	68.63
	C5	0.211	96.55	0.201	97.87	0.245	95.76	0.779	59.19

$$C2 = 4.52 - 6304 * C1$$

$$R \text{ SQUARE} = 92.1\%$$

K VALUE AND R SQUARE DATA FOR 2ND ORDER AND "HCCMF" SAMPLE

TEMP (C)	SAMPLE	128(S)		192(S)		256(S)		384(S)	
		K	R	K	R	K	R	K	R
400	C2	0.0202	94.46	0.0291	93.24	0.0434	86.59	0.0734	82.91
	C3	0.0174	98.02	0.0188	98.51	0.0214	97.59	0.0314	88.17
	C4	0.0147	98.37	0.0154	99.01	0.0169	98.54	0.0222	93.03
	C5	0.0196	98.17	0.0205	98.9	0.0227	98.37	0.0316	90.43
458	C2	0.0172	96.54	0.02	96.58	0.0417	90.4	0.0652	83.39
	C3	0.0233	94.51	0.0304	92.28	0.0235	96.31	0.0324	90.47
	C4	0.0201	97.26	0.0232	97	0.0278	95.81	0.0411	87.55
	C5	0.0226	97.51	0.0258	97.35	0.0305	96.4	0.0437	88.48
542	C2	0.035	97.84	0.0337	98.66	0.0342	99.25	0.042	95.03
	C3	0.0456	97.14	0.0452	98.49	0.0475	98.96	0.0618	92.6
	C4	0.0586	96.14	0.0611	97.97	0.0663	98.33	0.0937	86.56
	C5	0.054	96.31	0.0555	98.11	0.0603	98.33	0.085	88.68
625	C2	0.0821	96.29	0.0763	97.22	0.0747	98.41	0.0861	96.66
	C3	0.0913	96.26	0.0852	97.27	0.0855	98.5	0.105	95.04
	C4	0.0994	96.62	0.0977	98.14	0.102	98.83	0.131	93.23
	C5	0.113	96.8	0.112	98.28	0.121	98.58	0.169	89.4
765	C2	0.159	95.63	0.151	97.12	0.162	97.89	0.237	87.66
	C3	0.132	93.27	0.118	94.06	0.113	96.34	0.138	93.43
	C4	0.156	95.27	0.143	96.28	0.14	97.85	0.172	94.03
	C5	0.171	95.6	0.159	96.74	0.156	98.17	0.186	95.22
805	C2	0.103	94.74	0.1	96.9	0.115	96.42	0.232	70.46
	C3	0.0951	91.49	0.0839	92.65	0.082	95.72	0.106	91.28
	C4	0.112	91.82	0.0978	92.41	0.0932	95.24	0.114	93.26
	C5	0.121	92.8	0.107	93.54	0.103	96.05	0.132	91.49

$$C2 = 2.09 - 4082 * C1$$

$$R \text{ SQUARE} = 95.0\%$$

APPENDIX C. CONVERSION EXPERIMENT DATA

APPENDIX C: CONVERSION EXPERIMENT DATA

Table A: Total Carbon Analysis of CMF Sample

TEMPERATU	XA	XB	XC	XD
805	5.9336	6.1245	6.1472	6.7855
765	6.2484	6.186	6.6864	6.2688
625	6.8597	6.6132	6.5536	6.2446
542	7.543	7.3403	7.0964	6.9441
458	7.6662	7.4524	7.4462	7.0208
430	8.704	8.0774	8.8577	7.6559
400	15.1581	19.6587	13.8473	18.9225
370	25.1244	25.1184	10.0885	12.1315

Table B: Total Carbon Analysis of MF Sample

TEMPERATU	XA	XB	XC	XD	XE	XF
805	4.2702	2.5976	4.0089	3.4337	3.4938	
765	3.8882	3.4614	4.6359	3.8788	1.5111	2.1059
625	6.1696	6.1223	6.1079	5.2436	3.4611	
542	6.034	6.0383	7.8196	8.9898	3.9622	4.6061
458	8.08463	8.0627	10.2997	9.9635	7.2304	
430	11.0839	10.8998	10.757	11.1147		
400	13.5221	13.692	13.0109	12.0369	12.9294	
370	21.5292	22.4749	22.5189	21.0866		

Table C: Total Carbon Analysis of HCMF Sample

TEMPERATU	XA	XB	XC	XD	XE
805	4.8752	4.8755	5.1337	5.0511	
765	5.2965	5.4456	5.7664	6.0504	
625	6.0558	6.0081	5.9831	5.8886	
542	6.2384	5.7051	6.0239	6.196	
458	6.9799	6.6835	6.6	6.734	
425	8.0833	7.8359	7.6351	7.4635	
400	11.9348	12.2943	11.7255	12.3984	
370	19.6419	26.0467	19.5181	26.1477	17.8182

Table D: Total Carbon Analysis of HCCMF Sample

TEMPERATU	XA	XB	XC	XD
805	9.3437	9.3102	8.8765	8.9006
765	9.4096	9.4574	9.3778	9.4767
625	9.6239			
542	9.6045	9.7623	9.8851	
458	9.9554	9.8402	9.9951	9.8663
425	10.0602	8.7395	10.2942	
400	14.033	13.7478	13.7188	13.3571
372	26.1319	26.2385	24.7234	

