

Isothermal and Nonisothermal Kinetic Analyses of Mahogany Oil Shale with TGA

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Oil shale: Source of unconventional energy

- **Organic matter**

- Bitumen (soluble in organic solvent)
- **Kerogen** (significant portion of TOC, total organic carbon)

- **Mineral constituents**

- Carbonates: calcite, dolomite, etc.

- **Kerogen**, A chemically immature hydrocarbon - essentially, oil's geological ancestor
- **Thermal/Chemical** decomposition- Released petroleum-like substance

- **Retorting (Pyrolysis)**

- » In-Situ retorting
- » Surface retorting

- Products include

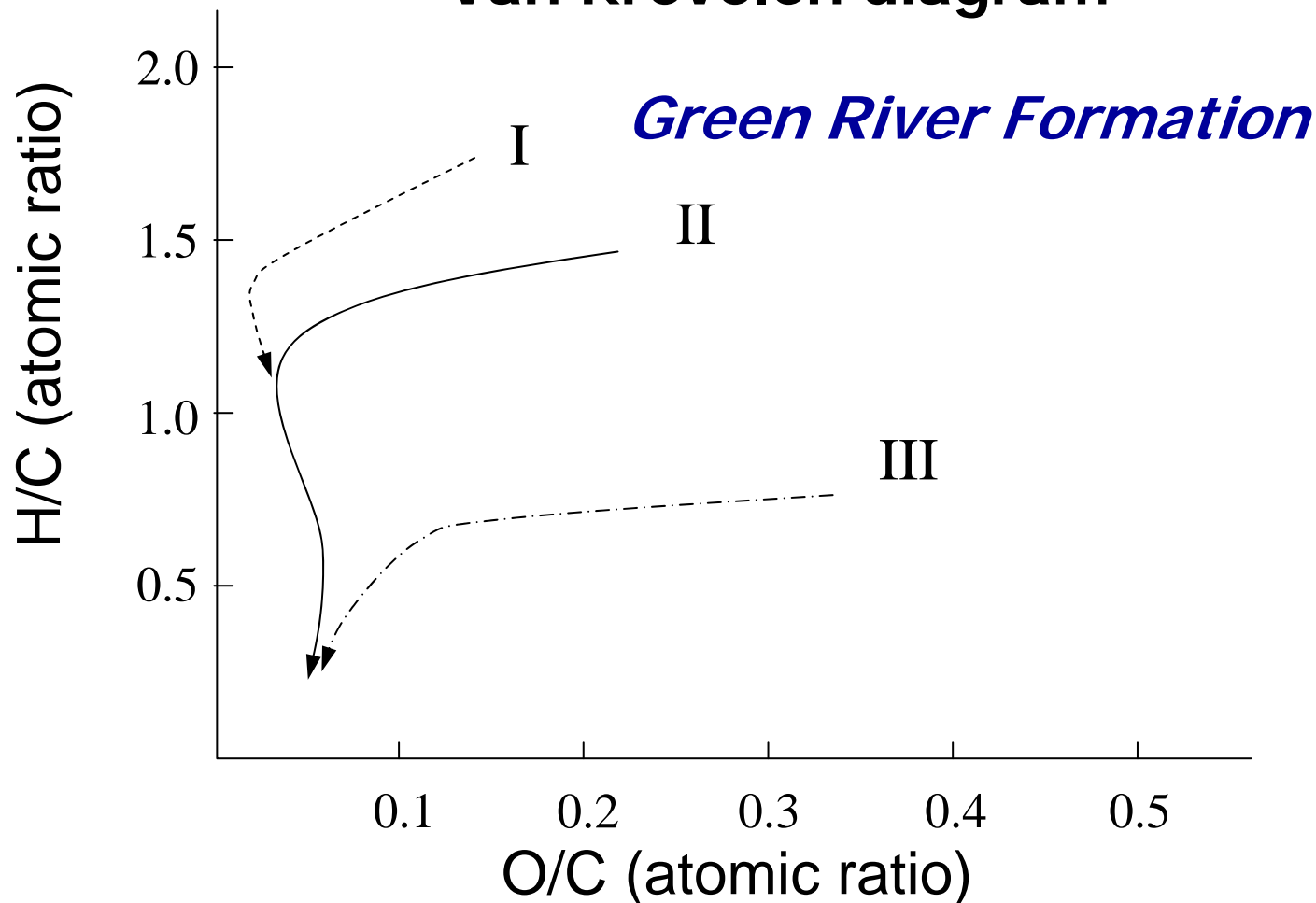
- Synthetic crude oil liquid
- Gases
- Residual solid



Oil Shale → **Shale Oil**

Kerogen classification

Van Krevelen diagram



Previous studies: Mechanism

Approach 1.

- *Kerogen* \rightarrow *Heavy Oil* + *Light Oil* + *gas* + CH_4 + *char*
- *Heavy Oil* \rightarrow *Light Oil* + *gas* + CH_4 + *char*
- *Light Oil* \rightarrow *gas* + CH_4 + *char*
- *Gas* \rightarrow CH_4 + *char*
- *Char* \rightarrow CH_4 + *gas* + *coke*

All reactions are assumed to be first order

Approach 2.



Approach 3.



Approach n.

And many others

First order reaction with respect to decomposition of the reactants

Kinetic study

- **Rate constant (K)**
- **Reaction order (n)**
- **Activation energy (Ea)**
- The rate at which a kinetic process proceeds depends on time-temperature history
- The knowledge of kinetic parameters is important to optimize the process – well locations, heat input rates, etc.

Thermo Gravimetric Analysis (TGA)

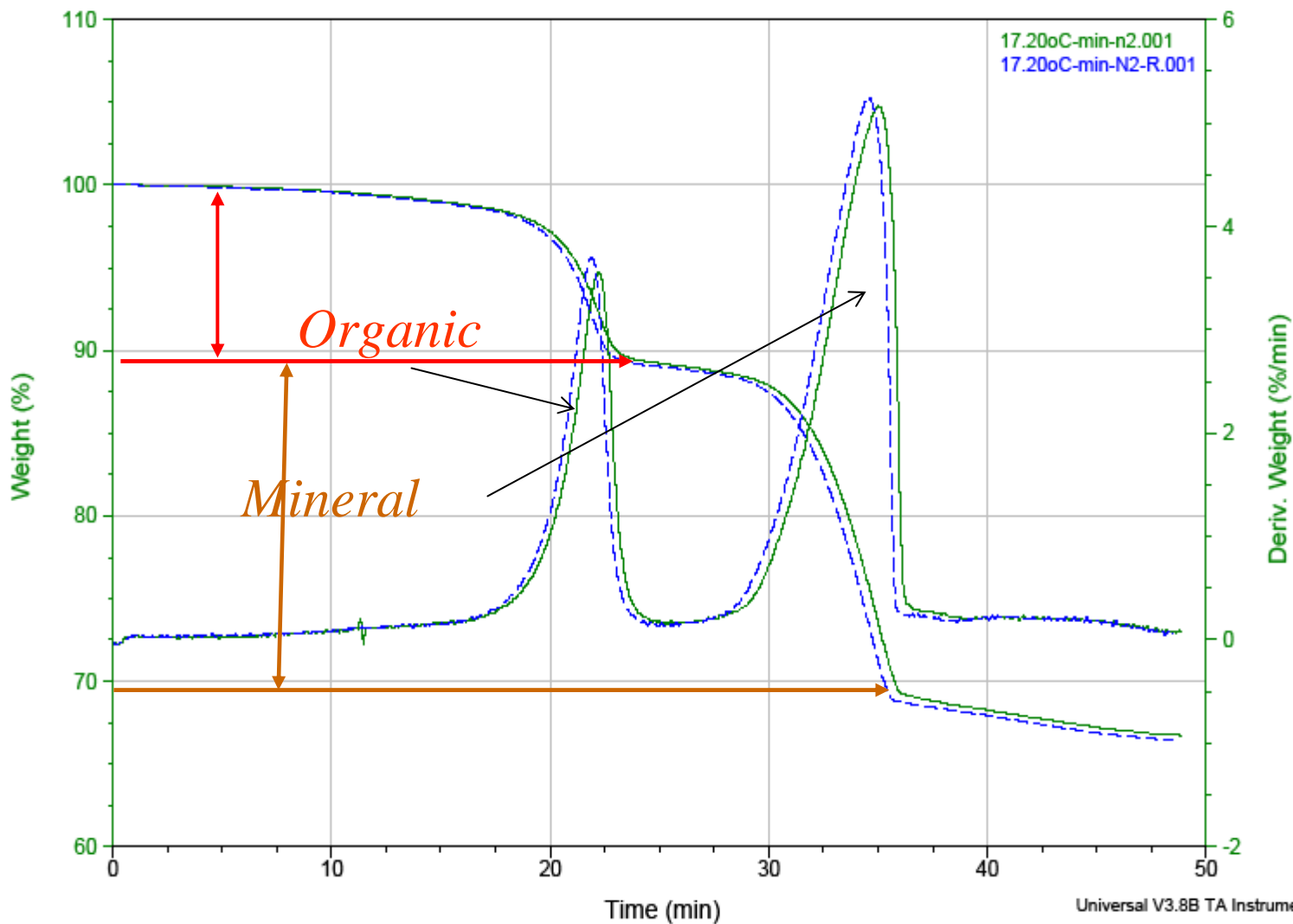
Weight loss/derivative versus Time/Temperature

