

Variable Activation Energy to Model Oil Shale Pyrolysis Kinetics

Omar S. Al-Ayed[†] and Sulieman Q. Abu Ein
Faculty of Engineering Technology

Al-Balqa Applied University

P.O. Box 15008 Marka 11134.

Jordan

[†] E-mail: osalayed@fet.edu.jo

Introduction

- ❖ Most of the reported modeling studies are based on TGA, DGA, DSC and Rock-Eval Analyzer results.
- ❖ Integral and differential methods, the method of maximum rate have been used.
- ❖ These models have assumed a first-order depletion of kerogen to form oil and gas products.

Previous Work

- ❖ Allred (1966) reported that the process of oil evolution is the sum of two separate steps.
 - ❖ The first involves degradation and
 - ❖ The second is the evaporation of the products,
 - ❖ Each has different activation energies.
 - ❖ As the temperature increases, this latter process is claimed to be the rate-determining step
- ❖ Braun and Rothman (1975), reported 44.6 kJmol^{-1} activation energy below 490°C reaction Temperature.
 - ❖ Decomposition of bitumen involves breaking of relatively weak chemical bonds,
 - ❖ Higher activation energy, 177.6 kJmol^{-1} involves breaking of much stronger chemical bonds in kerogen.

Previous Work (cont.)

- ❖ Weight loss in low temperature pyrolysis region attributed to loss of moisture, interlayer water and decomposition of nahcolite (NaHCO_3) which takes place up to 120 °C.
- ❖ Physical changes, such as softening and molecular rearrangement associated with the release of gases and structural water are attributed to the rapid evaporation of organic material not chemically bonded to the kerogen network.
- ❖ Campbell and co-workers (1980), studied rate of evolution of CH_4 , H_2 , CO , CO_2 , and C_2 , C_3 hydrocarbons during pyrolysis of Colorado Oil Shale at linear heating rates varying from 0.5 to 4.0°Cmin⁻¹.
- ❖ Dawsonite, $\text{NaAl}(\text{OH})_2\text{CO}_3$ decomposes to Na_2CO_3 , Al_2O_3 , H_2O , CO_2 between 350- 400 °C

Additional studies

- ❖ Decomposition of oil shale involves large number of reactions in parallel and in series,
 - ❖ TGA measures overall weight loss due to these reactions.
 - ❖ Therefore activation energies derived from TGA data are apparent activation energies.
- ❖ Li and Yue 2003, studied pyrolysis kinetics of different Chinese oil shale samples at a constant heating rate of $5^{\circ}\text{Cmin}^{-1}$.
 - ❖ The TGA data obtained used to develop a kinetic model which assumes 11 first order parallel reactions with changed activation energies and frequency factors.
 - ❖ They reported apparent activation energies in $80 - 280 \text{ kJmol}^{-1}$ range and apparent frequency factor in the range $1.3 \cdot 10^4$ to $1.4 \cdot 10^{19}$.
 - ❖ The calculated fractional conversion of each reaction is a complex function of activation energy.

Chemical Reactions and Variable Activation Energy Idea

- ▶ Low activation energies, rupture of weak cross linked bonds, such as, C-O, C-S, (17,18) etc.
 - ▶ Also, rupture of branched functional groups in kerogen long molecular structure.
 - ▶ These bonds have low rupture energy that produces gases such as H₂O, CO₂, H₂S, H₂ and light hydrocarbons
- ▶ Medium activation energy values are associated with
 - ▶ break up of the side chains in β-site of aromatics,
 - ▶ decomposition of normal alkane with large molecular weight,
 - ▶ Diels-Alder cyclation reaction and the rupture of alicyclic hydrocarbon.
- ▶ This corresponds to pyrolysis temperature between 420 – 480 °C

Chemical Reactions and Variable Activation Energy Idea

- ➔ High apparent activation energies are mainly the aromatization of alicyclic compounds, dehydrogenation and combination of aromatic rings, rupture of heterocyclic compounds coke formation reactions.