Table E: Inorganic Carbon Analysis of MF Sample

TEMPERATU	XA	XB	XC	XD	XE	X(AVG)
805	0	0.3796	0.2086			0.1961
765	0	0	0.7156	0.532		0.3119
625	1.7764	1.3066	1.4268	1.9868	1.188	1.5369
542	4.1453	4.6089	4.1009	4.0949		4.2375
458	5.0768	4.5962	4.4878	5.2064	5.115	4.8964
425	4.7217	5.0842	5.296	4.653	4.3445	4.8199
400	4.3204	5.0345	4.2087	4.6409	4.4766	4.5364
372	4.0127	4.1351	4.1824	4.2423		4.1431
350	4.0256	3.8329	4.1511	4.023	4.2664	4.0598

APPENDIX D. EXAMPLE OF MINI-TAB

MTB > PAPER

MTB > READ THCCMF625.DAT C1-C5

73 ROWS READ

ROW	C1	C2	C3	C4	C5
1	0.64	0.0000	0.0000	0.0000	0.0000
2	3.84	0.0003	0.0004	0.0004	0.0001
3	7.04	0.0006	0.0007	0.0006	0.0001
4	10.24	0.0111	0.0044	0.0011	0.0011

MTB > LET C2=C2/(0.7104*(0.7104-C2))

MTB > LET C3=C3/(0.7104*(0.7104-C3))

MTB > LET C4=C4/(0.7104*(0.7104-C4))

MTB > LET C5=C5/(0.7104*(0.7104-C5))

MTB > PRINT C1 C2 C3 C4 C5

ROW	C1	C2	C3	C4	C5
1	0.64	0.0000	0.0000	0.0000	0.0000
2	3.84	0.0006	0.0008	0.0008	0.0002
3	7.04	0.0012	0.0014	0.0012	0.0002
4	10.24	0.0223	0.0088	0.0022	0.0022
5	10.88	0.0412	0.0179	0.0032	0.0048
6	11.52	0.0686	0.0316	0.0050	0.0092
7	12.16	0.1036	0.0516	0.0084	0.0162
8	12.80	0.1463	0.0798	0.0140	0.0264
9	13.44	0.1964	0.1167	0.0228	0.0408
10	14.08	0.2551	0.1704	0.0358	0.0612
11	14.72	0.3245	0.2387	0.0554	0.0891
12	15.36	0.4069	0.3263	0.0835	0.1275
13	16.00	0.5059	0.4363	0.1235	0.1789
14	16.64	0.6249	0.5706	0.1781	0.2461
15	17.28	0.7648	0.7303	0.2510	0.3318
16	17.92	0.9261	0.9141	0.3443	0.4391
17	18.56	1.1055	1.1189	0.4601	0.5702
18	19.20	1.2987	1.3404	0.6004	0.7259
19	19.84	1.5010	1.5694	0.7648	0.9077
20	20.48	1.7028	1.8016	0.9531	1.1138

Continue?