- Calibration
 - Mass
 - Temperature
- Operating condition
 - Purge gas – 60ml/min
 - Weight --20~30 mg
 - Particle size – ~100 mesh size
 - Environment – N₂ and Air
 - Temperature – Isothermal and Non-isothermal
- Reproducibility



TGA:Q-500

TGA: Reproducibility of data



Kinetic study with TGA

• Conversion and rate equation

Conversion

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_\infty)} \quad \text{or} \quad \alpha = \frac{(W_0 - W_t)}{(W_0 \cdot X)}$$

W_0 = Initial weight of the sample, mg

W_t = Weight of the sample at time 't', mg

W_∞ = Weight of the sample at the end of analysis, mg

X = Normalization Factor

Arrhenius dependency : $K = A \cdot \exp(-Ea/RT)$

First order assumption

$$\frac{d\alpha}{dt} = A \cdot \exp\left(\frac{-Ea}{RT}\right) \cdot (1 - \alpha) \quad \text{Constant Temperature}$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(\frac{-Ea}{RT}\right) \cdot (1 - \alpha) \quad \text{Constant Heating Rate}$$

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

Kinetic study with TGA

Conversion and rate equation

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_\infty)}$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(\frac{-E_a}{RT}\right) \cdot (1 - \alpha)$$

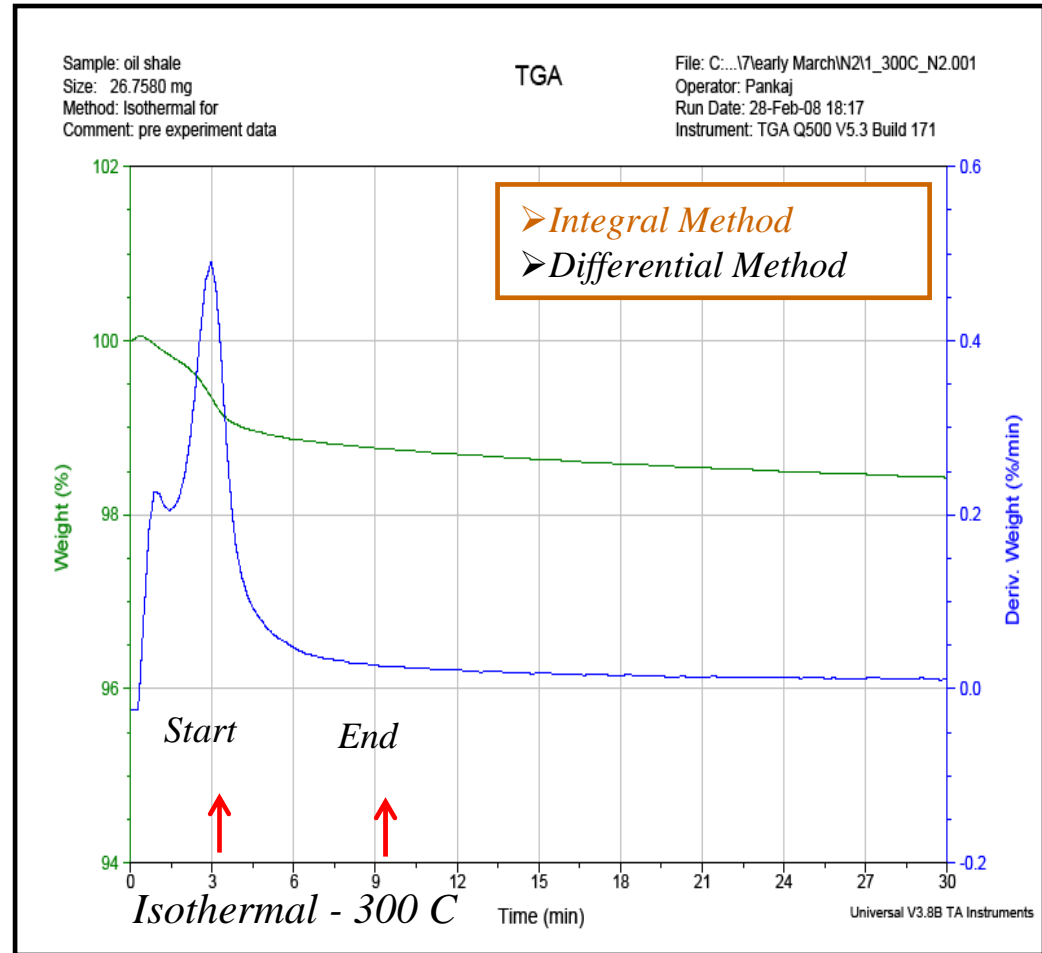
Isothermal TGA curve

Analysis criteria

- 100°C/min
- 1000°C (0.5°C/min)

Mathematical method

- Activation energy (E_a)
- Pre-exponential factor (A)



Kinetic study with TGA

Conversion and rate equation

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_\infty)}$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(\frac{-Ea}{RT}\right) \cdot (1-\alpha)$$

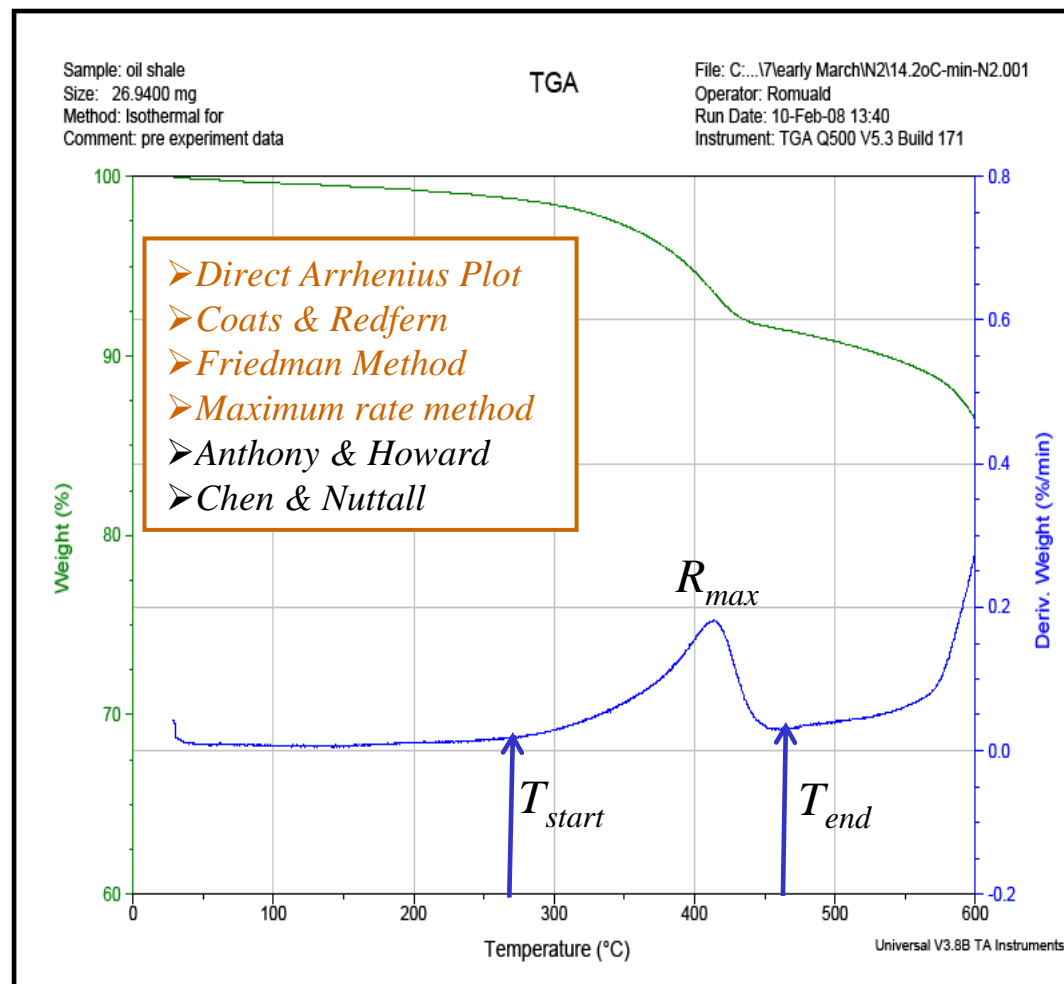
Analysis criteria

- 100°C/min
- 1000°C (0.5°C/min)