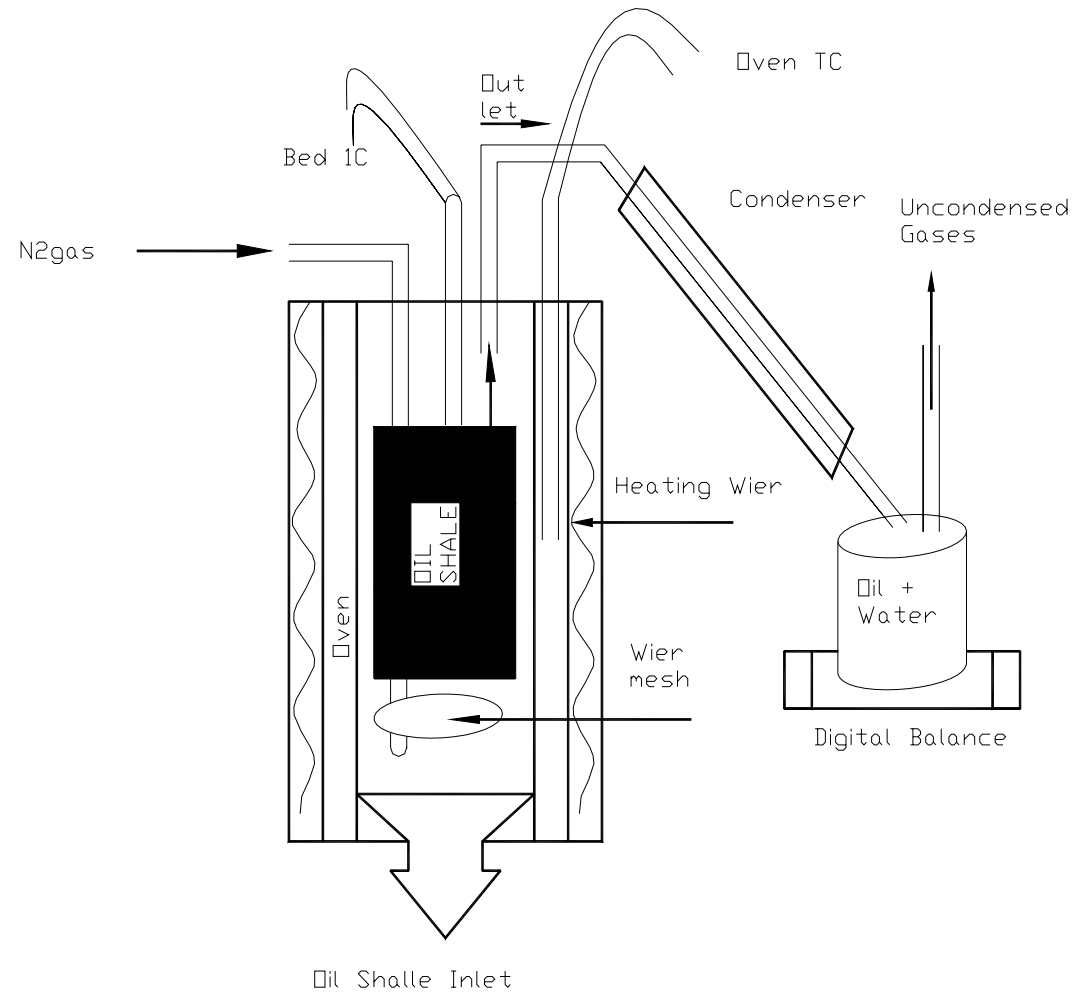
DTA Studies on Jordanian Oil Shale

- DTA thermal tests with a heating rate $10^{\circ}\text{Cmin}^{-1}$. conducted and the following heat effects recorded:
 - 30 – 150 °C endothermic – release of the absorbed water
 - 150 - 550 °C exothermic – reaction of first organic complex
 - 420 – 520 °C roasting of the pyrites
 - 480 - 520 °C dehydration of the phosphate complex
 - 450 – 800 °C reaction of the second organic complex
 - 790 – 940 °C endothermic dissociation of dolomite
 - 920 - endothermic dissociation of calcite

Experimental Conditions

- ✦ 400 g sample
- ✦ Particle size less than 3 mm
- ✦ N₂ gas and 350 -550 °C temperature range
- ✦ Stainless Steel cylindrical retort
- ✦ Digital Balance
- ✦ Circulating coolant with anti freeze at 2 °C
- ✦ Glass condenser
- ✦ Electrical heater.
- ✦ Heating rates varied between 2.6 – 5 °Cmin⁻¹

Experimental Setup (1)



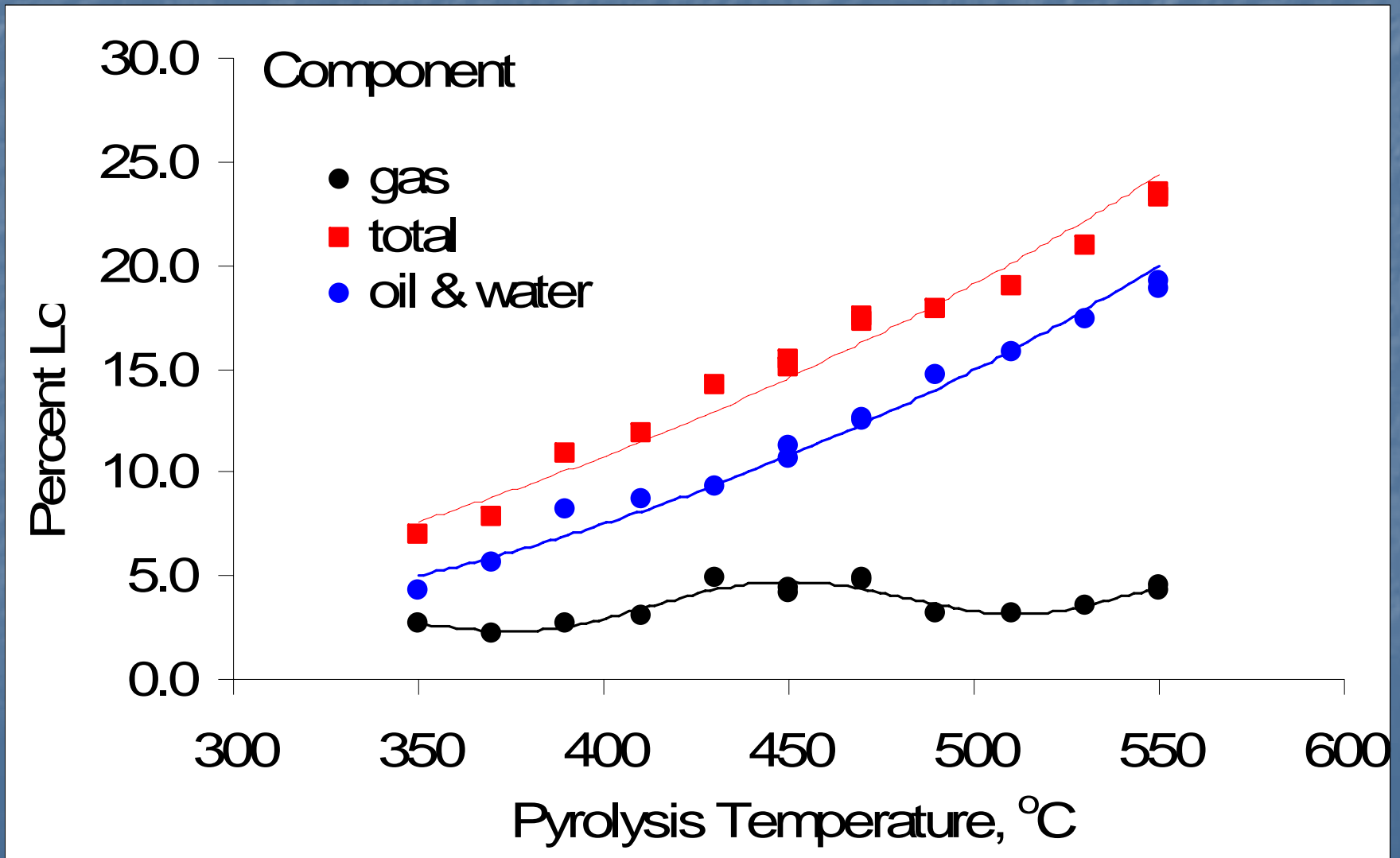
Experimental Setup(2)