21	21.12	1.9003	2.0276	1.1617	1.3419
22	21.76	2.0864	2.2420	1.3872	1.5281
23	22.40	2.2594	2.4400	1.6236	1.8465
24	23.04	2.4179	2.6214	1.8646	2.1110
25	23.68	2.5590	2.7835	2.1011	2.3745
26	24.32	2.6873	2.9307	2.3321	2.6295
27	24.96	2.8011	3.0606	2.5496	2.8732
28	25.60	2.9008	3.1795	2.7521	3.1009
29	26.24	2.9918	3.2850	2.9402	3.3115
30	26.88	3.0766	3.3816	3.1091	3.5039
31	27.52	3.1544	3.4704	3.2631	3.6788
32	28.16	3.2263	3.5527	3.4070	3.8417
33	28.80	3.2960	3.6301	3.5355	3.9890
34	29.44	3.3611	3.7022	3.6531	4.1264
35	30.08	3.4233	3.7737	3.7630	4.2485
36	30.72	3.4823	3.8417	3.8694	4.3660
37	31.36	3.5428	3.9058	3.9658	4.4747
38	32.00	3.5973	3.9687	4.0538	4.5768
39	32.64	3.6505	4.0301	4.1417	4.6751
40	33.28	3.7022	4.0929	4.2230	4.7690
41	33.92	3.7496	4.1510	4.3001	4.8580
42	34.56	3.7980	4.2072	4.3760	4.9415
43	35.20	3.8472	4.2645	4.4506	5.0273
Continue?					
44	35.84	3.8946	4.3164	4.5235	5.1070
45	36.48	3.9428	4.3693	4.5947	5.1843
46	37.12	3.9890	4.4198	4.6603	5.2590
47	37.76	4.0360	4.4712	4.7311	5.3354
48	38.40	4.0808	4.5235	4.7958	5.4090
49	39.04	4.1264	4.5768	4.8580	5.4841
50	39.68	4.1741	4.6301	4.9230	5.5615
51	40.32	4.2233	4.6845	4.9900	5.6415
52	40.96	4.2740	4.7399	5.0590	5.7235
53	41.60	4.3263	4.7964	5.1300	5.8075
54	42.24	4.3801	4.8539	5.2030	5.8935
55	42.88	4.4354	4.9124	5.2780	5.9815
56	43.52	4.4923	4.9719	5.3550	6.0715
57	44.16	4.5508	5.0324	5.4340	6.1635
58	44.80	4.6109	5.0939	5.5150	6.2575
59	45.44	4.6726	5.1564	5.5980	6.3535
60	46.08	4.7359	5.2209	5.6830	6.4515
61	46.72	4.8008	5.2874	5.7700	6.5515
62	47.36	4.8673	5.3559	5.8590	6.6535
63	48.00	4.9354	5.4264	5.9500	6.7575
64	48.64	5.0051	5.4989	6.0430	6.8635
65	49.28	5.0764	5.5734	6.1380	6.9715
66	49.92	5.1493	5.6499	6.2350	7.0815
67	50.56	5.2238	5.7284	6.3340	7.1935
68	51.20	5.2999	5.8089	6.4350	7.3075
69	51.84	5.3776	5.8914	6.5380	7.4235
70	52.48	5.4569	5.9759	6.6430	7.5415
71	53.12	5.5378	6.0624	6.7500	7.6615
72	53.76	5.6193	6.1509	6.8590	7.7835
73	54.40	5.7024	6.2414	6.9700	7.9075
74	55.04	5.7871	6.3339	7.0830	8.0335
75	55.68	5.8734	6.4284	7.1980	8.1615
76	56.32	5.9613	6.5249	7.3150	8.2915
77	56.96	6.0508	6.6234	7.4340	8.4235
78	57.60	6.1419	6.7239	7.5550	8.5575
79	58.24	6.2346	6.8264	7.6780	8.6935
80	58.88	6.3289	6.9309	7.8030	8.8315
81	59.52	6.4248	7.0374	7.9300	8.9715
82	60.16	6.5223	7.1459	8.0590	9.1135
83	60.80	6.6214	7.2564	8.1900	9.2575
84	61.44	6.7221	7.3689	8.3230	9.4035
85	62.08	6.8244	7.4834	8.4580	9.5515
86	62.72	6.9283	7.5999	8.5950	9.7015
87	63.36	7.0338	7.7184	8.7340	9.8535
88	64.00	7.1409	7.8389	8.8750	10.0075
89	64.64	7.2496	7.9614	9.0180	10.1635
90	65.28	7.3599	8.0859	9.1630	10.3215
91	65.92	7.4718	8.2124	9.3100	10.4815
92	66.56	7.5853	8.3409	9.4590	10.6435
93	67.20	7.7004	8.4714	9.6100	10.8075
94	67.84	7.8171	8.6039	9.7630	10.9735
95	68.48	7.9354	8.7384	9.9180	11.1415
96	69.12	8.0553	8.8749	10.0750	11.3115
97	69.76	8.1768	9.0134	10.2340	11.4835
98	70.40	8.2999	9.1539	10.3950	11.6575
99	71.04	8.4246	9.2964	10.5580	11.8335
100	71.68	8.5509	9.4409	10.7230	12.0115
101	72.32	8.6788	9.5874	10.8900	12.1915
102	72.96	8.8083	9.7359	11.0590	12.3735
103	73.60	8.9394	9.8864	11.2300	12.5575
104	74.24	9.0721	10.0389	11.4030	12.7435
105	74.88	9.2064	10.1934	11.5780	12.9315
106	75.52	9.3423	10.3499	11.7550	13.1215
107	76.16	9.4798	10.5084	11.9340	13.3135
108	76.80	9.6189	10.6689	12.1150	13.5075
109	77.44	9.7596	10.8314	12.2980	13.7035
110	78.08	9.9019	10.9959	12.4830	13.9015
111	78.72	10.0458	11.1624	12.6700	14.1015
112	79.36	10.1913	11.3309	12.8590	14.3035
113	80.00	10.3384	11.4994	13.0500	14.5075
114	80.64	10.4871	11.6699	13.2430	14.7135