Mathematical method

- Activation energy (Ea)
- Pre-exponential factor (A)

Non-isothermal TGA curve



Kinetic study with TGA

• Conversion *and* rate equation

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_\infty)}$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(\frac{-E_a}{RT}\right) \cdot (1-\alpha)$$

Isothermal $_N_2$

• Analysis criteria

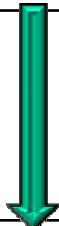
- 100°C/min
- 1000°C (0.5°C/min)

• Mathematical method

- Activation energy (E_a)
- Pre-exponential factor (A)

• Experimental conditions

- Isothermal
- Nonisothermal

ISOTHERMAL			N_2 Normalized data		
T	Total time	Initial weight	Start Isothermal condition		Normalization factor X
°C	min	mg	Time	Weight Loss	
300	720	26.75	3.33	99.17	0.0917
350	240	26.69	3.82	98.75	0.0875
400	240	22.64	4.36	98.21	0.0821
450	240	24.68	4.96	96.01	0.0601
500	240	25.00	5.59	89.29	
550	180	23.95	6.3	88.38	
600	30	24.10	6.96	87.89	

Isothermal analyses cannot be performed at these temperatures, because most of the organic matter decomposes before this temperature is attained

Kinetic study with TGA

- Conversion *and* rate equation Non-isothermal N_2

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_\infty)}$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(\frac{-Ea}{RT}\right) \cdot (1-\alpha)$$

- Analysis criteria

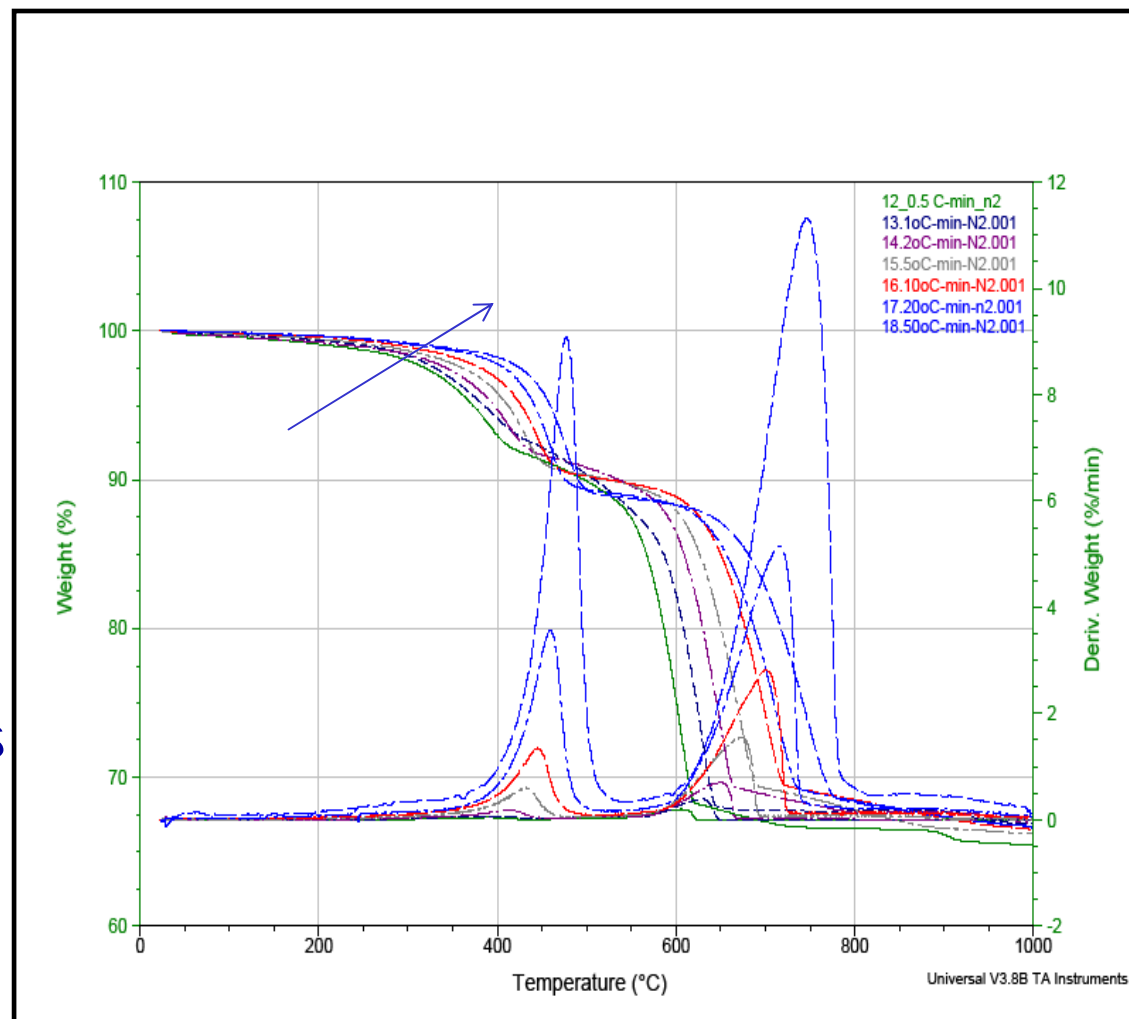
- 100°C/min
- 1000°C (0.5°C/min)

- Mathematical method

- Activation energy (Ea)
- Pre-exponential factor (A)