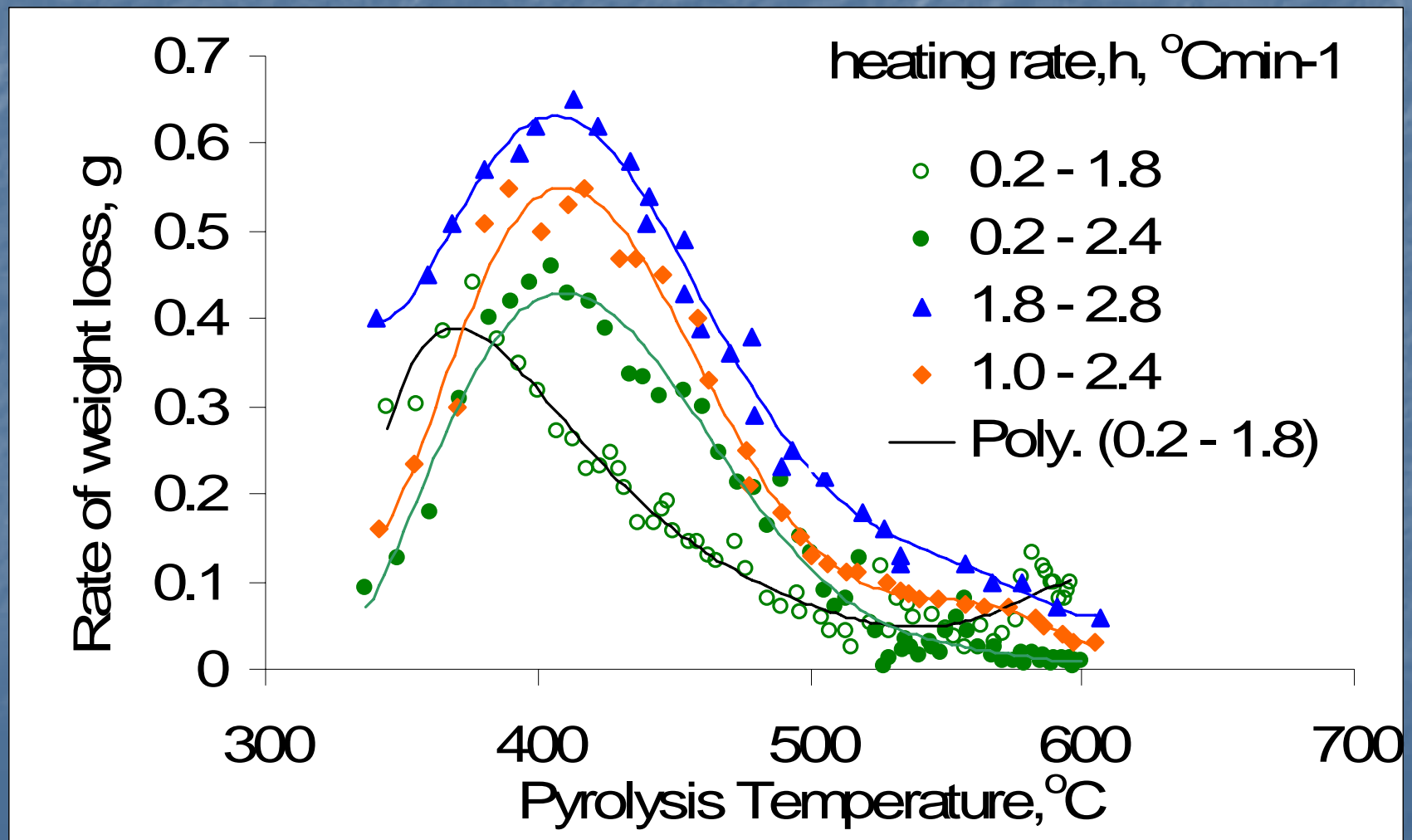
Oil Shale Characteristics

Component	Raw Shale
Moisture Content	1.21
Total Water	3.0
Total Oil	12.18
Gas Loss	3.4
Spent Shale	86.3
Total Sulfur	2.29
Total Carbon	17.28
Total Organic Carbon	11.42
Hydrogen	1.76
CaCO ₃	46.31
Calorific Value, kJ/kg	5467