115	81.28	10.6374	11.8414	13.4380	14.9215
116	81.92	10.7893	12.0139	13.6350	15.1315
117	82.56	10.9428	12.1874	13.8340	15.3435
118	83.20	11.0979	12.3629	14.0350	15.5575
119	83.84	11.2546	12.5394	14.2380	15.7735
120	84.48	11.4129	12.7169	14.4430	15.9915
121	85.12	11.5728	12.8954	14.6500	16.2115
122	85.76	11.7343	13.0759	14.8590	16.4335
123	86.40	11.8974	13.2584	15.0700	16.6575
124	87.04	12.0621	13.4429	15.2830	16.8835
125	87.68	12.2284	13.6294	15.4980	17.1115
126	88.32	12.3963	13.8179	15.7150	17.3415
127	88.96	12.5658	14.0084	15.9340	17.5735
128	89.60	12.7369	14.2009	16.1550	17.8075
129	90.24	12.9096	14.3954	16.3780	18.0435
130	90.88	13.0839	14.5919	16.6030	18.2815
131	91.52	13.2598	14.7904	16.8300	18.5215
132	92.16	13.4373	14.9909	17.0590	18.7635
133	92.80	13.6164	15.1934	17.2900	19.0075
134	93.44	13.7971	15.3979	17.5230	19.2535
135	94.08	13.9794	15.6044	17.7580	19.5015
136	94.72	14.1633	15.8129	17.9950	19.7515
137	95.36	14.3488	16.0234	18.2340	20.0035
138	96.00	14.5359	16.2359	18.4750	20.2575
139	96.64	14.7246	16.4494	18.7180	20.5135
140	97.28	14.9149	16.6649	18.9630	20.7715
141	97.92	15.1068	16.8824	19.2100	21.0315
142	98.56	15.2993	17.1019	19.4590	21.2935
143	99.20	15.4934	17.3234	19.7100	21.5575
144	99.84	15.6891	17.5469	19.9630	21.8235
145	100.48	15.8864	17.7724	20.2180	22.0915
146	101.12	16.0853	18.0009	20.4750	22.3615
147	101.76	16.2858	18.2314	20.7340	22.6335
148	102.40	16.4879	18.4639	20.9950	22.9075
149	103.04	16.6916	18.6984	21.2580	23.1835
150	103.68	16.8969	18.9349	21.5230	23.4615
151	104.32	17.1038	19.1734	21.7900	23.7415
152	104.96	17.3123	19.4139	22.0590	24.0235
153	105.60	17.5224	19.6564	22.3300	24.3075
154	106.24	17.7341	19.9009	22.6030	24.5935
155	106.88	17.9474	20.1474	22.8780	24.8815
156	107.52	18.1623	20.3959	23.1550	25.1715
157	108.16	18.3788	20.6464	23.4340	25.4635
158	108.80	18.5969	20.8989	23.7150	25.7575
159	109.44	18.8166	21.1534	23.9980	26.0535
160	110.08	19.0379	21.4099	24.2830	26.3515
161	110.72	19.2608	21.6684	24.5700	26.6515
162	111.36	19.4853	21.9289	24.8590	26.9535
163	112.00	19.7114	22.1914	25.1500	27.2575
164	112.64	19.9391	22.4559	25.4430	27.5635
165	113.28	20.1684	22.7224	25.7380	27.8715
166	113.92	20.3993	22.9909	26.0350	28.1815
167	114.56	20.6318	23.2614	26.3340	28.4935
168	115.20	20.8659	23.5339	26.6350	28.8075
169	115.84	21.1016	23.8084	26.9380	29.1235
170	116.48	21.3389	24.0849	27.2430	29.4415
171	117.12	21.5778	24.3634	27.5500	29.7615
172	117.76	21.8183	24.6439	27.8590	30.0835
173	118.40	22.0604	24.9264	28.1700	30.4075
174	119.04	22.3041	25.2109	28.4830	30.7335
175	119.68	22.5494	25.4974	28.7980	31.0615
176	120.32	22.7963	25.7859	29.1150	31.3915
177	120.96	23.0448	26.0764	29.4340	31.7235
178	121.60	23.2949	26.3689	29.7550	32.0575
179	122.24	23.5466	26.6634	30.0780	32.3935
180	122.88	23.7999	26.9599	30.4030	32.7315
181	123.52	24.0548	27.2584	30.7300	33.0715
182	124.16	24.3113	27.5589	31.0590	33.4135
183	124.80	24.5694	27.8614	31.3900	33.7575
184	125.44	24.8291	28.1659	31.7230	34.1035
185	126.08	25.0904	28.4724	32.0580	34.4515
186	126.72	25.3533	28.7809	32.3950	34.8015
187	127.36	25.6178	29.0914	32.7340	35.1535
188	128.00	25.8839	29.4039	33.0750	35.5075
189	128.64	26.1516	29.7184	33.4180	35.8635
190	129.28	26.4209	30.0349	33.7630	36.2215
191	129.92	26.6918	30.3534	34.1100	36.5815
192	130.56	26.9643	30.6739	34.4590	36.9435
193	131.20	27.2384	30.9964	34.8100	37.3075
194	131.84	27.5141	31.3209	35.1630	37.6735
195	132.48	27.7914	31.6474	35.5180	38.0415
196	133.12	28.0703	31.9759	35.8750	38.4115
197	133.76	28.3508	32.3064	36.2340	38.7835
198	134.40	28.6329			