- Experiment conditions

- Isothermal
- Nonisothermal

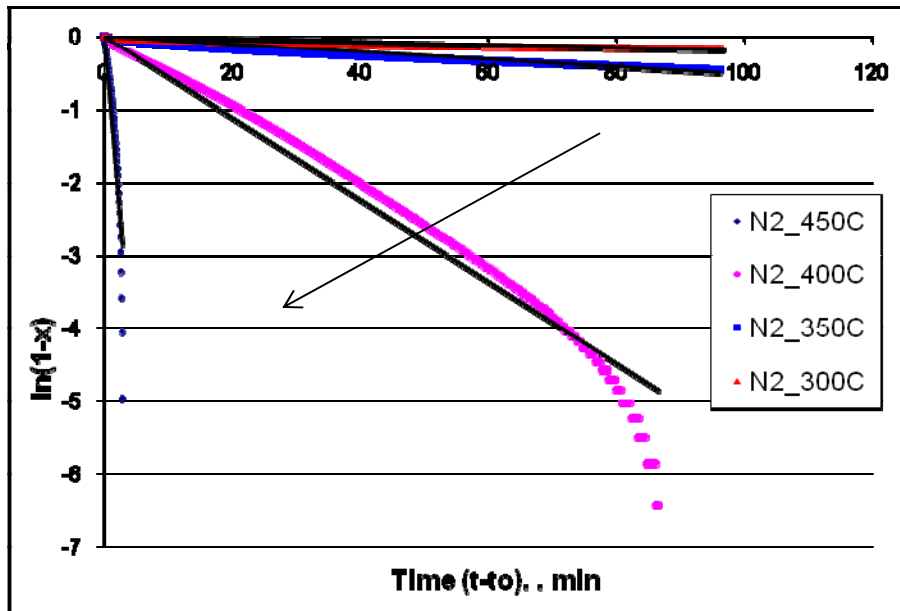


Kinetic study with TGA

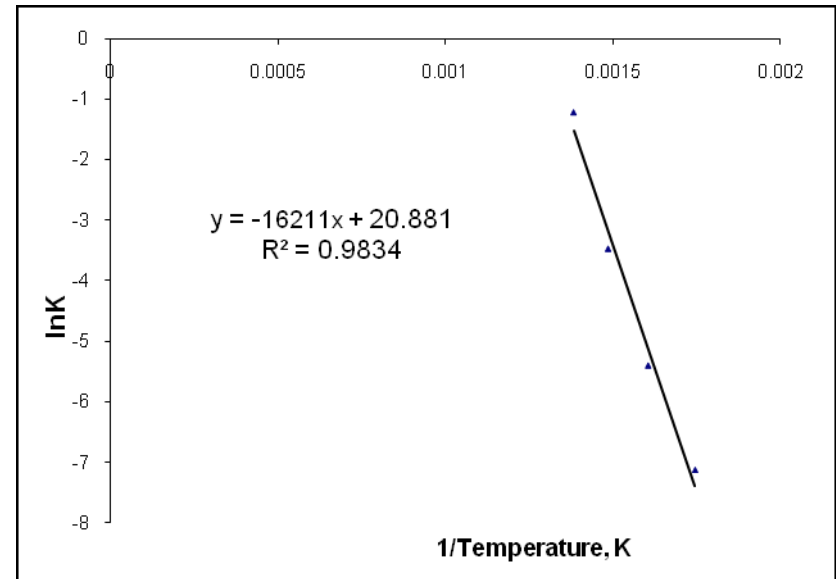
Isothermal: Integral method (first order)

$$\rightarrow \ln(1 - \alpha) = -k \cdot (t - t_0)$$

Integral method N_2



Arrhenius plot N_2



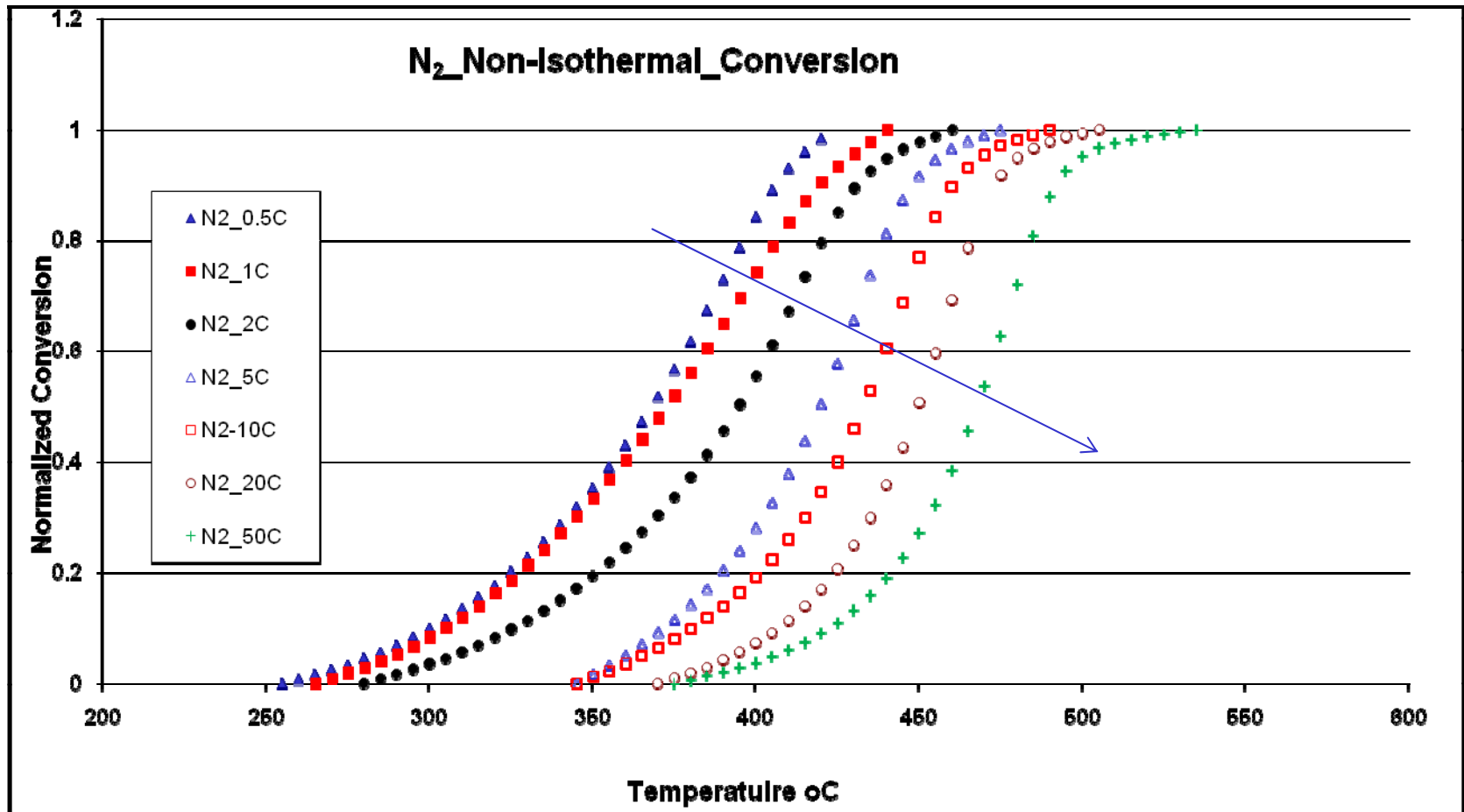
- ❖ t_0 is the time at the start of the constant- temperature period (isothermal condition).
- ❖ Thermal induction part is eliminated from the kinetic analysis and correspondingly the W_∞ is corrected.
- ❖ α and x , are same and representing conversion

N_2	
Ea, KJ/mol	A
134.778254	1.2E+09

Kinetic study with TGA

Non-isothermal

Conversion



Kinetic study with TGA

Non-isothermal: Differential method

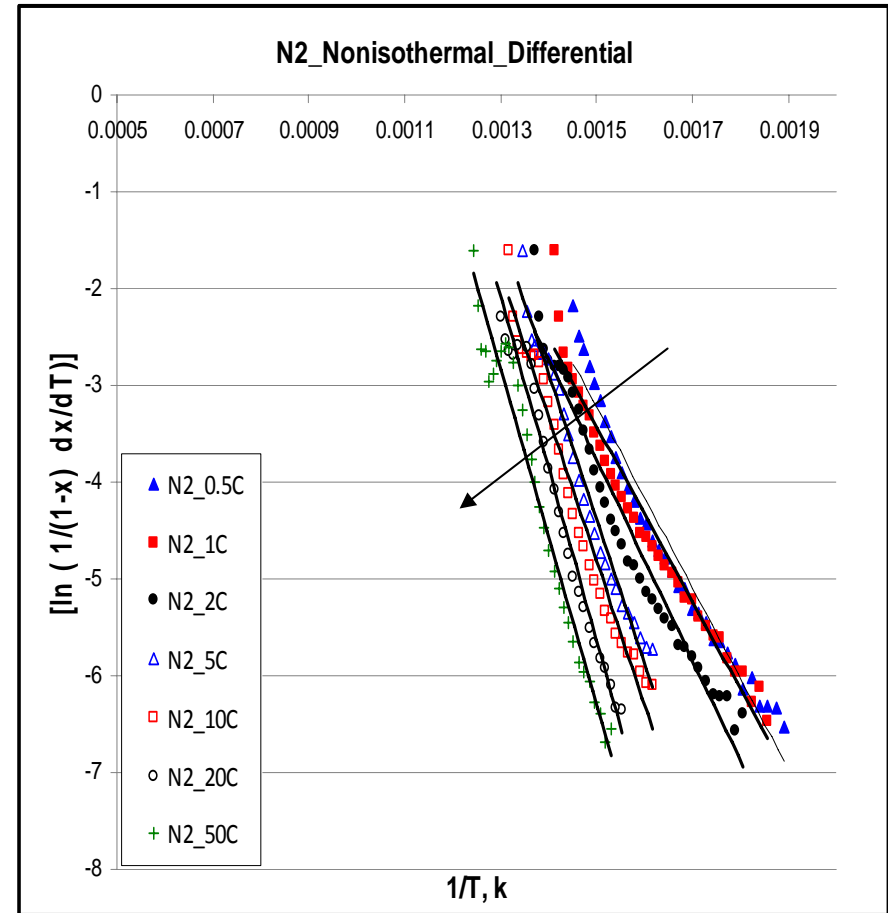
(Direct Arrhenius plot)

$$\rightarrow \frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(\frac{-Ea}{R \cdot T}\right) \cdot (1 - \alpha)$$