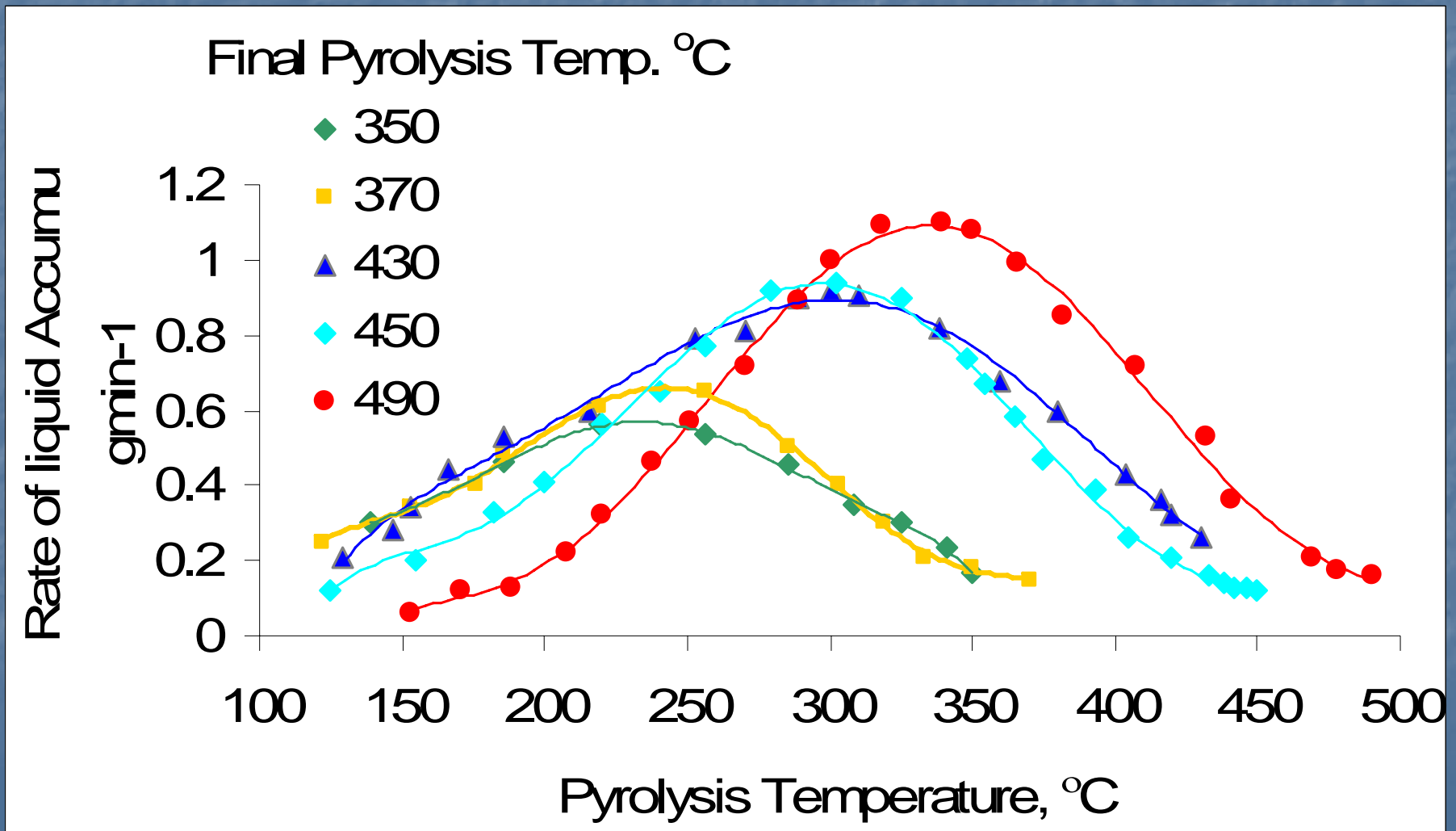
Sample Losses, Total, Liquids, Gases



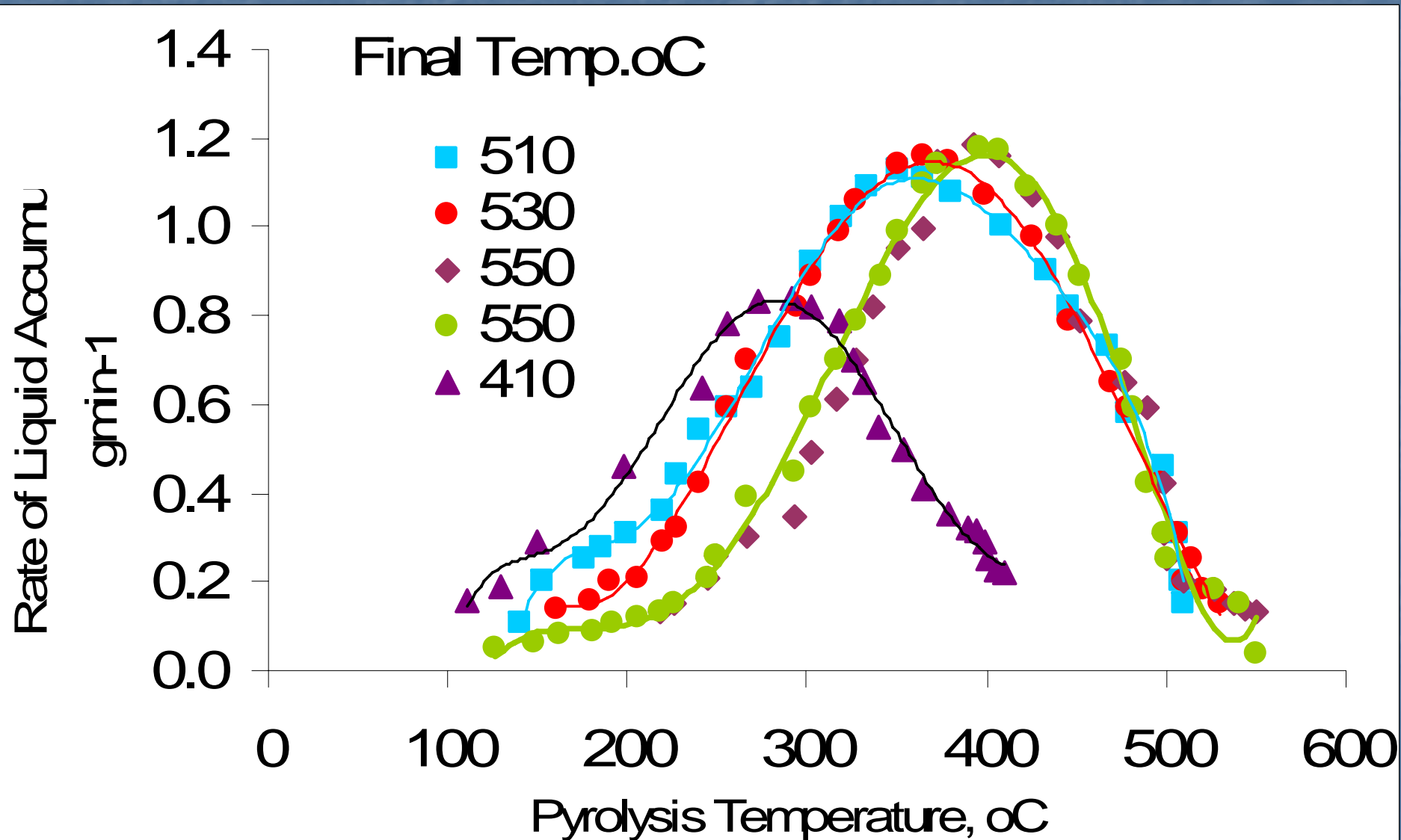
Rate of liquid condensation (gmin^{-1}) with temperature, at different heating rates ($^{\circ}\text{Cmin}^{-1}$)



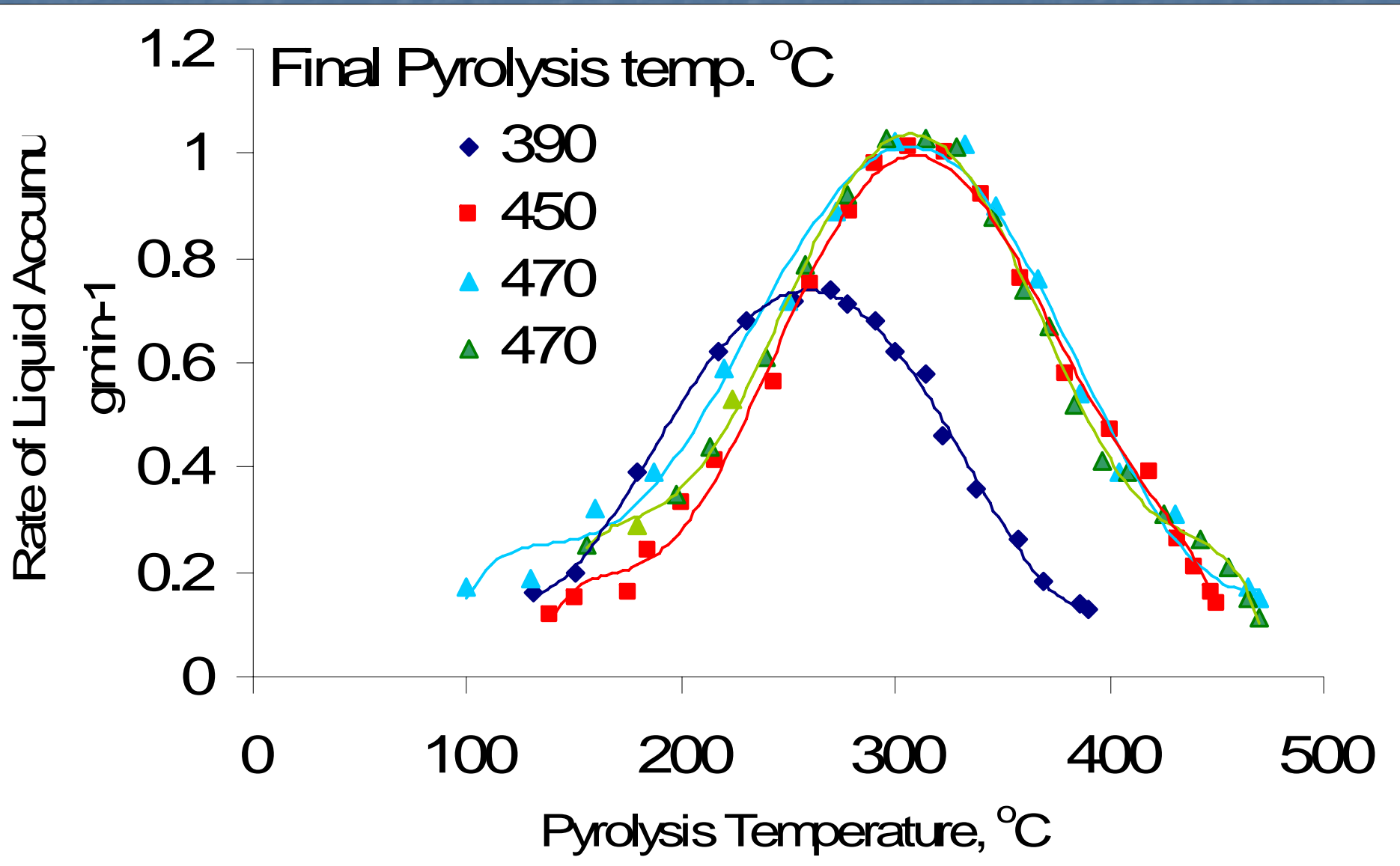
Final Pyrolysis Temperature °C, with 3.8 – 5 °Cmin⁻¹, heating rate