67	179.84	12.5979	14.1687	17.3893	20.1906
68	192.64	13.5400	15.3148	19.0008	22.1772
69	205.44	14.5413	16.6429	20.7162	24.4321
70	218.24	15.5992	18.0476	22.6887	26.9210
71	231.04	16.7412	19.6008	24.4991	29.4565
72	243.84	17.9722	21.3196	26.6036	32.3762
73	256.64	19.2963	23.2837	28.8954	35.6294

MTB > NOCONST

MTB > REGRESS C2 1 C1 IN C6 C7

The regression equation is
C2 = 0.0747 C1

Predictor	Coef.	Stdev	t-ratio
Noconstant			
C1	0.074715	0.001121	66.66

s = 0.8360

Analysis of Variance

SOURCE	DF	SS	MS
Regression	1	3105.9	3105.9
Error	72	50.3	0.7
Total	73	3156.2	

Unusual Observations

Obs.	C1	C2	Fit	Stdev.Fit	Residual	St.Resid
65	154	10.8774	11.5240	0.1729	-0.6467	-0.79 X
66	167	11.7329	12.4804	0.1872	-0.7474	-0.92 X
67	180	12.5979	13.4367	0.2016	-0.8388	-1.03 X
68	193	13.5400	14.3931	0.2159	-0.8531	-1.06 X
Continue?						
69	205	14.5413	15.3494	0.2303	-0.8081	-1.01 X
70	218	15.5992	16.3058	0.2446	-0.7066	-0.88 X
71	231	16.7412	17.2621	0.2590	-0.5210	-0.66 X
72	244	17.9722	18.2185	0.2733	-0.2463	-0.31 X
73	257	19.2963	19.1748	0.2877	0.1215	0.15 X

X denotes an obs. whose X value gives it large influence.

REGRESS C3 1 C1 IN C8 C9

The regression equation is
 C3 = 0.0855 C1

Predictor	Coef	Stdev	t-ratio
Nonconstant			
C1	0.085525	0.001243	68.79

s = 0.9273

Analysis of Variance

SOURCE	DF	SS	MS
Regression	1	4069.6	4069.6
Error	72	61.9	0.9
Total	73	4131.5	

Unusual Observations

Obs.	C1	C3	Fit	Stdev.Fit	Residual	St.Resid
65	164	12.088	13.191	0.192	-1.104	-1.25 X
66	167	13.085	14.286	0.208	-1.201	-1.33 X
67	180	14.169	15.381	0.224	-1.212	-1.35 X
68	193	15.315	16.475	0.239	-1.161	-1.30 X
Continue?						
69	205	16.643	17.570	0.255	-0.927	-1.04 X
70	218	18.048	18.665	0.271	-0.617	-0.70 X
71	231	19.601	19.760	0.287	-0.159	-0.18 X
72	244	21.320	20.854	0.303	0.465	0.53 X
73	257	23.284	21.949	0.319	1.335	1.53 X

X denotes an obs. whose X value gives it large influence.