Simplified form for first order

$$\rightarrow \ln\left[\frac{1}{(1-\alpha)} \cdot \frac{d\alpha}{dT}\right] = \ln\left(\frac{A}{\beta}\right) - \left(\frac{Ea}{R \cdot T}\right) \rightarrow$$

N ₂ _Nonisothermal_Differential					
β	R ²	slope	Intercept	Ea	A
0.5	0.961	9351	10.8	77.74	24510
1	0.959	9002	10.07	74.84	23624
2	0.962	10379	11.8	86.29	266505
5	0.977	14873	17.93	123.6	3E+08
10	0.972	14905	17.54	123.9	4E+08
20	0.979	17757	21	147.6	3E+10
50	0.967	17218	19.56	143.1	2E+10



Kinetic study with TGA

Non-isothermal: Integral method (Coats-Redfern)

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-Ea}{R \cdot T}\right) dT$$

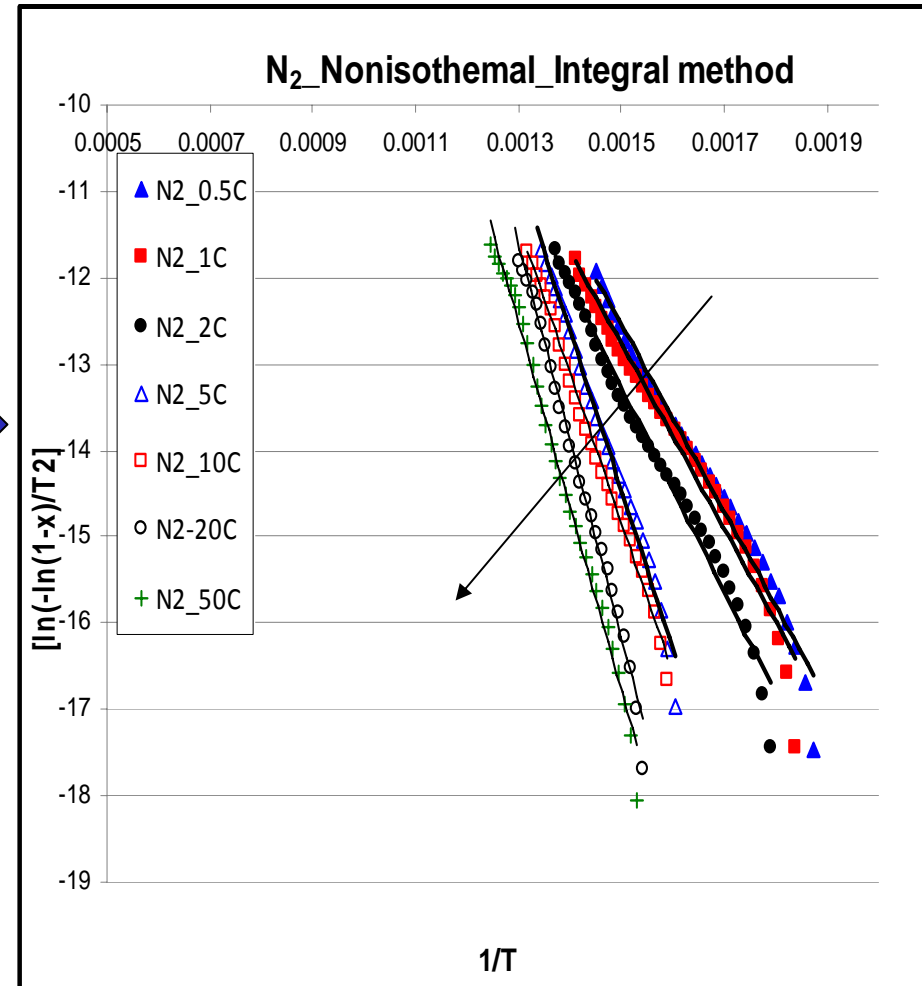
$$\ln\left[\frac{-\beta \cdot \ln(1-\alpha)}{R \cdot T^2}\right] - \ln\left(1 - \frac{2 \cdot R \cdot T}{Ea}\right) = \ln\left(\frac{A}{Ea}\right) - \left(\frac{Ea}{R \cdot T}\right)$$

Chen-Nuttall

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{A \cdot R}{Ea \cdot \beta}\right) - \left(\frac{Ea}{R \cdot T}\right)$$

Coats-Redfern

N ₂ _Nonisothermal_Integral method					
β	R ²	slope	Intercept	Ea	A
0.5	0.978	10837	3.714	90.098	222253.59
1	0.97	10708	3.302	89.022	290903.36
2	0.985	11818	4.46	98.254	2044218.8
5	0.988	18441	13.2	153.318	4.982E+10
10	0.995	17276	11.08	143.632	1.121E+10
20	0.991	22780	18.02	189.392	3.052E+13
50	0.991	21283	15.15	176.946	4.042E+12

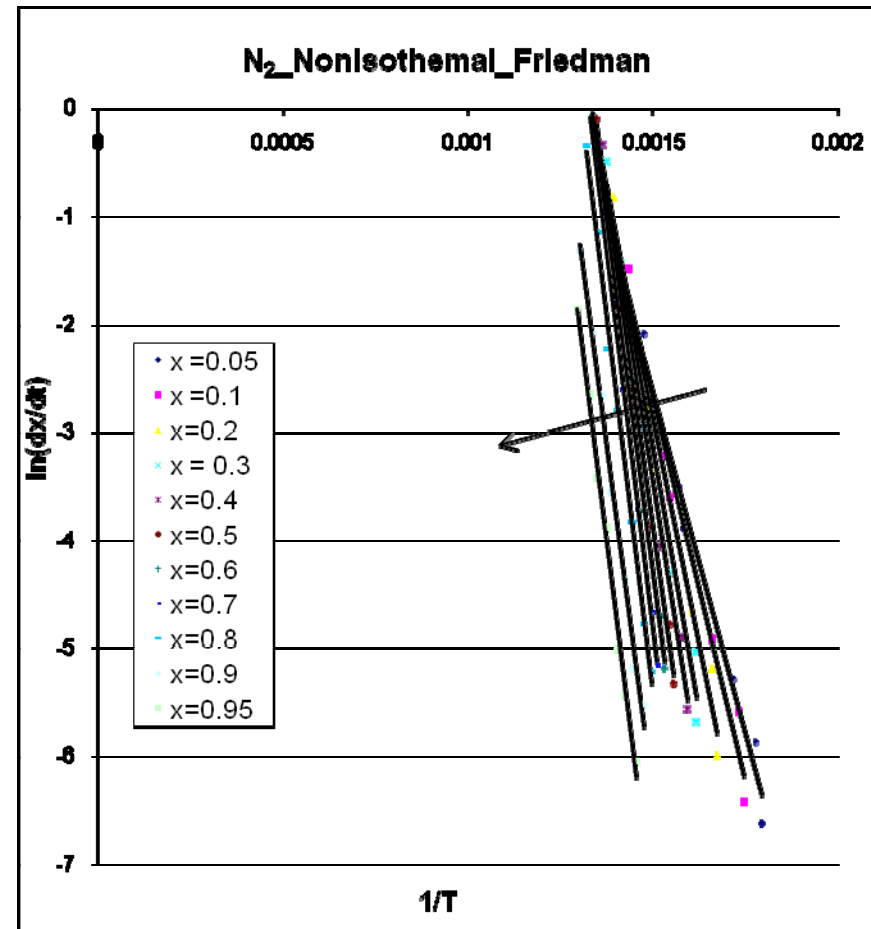


Kinetic study with TGA

Non-isothermal: Friedman method

$$\rightarrow \ln\left(\frac{d\alpha}{dt}\right) = \ln\left[A \cdot (1 - \alpha)\right] - \left(\frac{Ea}{R \cdot T}\right)$$