Final Pyrolysis Temperature °C, with 2.6 - 2.8 °Cmin⁻¹, heating rate



Final Pyrolysis Temperature °C, with 3.0 – 3.3 °Cmin⁻¹, heating rate



Kinetic Equations

$$\frac{dx}{dt} = k(1 - x)$$

$$k = k_o \exp\left(\frac{-E}{RT}\right)$$

$$h = \frac{dT}{dt}$$

$$\ln[-\ln(1 - x)] = \ln\left[\frac{k_o RT^2}{hE} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

Calculated $\ln[-\ln(1-x)]$ Vs. Predicted

Theoretical $\ln[-\ln(1-x)]$

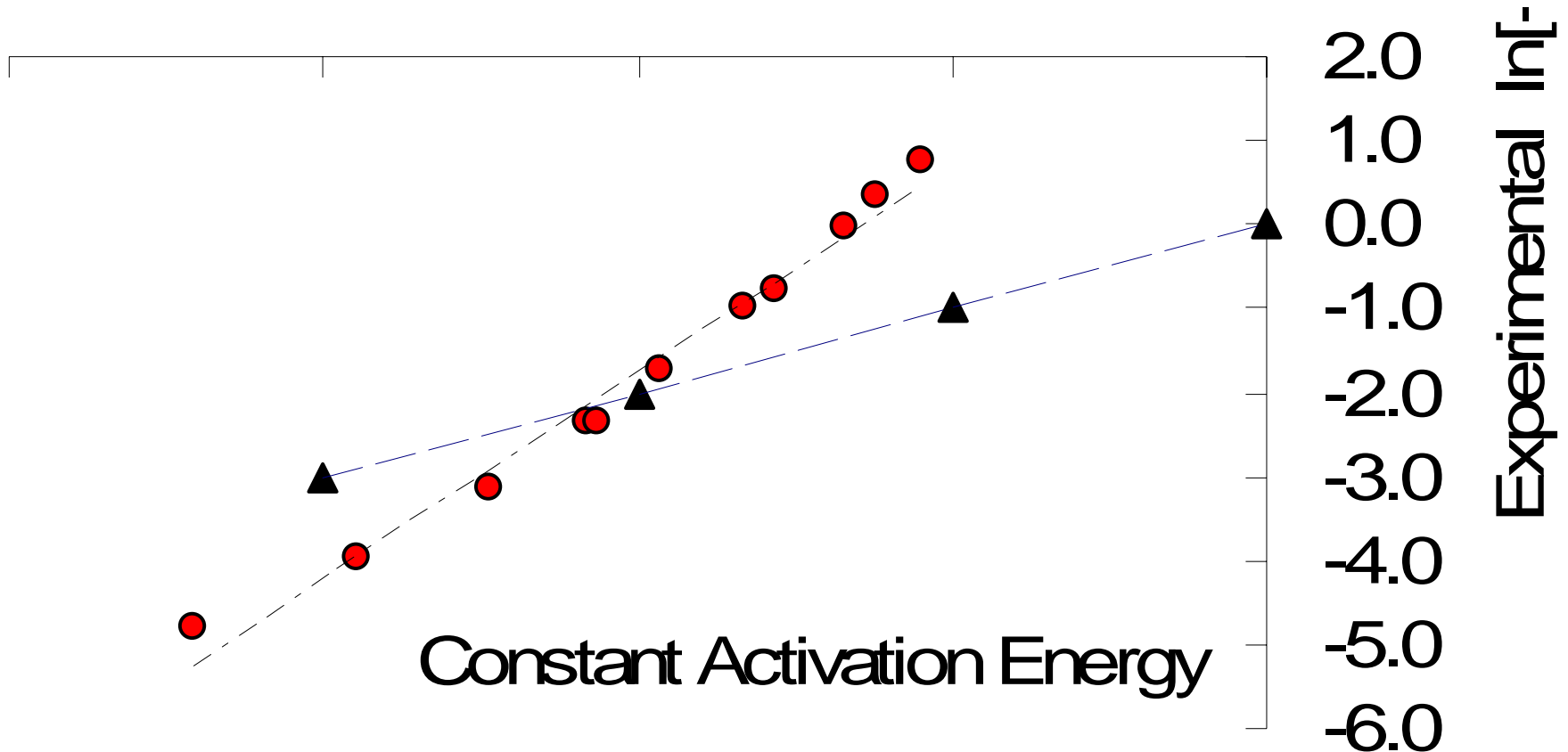
-4.0

-3.0

-2.0

-1.0

0.0



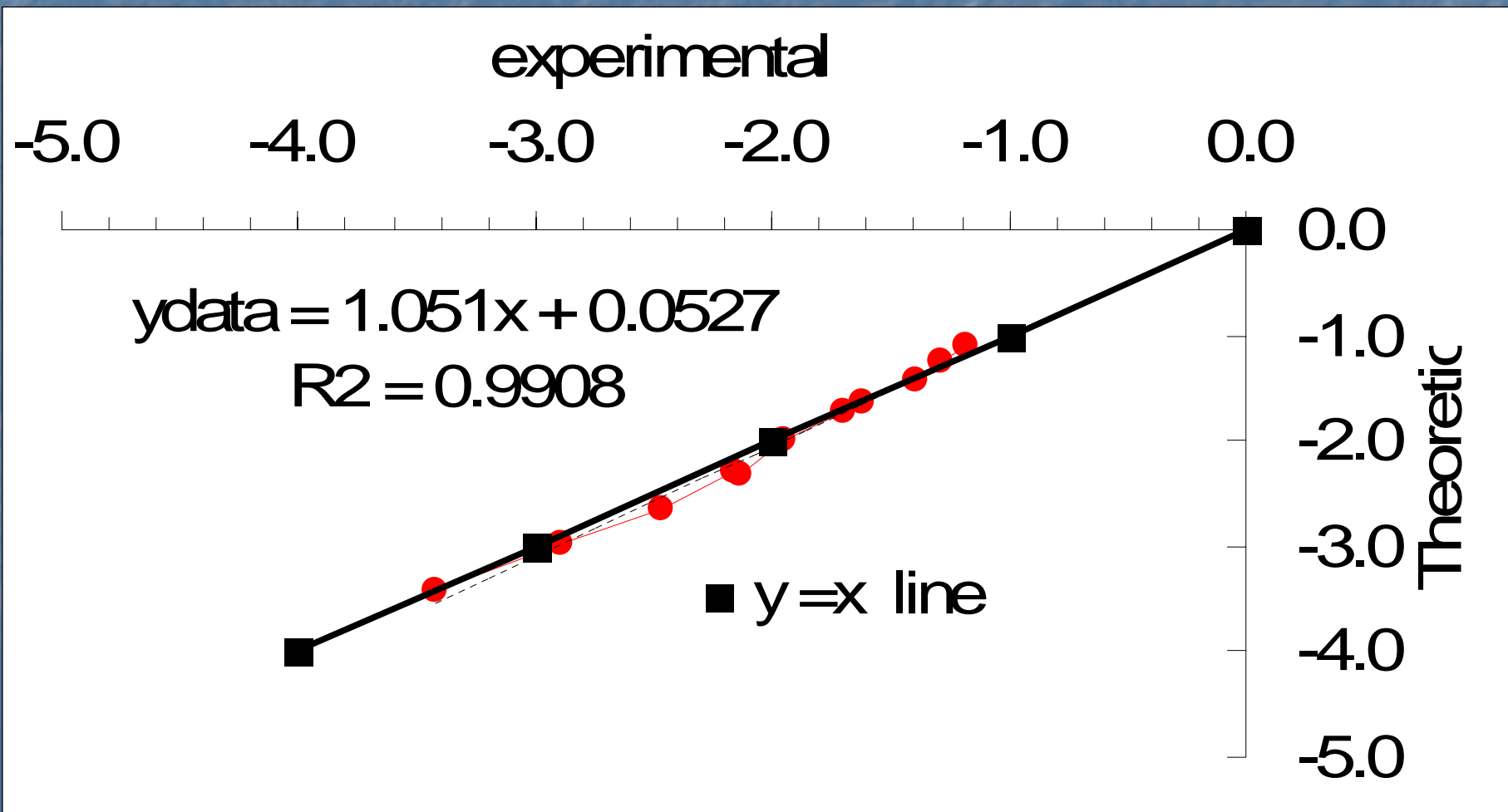
$$E = E_o(1+x)$$

Modified Kinetic Equation

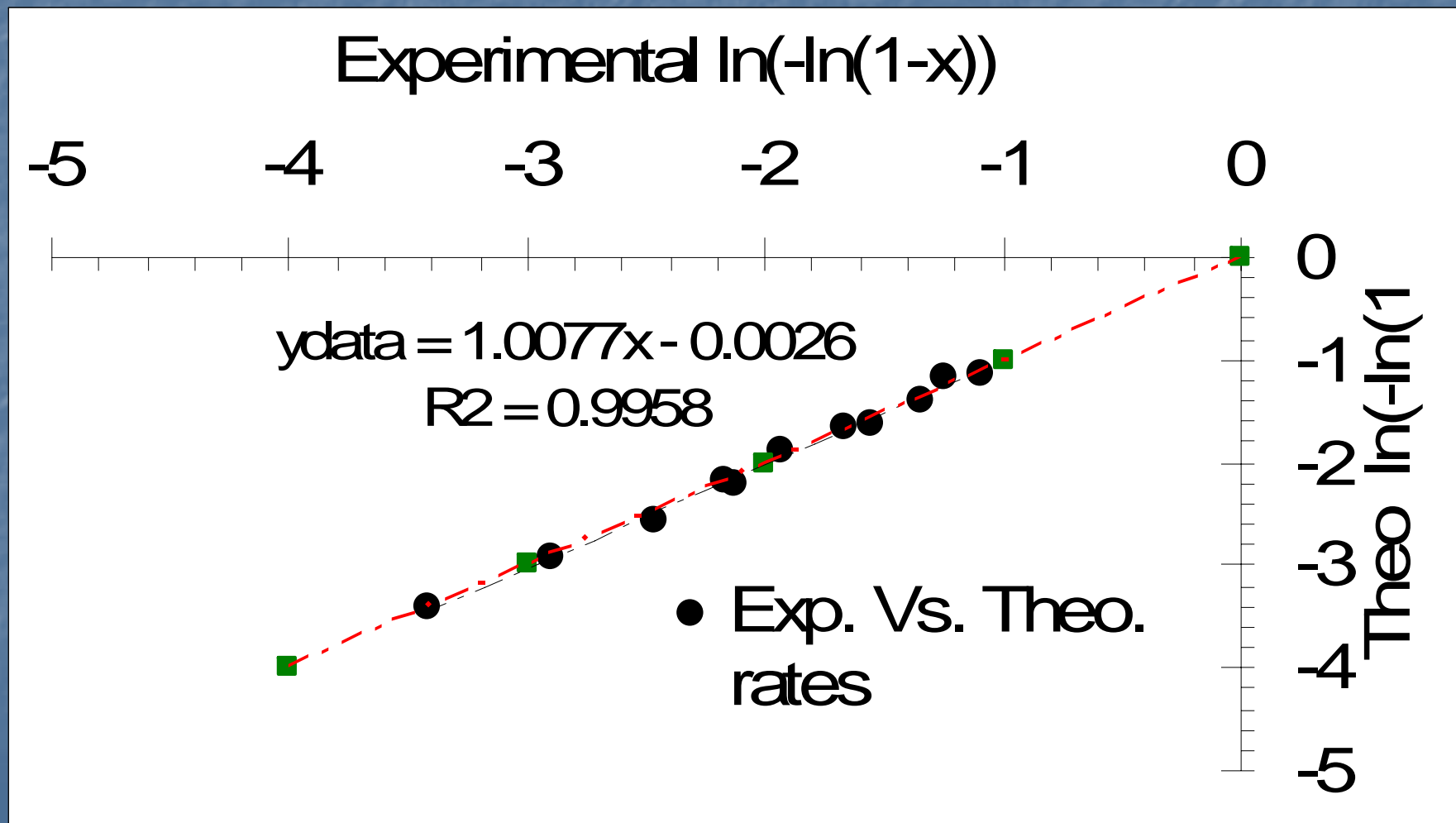
$$\ln[-\ln(1-x)] = \ln \left[\frac{k_o RT^2}{hE(x)} \left(1 - \frac{2RT}{E(x)} \right) \right] - \frac{E(x)}{RT}$$