MTB >

REGRESS VC4 I C1 IN C10 C11

The regression equation is
 $C4 = 0.102 C1$

Predictor	Coef	Stdev	t-ratio
Noconstant			
C1	0.102261	0.001311	78.02

s = 0.9777

Analysis of Variance

SOURCE	DF	SS	MS
Regression	1	5818.2	5818.2
Error	72	48.8	1.0
Total	73	5887.0	

Unusual Observations

Obs.	C1	C4	Fit	Stdev.Fit	Residual	St.Resid
65	154	14.465	15.773	0.202	-1.307	-1.37 X
66	167	15.893	17.082	0.219	1.188	-1.25 X
67	180	17.389	18.391	0.236	-1.001	-1.06 X
68	193	19.001	19.699	0.253	-0.699	-0.74 X
Continue?						
69	205	20.716	21.008	0.269	-0.292	-0.31 X
70	218	22.689	22.317	0.286	0.371	0.40 X
71	231	24.499	23.626	0.303	0.873	0.94 X
72	244	26.604	24.935	0.320	1.668	1.81 X
73	257	28.895	26.244	0.336	2.651	2.89RX

R denotes an obs. with a large st. resid.

X denotes an obs. whose X value gives it large influence.

MTB >

REGRESS C5 1 C1 IN C12 C13

The regression equation is
 C5 = 0.121 C1

Predictor	Coef	Stdev	t-ratio
Noconstant			
C1	0.120603	0.001706	70.70

s = 1.272

Analysis of Variance

SOURCE	DF	SS	MS
Regression	1	8092.6	8092.6
Error	72	116.6	1.6
Total	73	8209.2	

Unusual Observations

Obs.	C1	C5	Fit	Stdev.Fit	Residual	St.Resid
65	154	16.774	18.602	0.263	-1.828	-1.47 X
66	167	18.394	20.146	0.285	-1.751	-1.41 X
67	180	20.191	21.689	0.307	-1.499	-1.21 X
68	193	22.177	23.233	0.329	-1.056	-0.86 X
Continue?						
69	205	24.432	24.777	0.350	-0.345	-0.28 X
70	218	26.921	26.320	0.372	0.601	0.49 X
71	231	29.457	27.864	0.394	1.592	1.32 X
72	244	32.376	29.408	0.416	2.968	2.47RX
73	257	35.629	30.952	0.438	4.678	3.92RX

R denotes an obs. with a large st. resid.

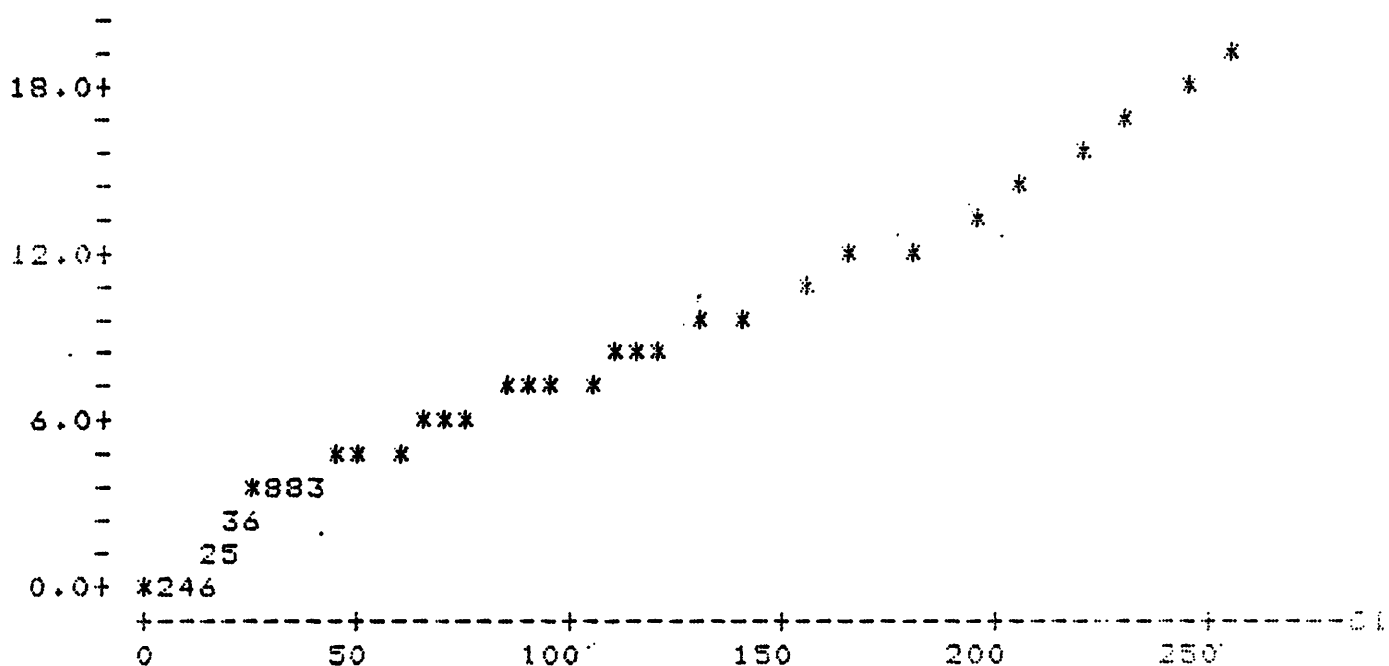
X denotes an obs. whose X value gives it large influence.