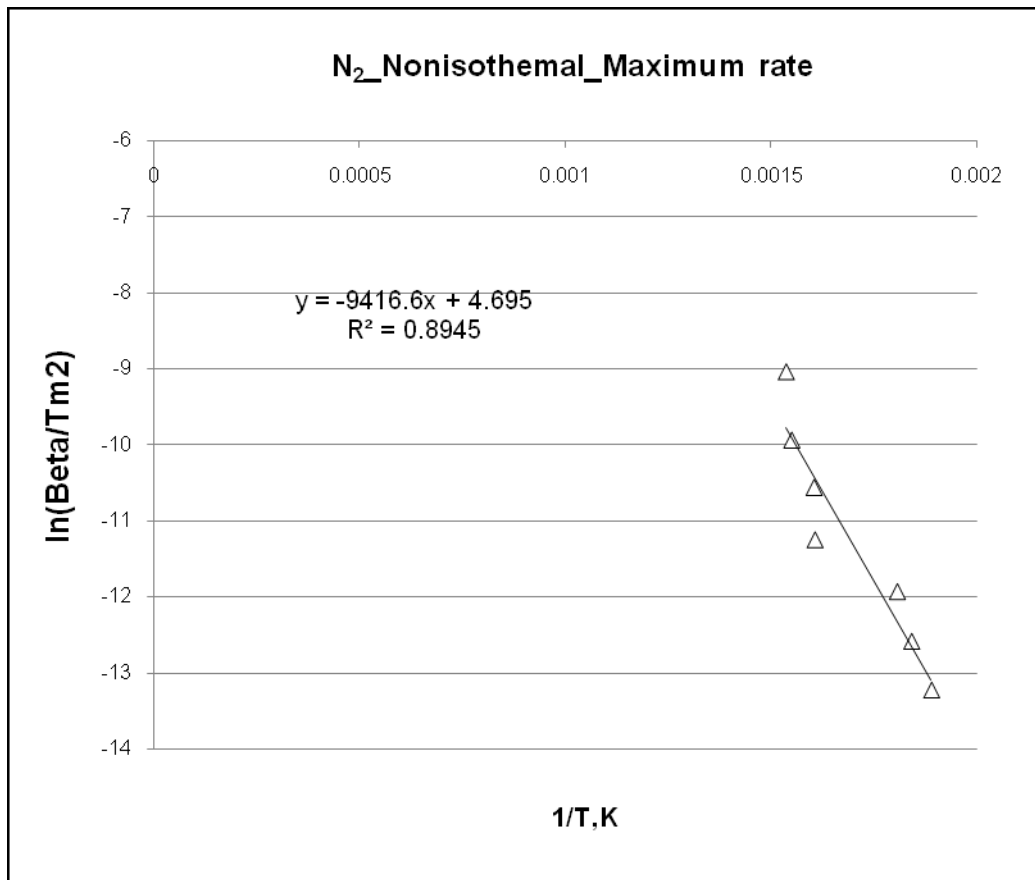
N ₂ _Nonisothermal_Friedman						
α	Slope	Intercept	R ²	Ea kJ/mol	A	LnA
0.05	12767	16.49	0.983	106.14	1.5E+07	16.54
0.1	14197	18.57	0.981	118.08	1.3E+08	18.68
0.2	16912	22.46	0.983	140.60	7.1E+09	22.68
0.3	19417	25.93	0.982	161.43	2.62E+11	26.29
0.4	21671	28.99	0.989	180.17	6.55E+12	29.50
0.5	24326	32.55	0.997	202.24	2.75E+14	33.24
0.6	26110	34.82	0.998	217.07	3.34E+15	35.74
0.7	28020	37.10	0.996	232.95	4.33E+16	38.30
0.8	27740	36.16	0.990	230.63	2.53E+16	37.77
0.9	25843	32.35	0.986	214.85	1.13E+15	34.65
0.95	27102	33.17	0.991	225.32	5.09E+15	36.16



Kinetic study with TGA

Non-isothermal: Maximum rate method (First order)

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{A \cdot R}{Ea}\right) - \left(\frac{Ea}{R \cdot T_m}\right)$$