$$E(x) = E_o(1+x)$$

Variable Activation Energy with Const. k_0



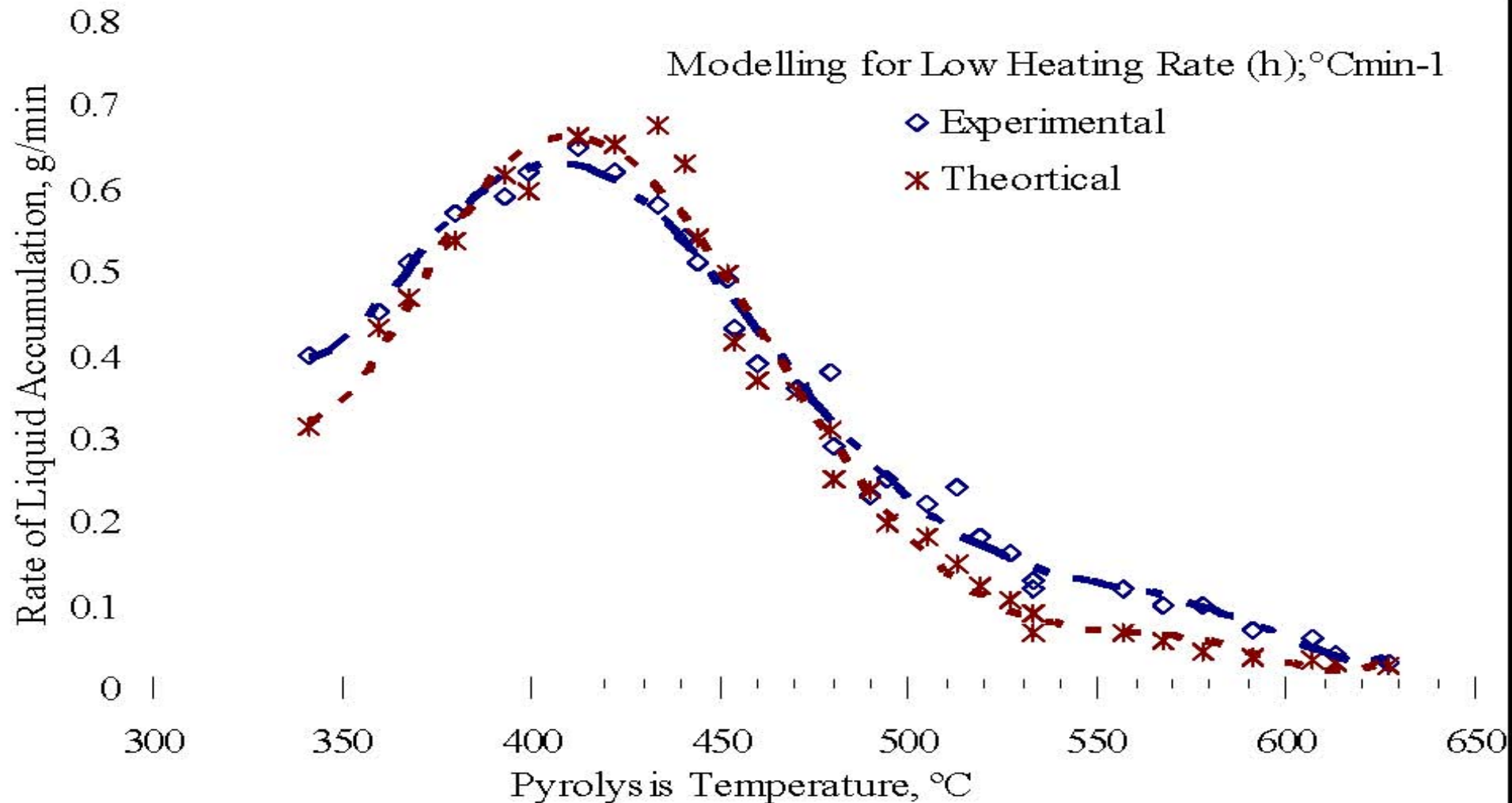
Activation Energy and k_0 are function of x