MTB >

PLOT C2 V SCI

Continue?

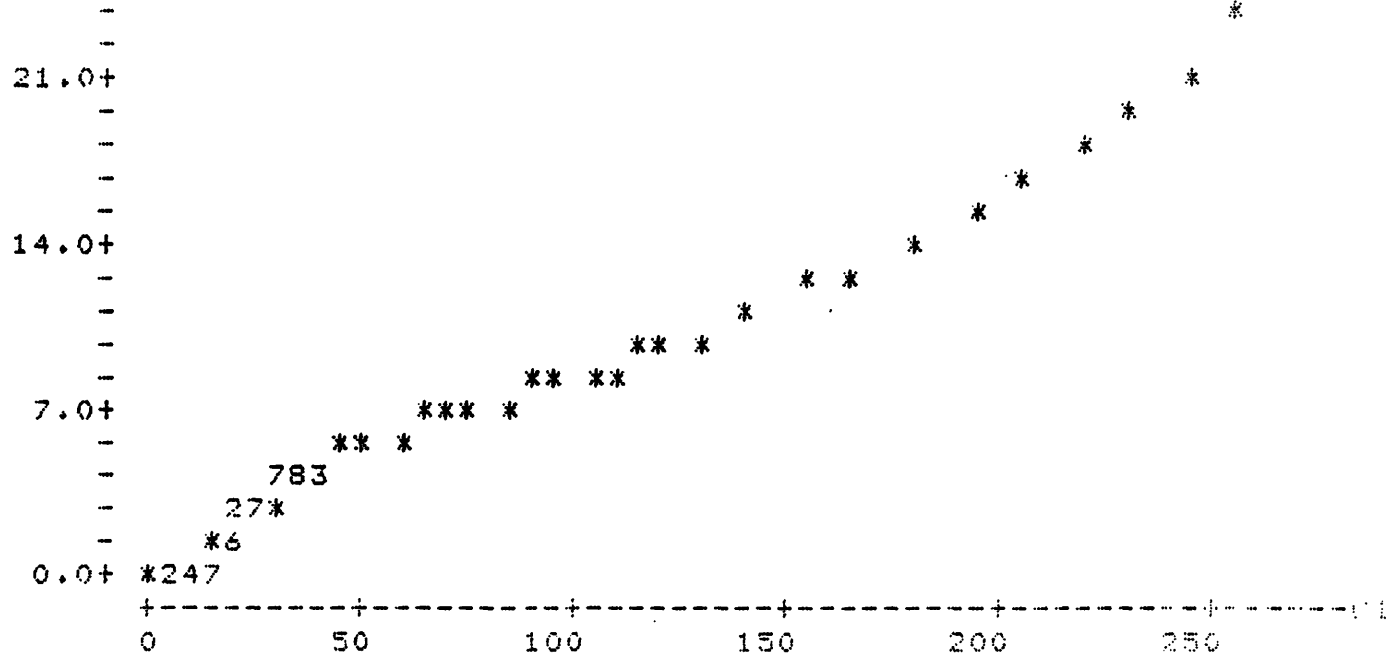
C2



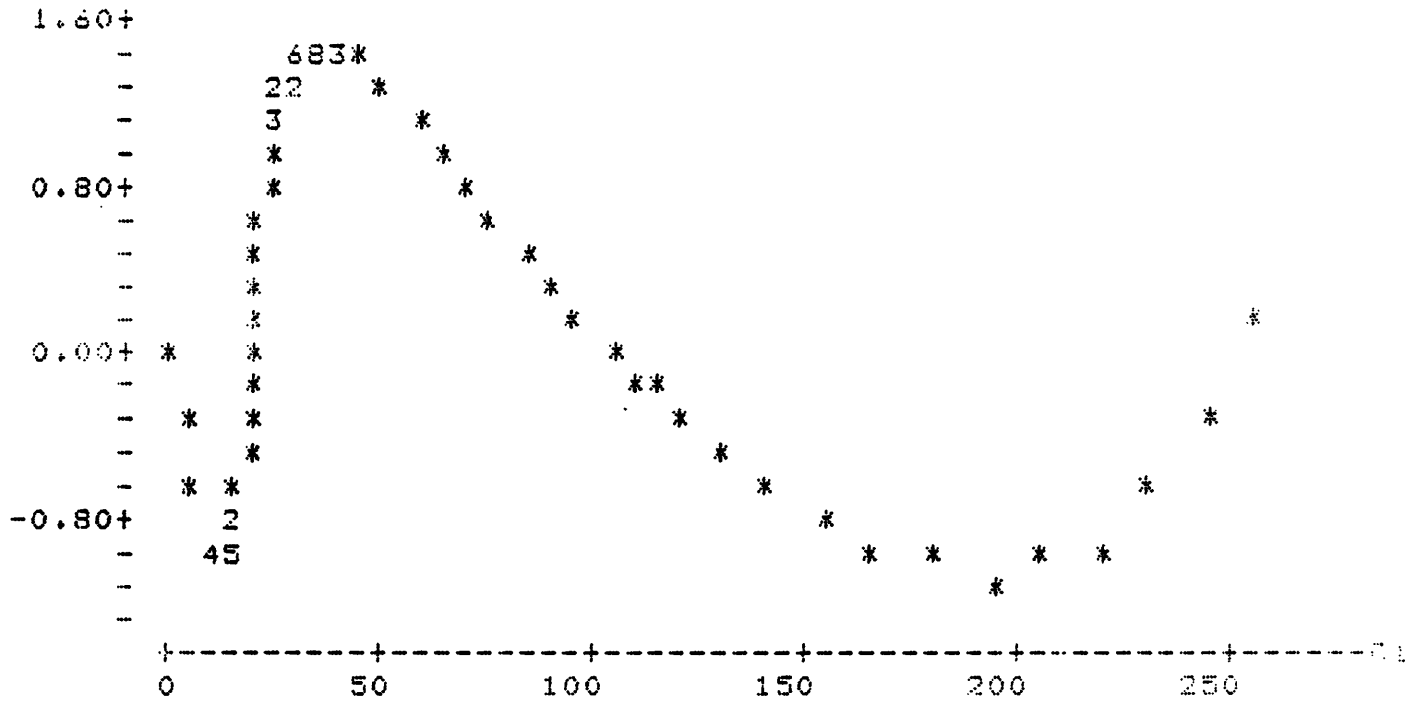
MTB > PLOT C3 VS C1

Continue?