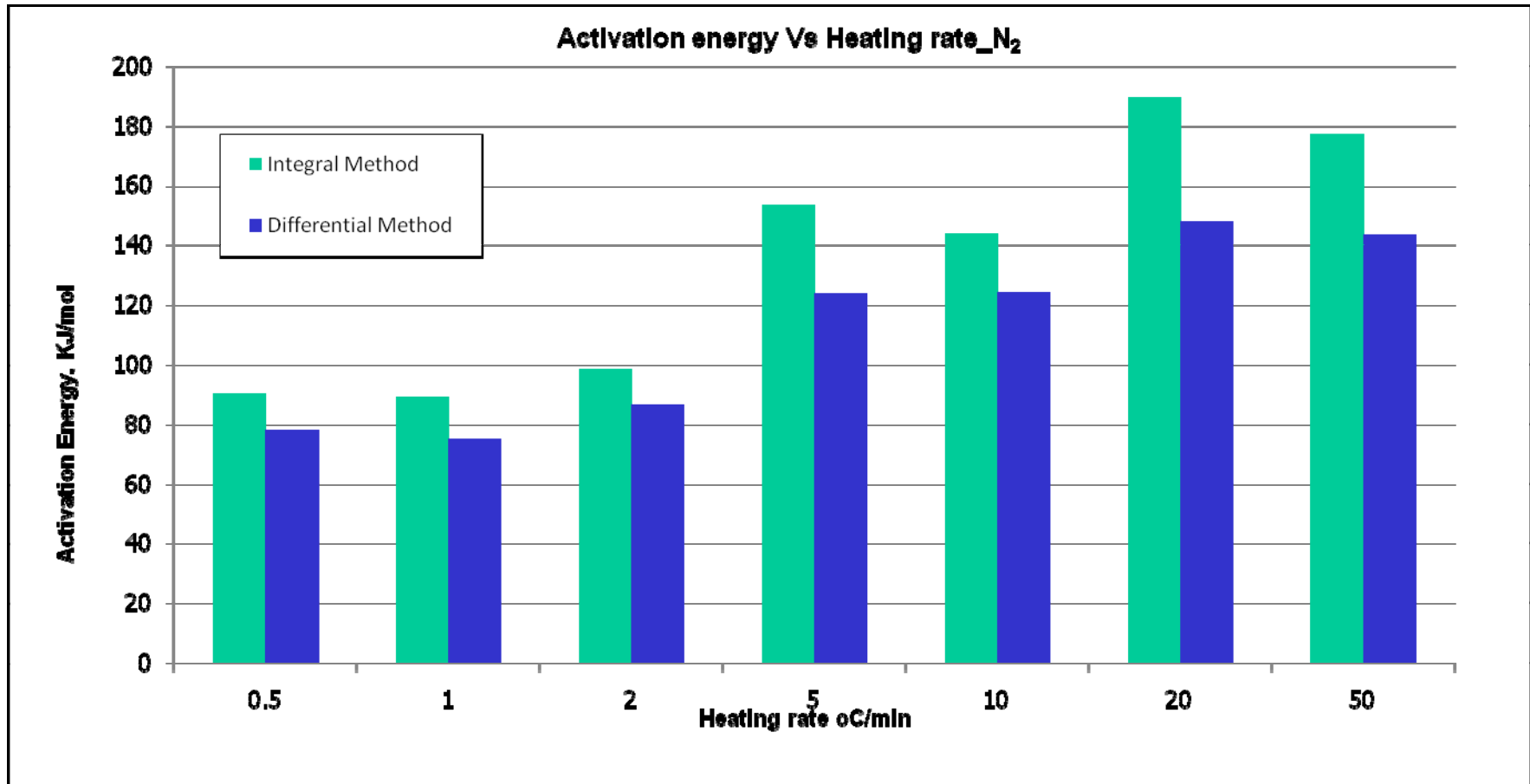


N ₂ _Nonisothermal_Maximum rate	
Ea, KJ/mol	78.2846
A	1.03E+06

Results and Discussion

Non-isothermal: Integral vs Differential method

Activation Energies

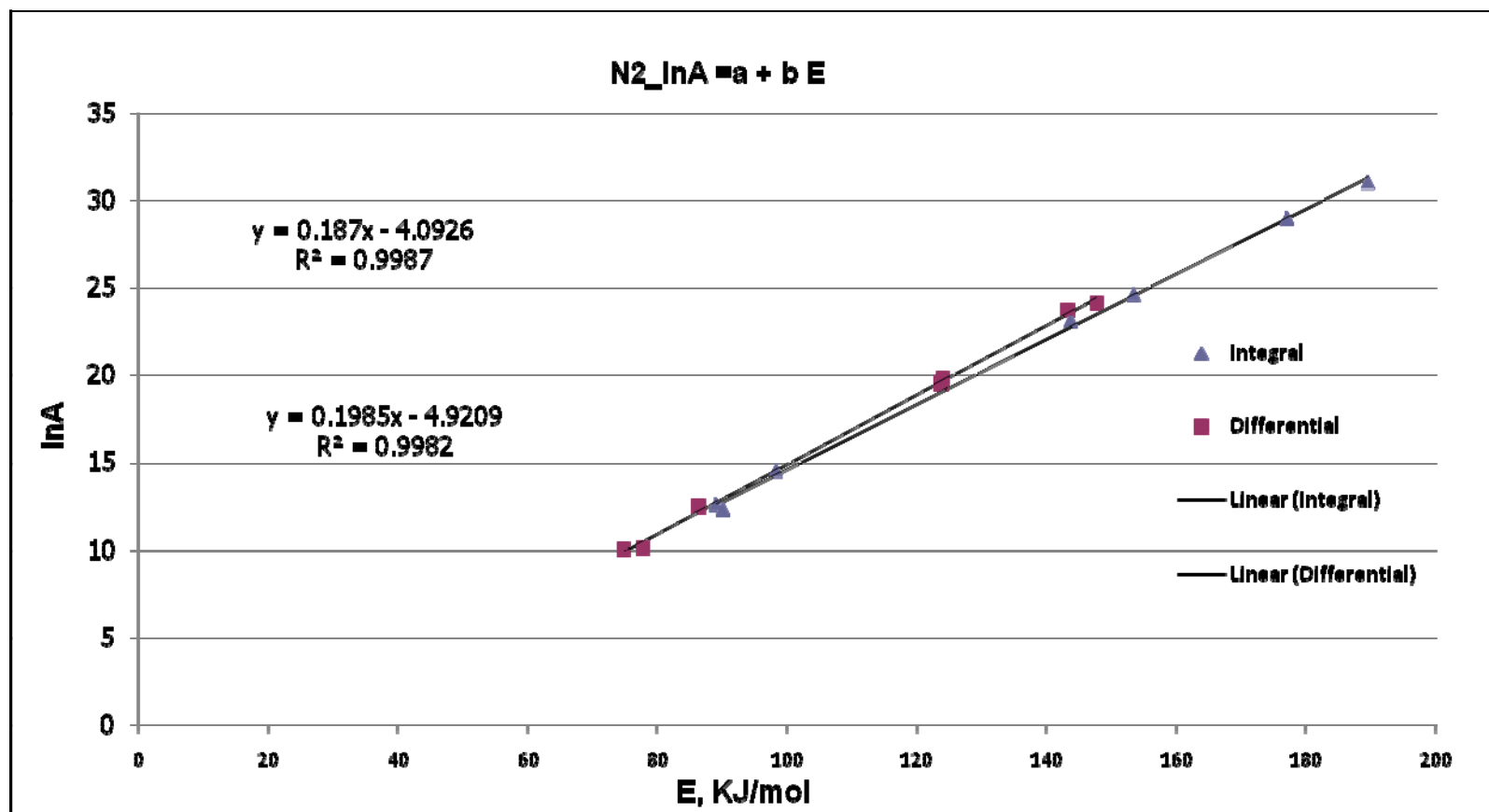


- Activation energy increases as heating rate increase
- Higher activation energy using the integral method

Results and Discussion

Non-isothermal: Integral vs Differential method

Trade-off between A and E [$\ln A = a + bE$]



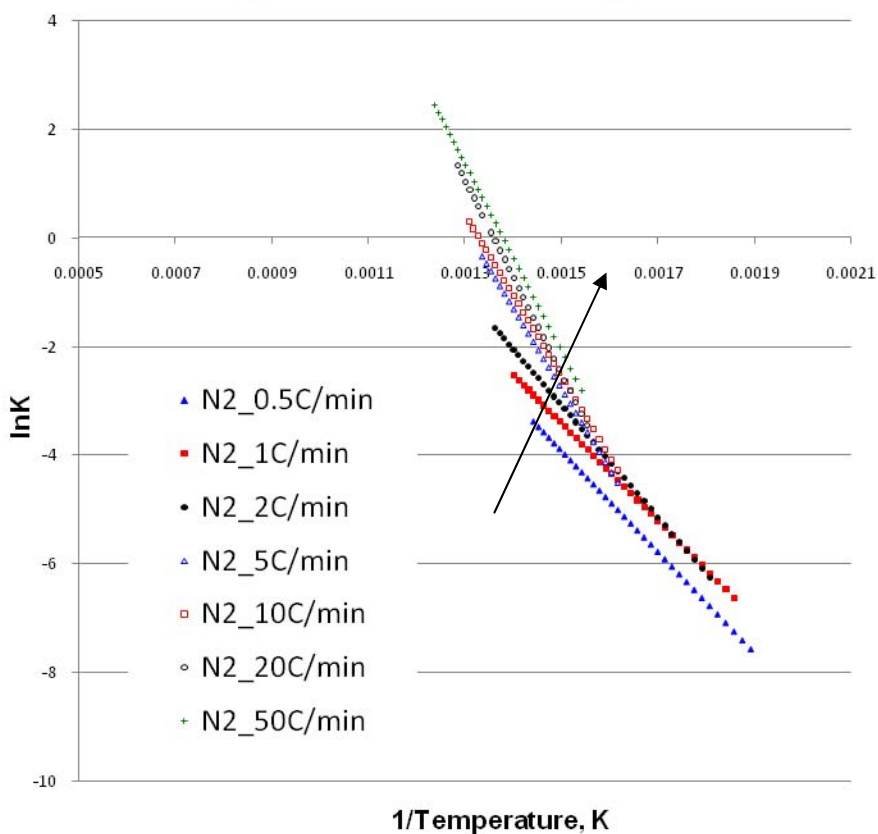
Good fit using both the methods

Results and Discussion

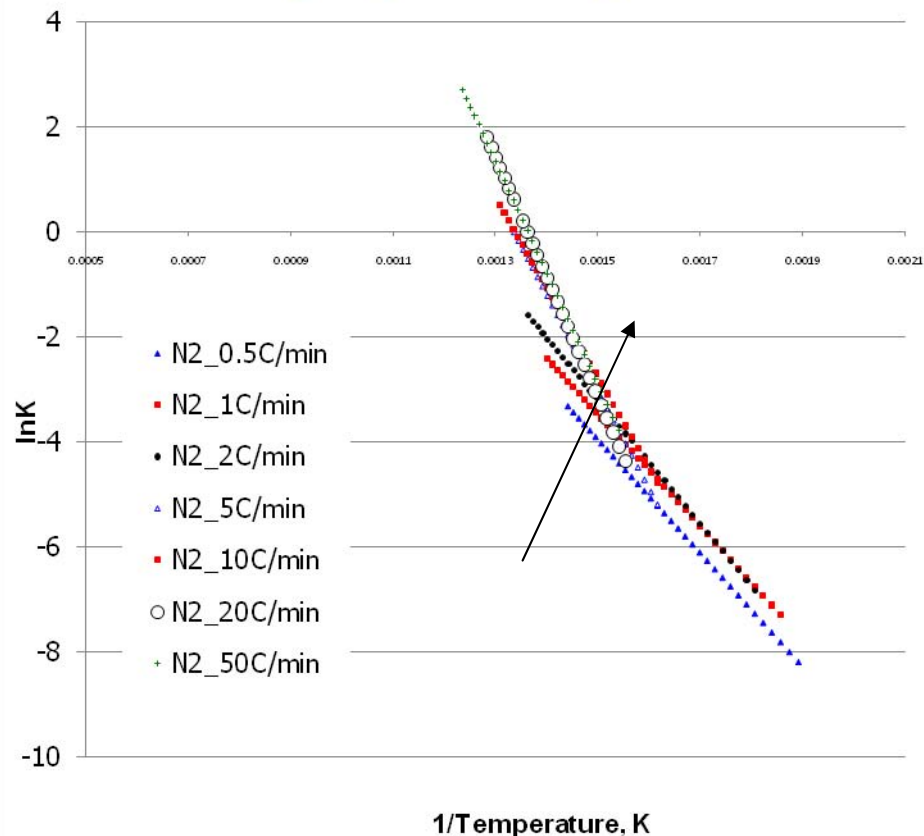
Non-isothermal: Integral vs Differential method