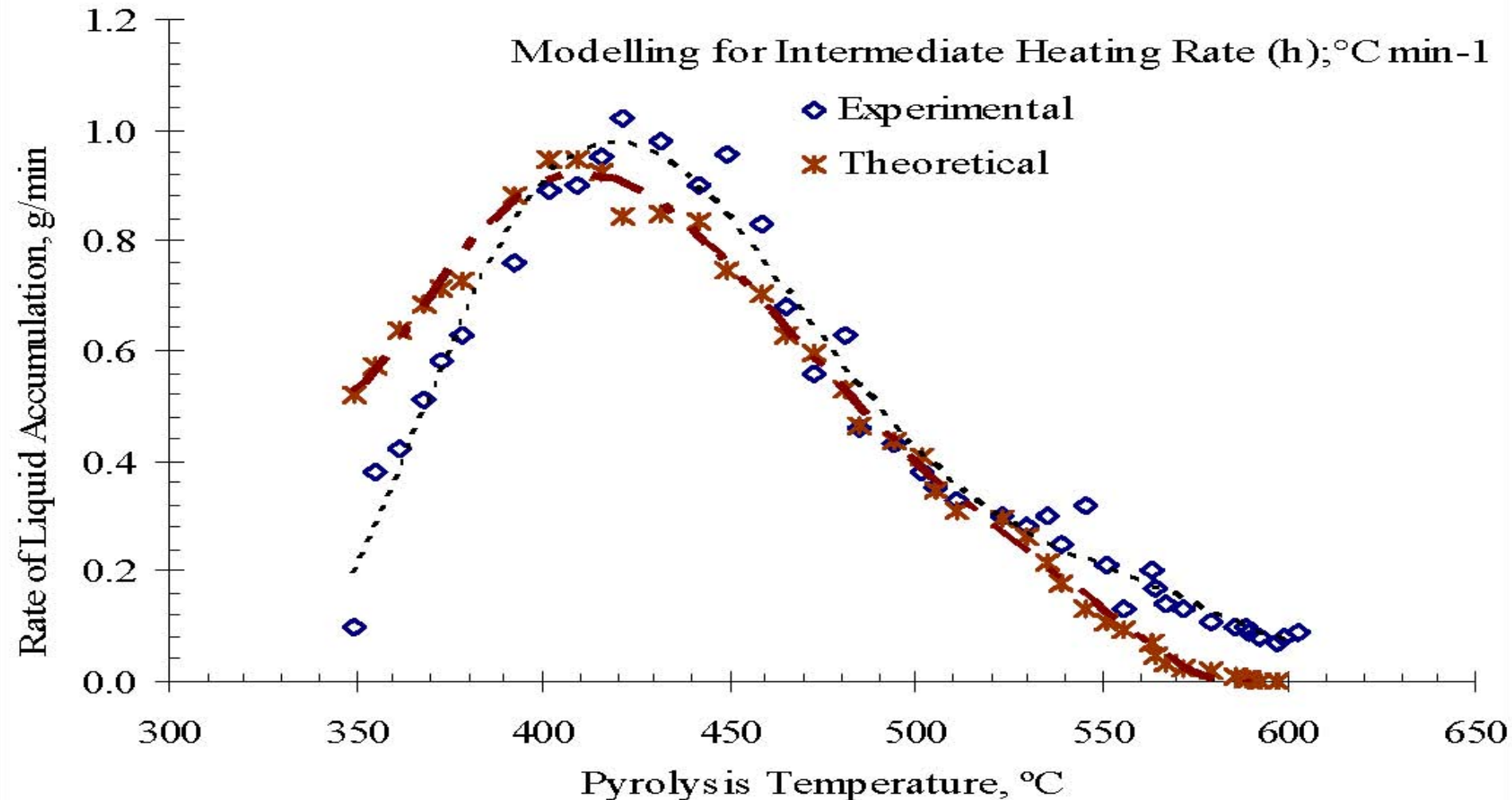
Rate of Liquid Production

$$\frac{dw_l}{dt} = k_{ol} \exp\left(-\frac{E}{RT}\right) (1-x)^2$$

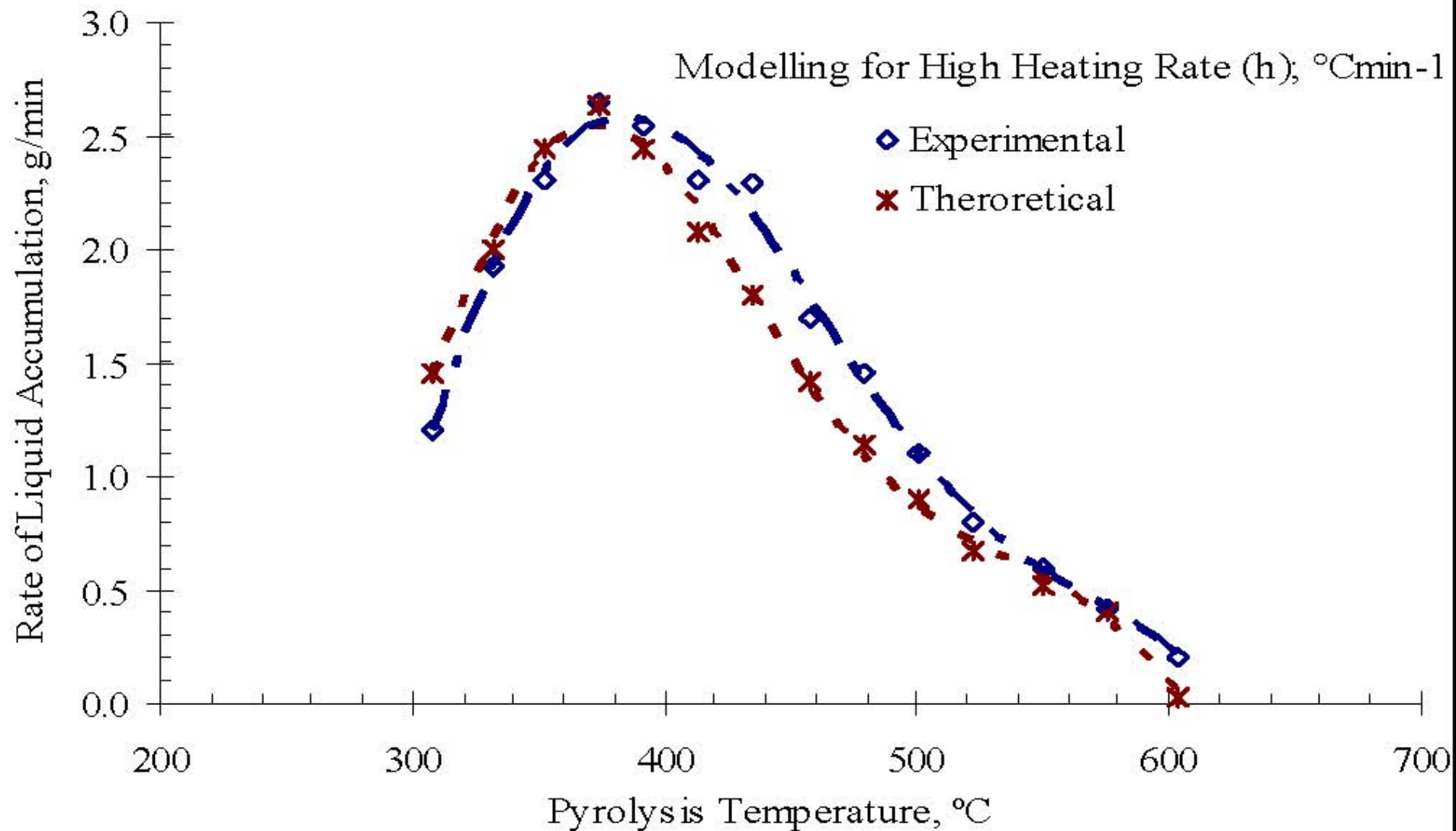
Liquid modeling for h 2.6-2.8 °Cmin⁻¹



Liquid modeling for h 2.5-5 °Cmin⁻¹



Liquid modeling for (h) 9-14 °Cmin⁻¹



Calculated parameters

Low and intermediate heating rate calculated parameters:

$$\#k_{0l} = 1.15 \cdot 10^6$$

$$\#E = 77 \text{ kJmol}^{-1}$$

High heating rate calculated parameters:

$$\#K_{0l} = 3.0 \cdot 10^6$$

$$\#E = 96.5 \text{ kJmol}^{-1}$$

Conclusions and Recommendations

1. Total oil shale weight loss data have been fitted to a standard first order equation with new modifications for Activation Energy and Frequency factor.
 - The complexity of reactions during pyrolysis dictate such thinking
 - Excellent agreement is obtained between developed model and experimental data.
2. Rate of liquid accumulation has been modeled with a standard second order reaction model.
 - 77 kJmol^{-1} activation energy calculated for heating rate less than $5 \text{ }^{\circ}\text{Cmin}^{-1}$.
 - 96.5 kJmol^{-1} calculated for heating rate in $9 - 14 \text{ }^{\circ}\text{Cmin}^{-1}$ range.
3. Gaseous production rate has not been modeled yet.
4. Mathematical treatment of the model is required.

Thanks and Gratitude to:

- Chairman of Symposium and Organizers.

Chapter Four



Oil Shale in Jordan