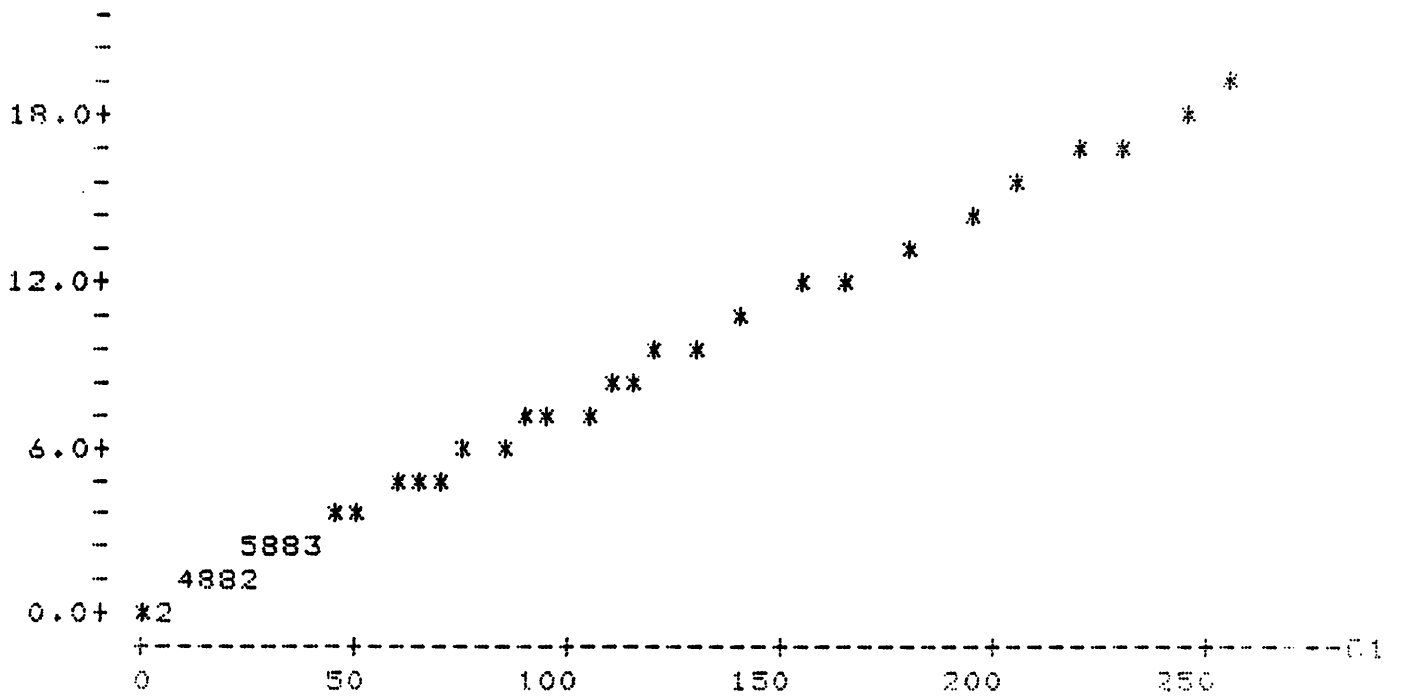
C3



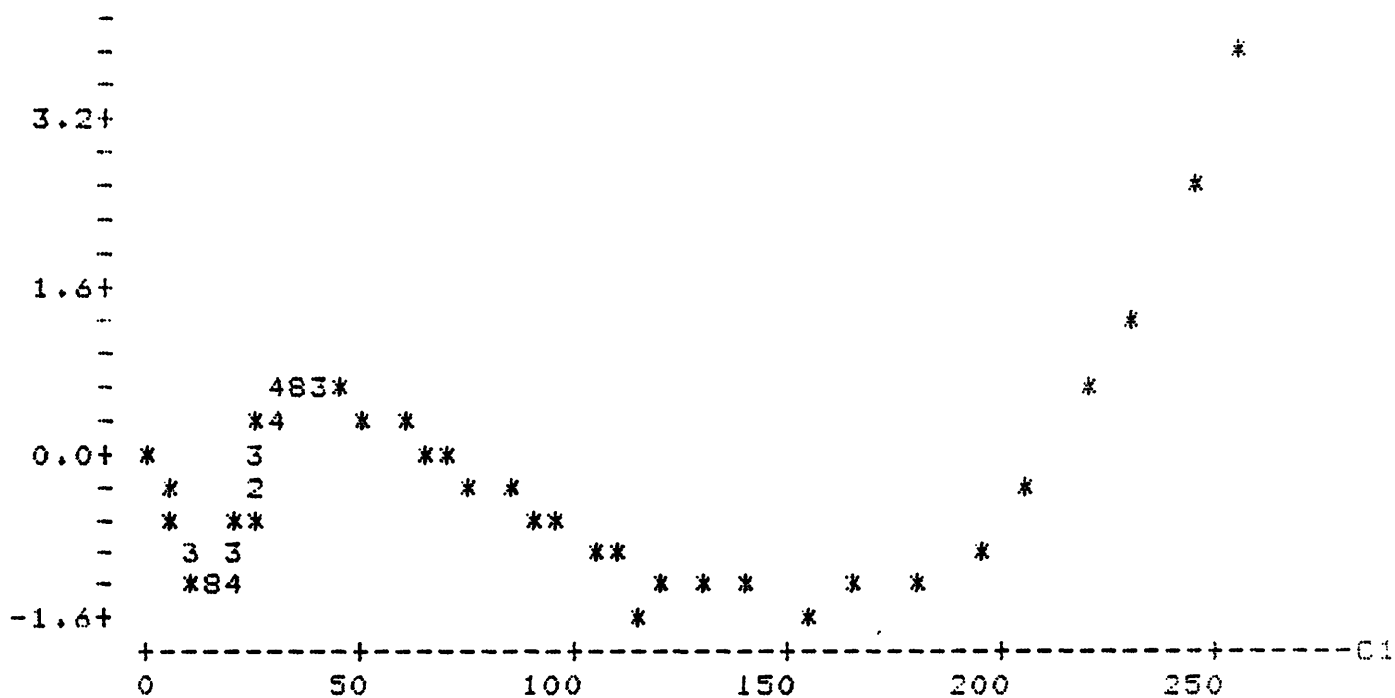
PLOT C6 VS C1



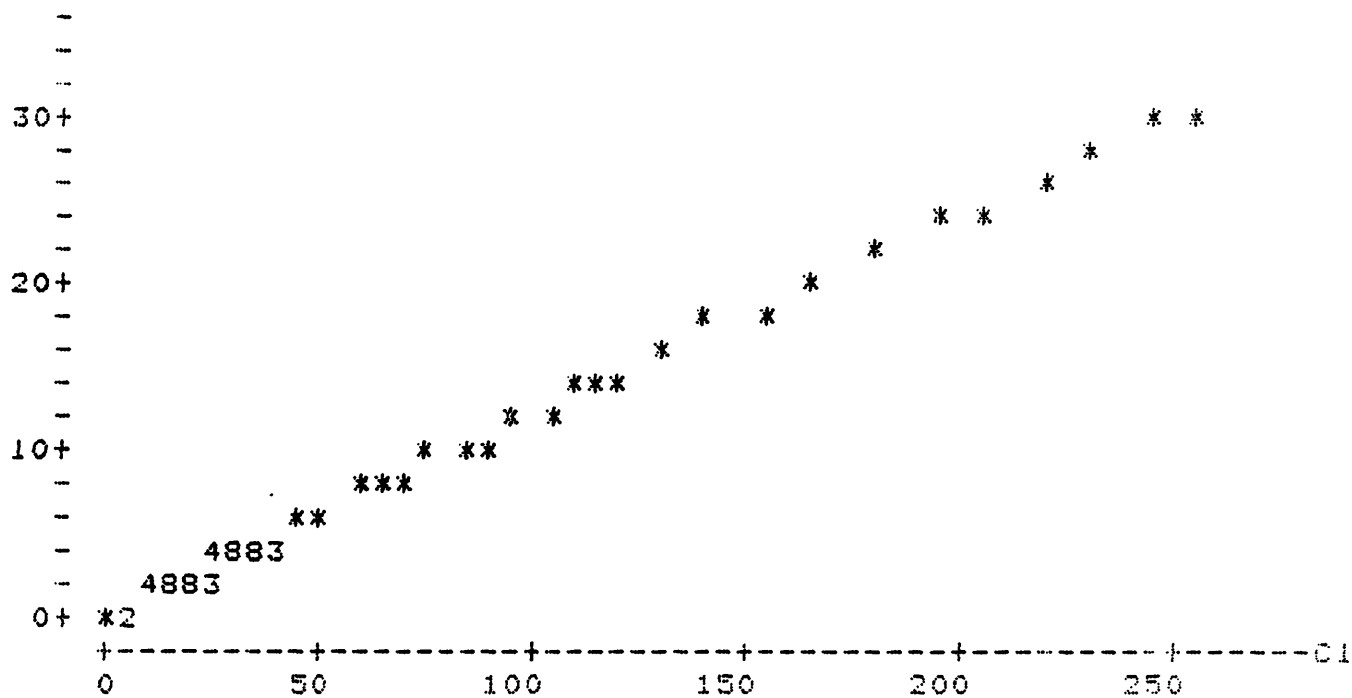
MTB > PLOT C7 VS C1



PLOT C12 VS C1



MTB > PLOT C13 VS C1



APPENDIX E. FLOW SHEET OF DATA TREATMENT