In K vs 1/T relationship

N2_Differential method_InK vs 1/T



N2_Integral method_InK vs 1/T



Both the methods suggest/support , pyrolysis is single stage process

Results and Discussion

Isothermal_N₂

- *Weight loss increases as temperature increase*
- *10-12% weight loss (TOC) at around 400-450 °C*
- *lnK vs 1/T plot suggests its single stage process*
- *Integral method gives 134 KJ/mol, activation energy*

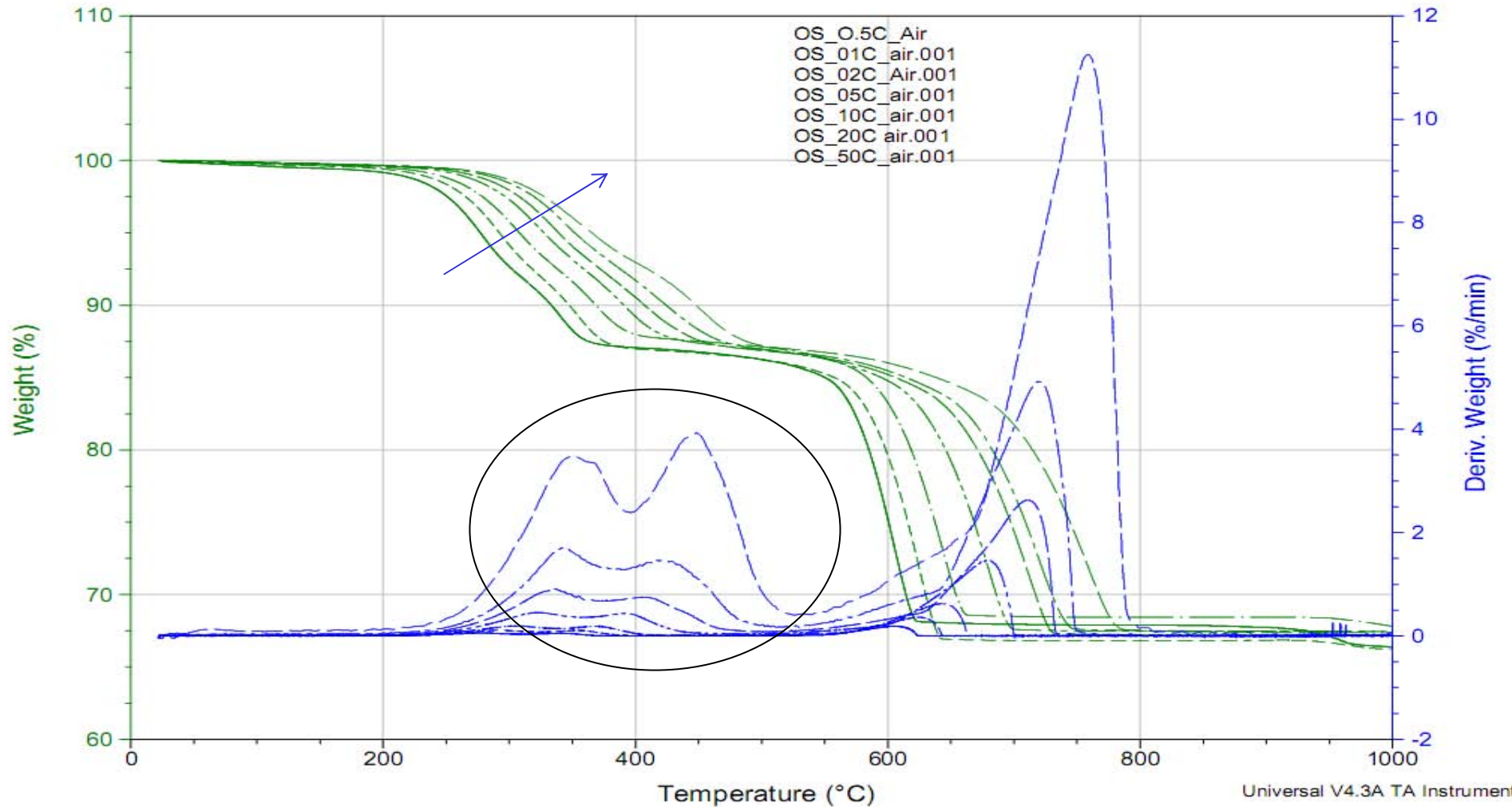
Results and Discussion

Non-isothermal_N₂

- 10-12% *weight loss (TOC)*
- *Maximum rate of weight loss is higher at higher temperature*
- *Pyrolysis temperature shifts to higher temperature as heating rate increase*
- *Four methods were used and they give distribution of activation energy*
 - *Differential – (74- 147, KJ/mol)*
 - *Integral – (89- 189, KJ/mol)*
 - *Friedman – (106- 233, KJ/mol)*
 - *Maximum rate method – (78, KJ/mol)*
- *Activation energy increases as heating rate increase*
- *Differential and integral methods fit the data best*
- *Integral method gives higher activation energy than the differential method*

Kinetic study with TGA

Non-isothermal_Air

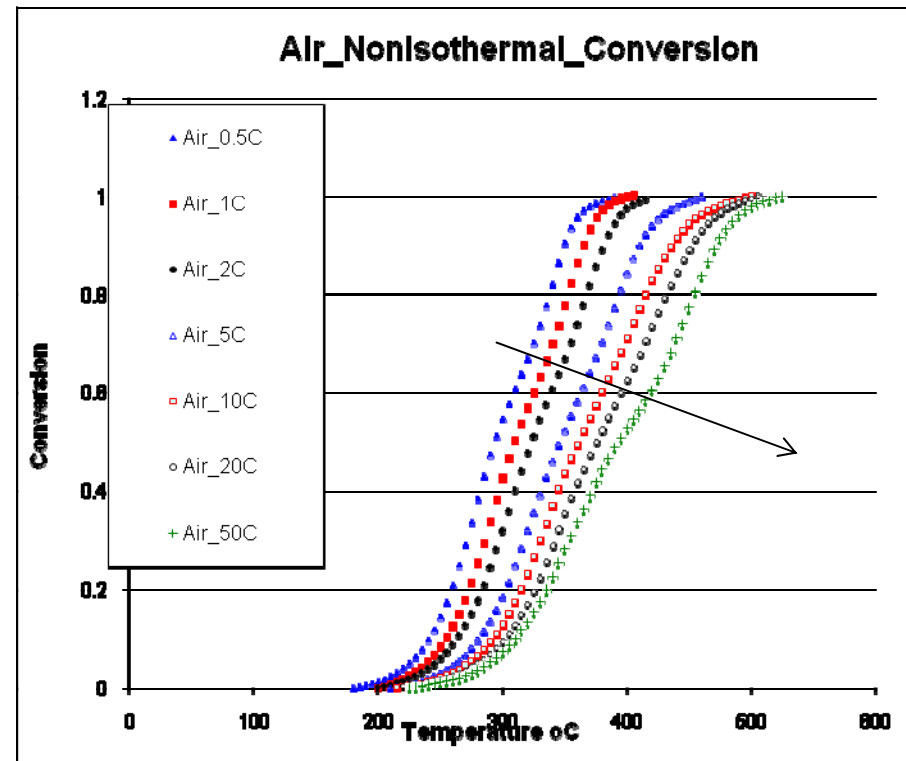


Results and Discussion

Isothermal_Air

Integral method_Air	
Ea, KJ/mol	A
100.47469	5.1E+07

Non-isothermal_Air



Conclusions

- *TGA gives intrinsic kinetics with effective kinetic parameters*
- *Pyrolysis of Mahogany oil shale is single stage and first order process*
- *Integral method gives higher activation energy than differential method*
- *Friedman approach gives highest activation energy values*
- *Kinetic parameters are in the range of values reported in the literature*
- *Pyrolysis, mechanism and kinetic parameters depend on origin and geological condition*
- *More weight loss in air environment than N₂ environment*
- *Activation energy is less in air environment than N₂ for isothermal*

Acknowledgement

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www.heavyoil.utah.edu
- *Petroleum Research Center members*
www.perc.utah.edu

Thank you

➤ Back up