TG/DTG studies of Fresh Fishing Net and Waste Fishing Net

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Introduction

▶ Ocean pollution poses serious environmental problems in Korea

→ Need to treat marine wastes in more environmentally friendly manner

▶ Main composition of marine wastes

→ Waste fishing nets (WFN), waste fishing tackles and waste lopes

▶ Characteristics of marine wastes

→ Floating, deposition and moving on seashore

→ Damage of marine ecosystem, cause of loss in the fishing industry

- Fishing nets: production, consignment(1997~2000 yr) [unit : Ton]

Year	Production	Consignment	Remark
1997	11,057	11,571	-
1998	9,607	9,895	-
1999	10,066	10,442	-
2000	10,916	11,033	-

자료 : 통계청, “한국산업통계연보”, 2001, p450

Experimental

- **Thermogravimetric Analysis**
  → Thermogravimetric Analyzer (TGA; Cahn, TG-2171)
  → Sample : Fresh Fishing Net(Nylon-6), Waste Fishing Net(Nylon-6)
  → Mass : 400 mg
  → Heating rates : 0.5~2.0 ℃/min (<500℃)
- **M**icro-scale tubing reactor
  → Reaction temperature : 440℃
  → Reaction time : 60~100 min
- Product Analysis
  → Carbon number distribution : GC (Younglin, M600D)
  → FT-IR (Thermo Mattson, 60AR)

Experimental

- Elemental analysis : fresh fishing nets(FFN), waste fishing nets**(WFN)**

	Element (wt%)					H/C ratio
	C	H	N	S	O	
FFN	62.68	10.66	12.24	–	14.42	2.04
WFN	56.28	8.86	10.92	0.05	14.83	1.89

Activation Energy

- **Conversion: X**

$$X = \frac{W - W_t}{W_0 - W_t} \qquad (1)$$

- **Pyrolysis rate:**

$$\frac{dX}{dt} = k\, f(X) \qquad (2)$$

- **Reaction constant: k**

$$k = A \exp\left(\frac{-E}{RT}\right) \qquad (3)$$

- **Conversion function: f(X)**

$$f(X) = (1 - X)^n \qquad (4)$$

- Eq.(3), Eq.(4) → Eq.(2)

$$\frac{dX}{dt} = A \exp\left(\frac{-E}{RT}\right)(1 - X)^n \qquad (5)$$

- **Take logarithm Eq.(6)**

$$\ln\left(\frac{dX}{dt}\right) = \ln\left[A(1 - X)^n\right] - \frac{E}{R}\frac{1}{T} \qquad (6)$$

A : pre-exponential factor (sec^{-1})

n : reaction order

E : activation energy (kJ/mol)

R : gas constant (8.314Jg/mol K)

T : temperature (K)

t : time (sec)

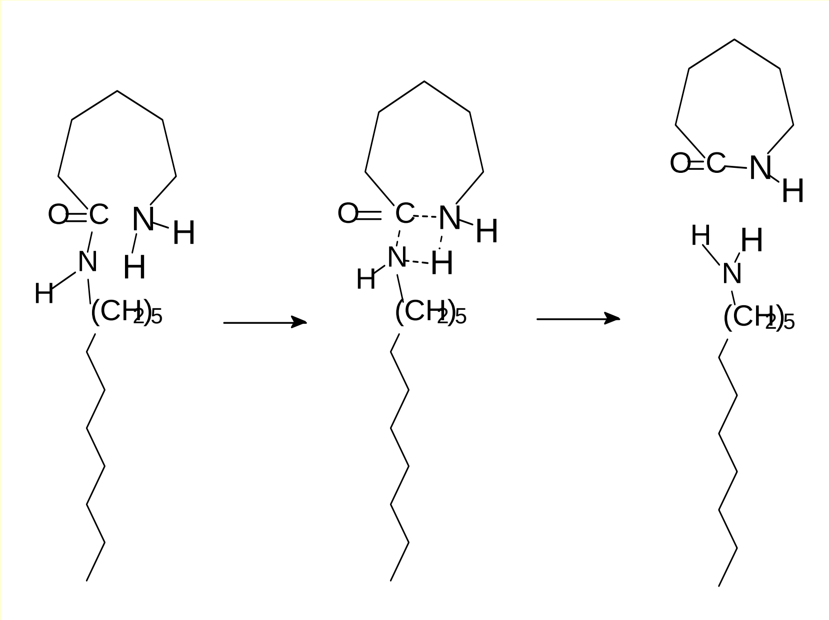
- **Intercept of Eq.(6) is**

$$\ln\left[A(1 - X)^n\right] = \ln(A) + n\ln(1 - X) \qquad (7)$$

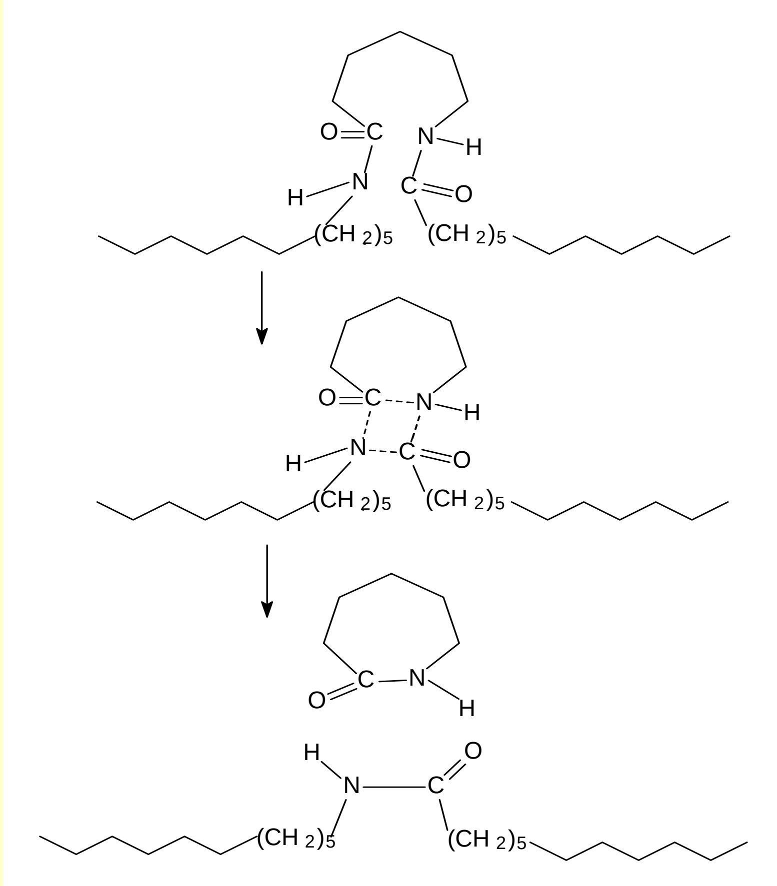
Decomposition mechanism of Nylon -6:

R.S Lehrle et al., *Polymer Degradation and Stability*, **67**, 21(2000)

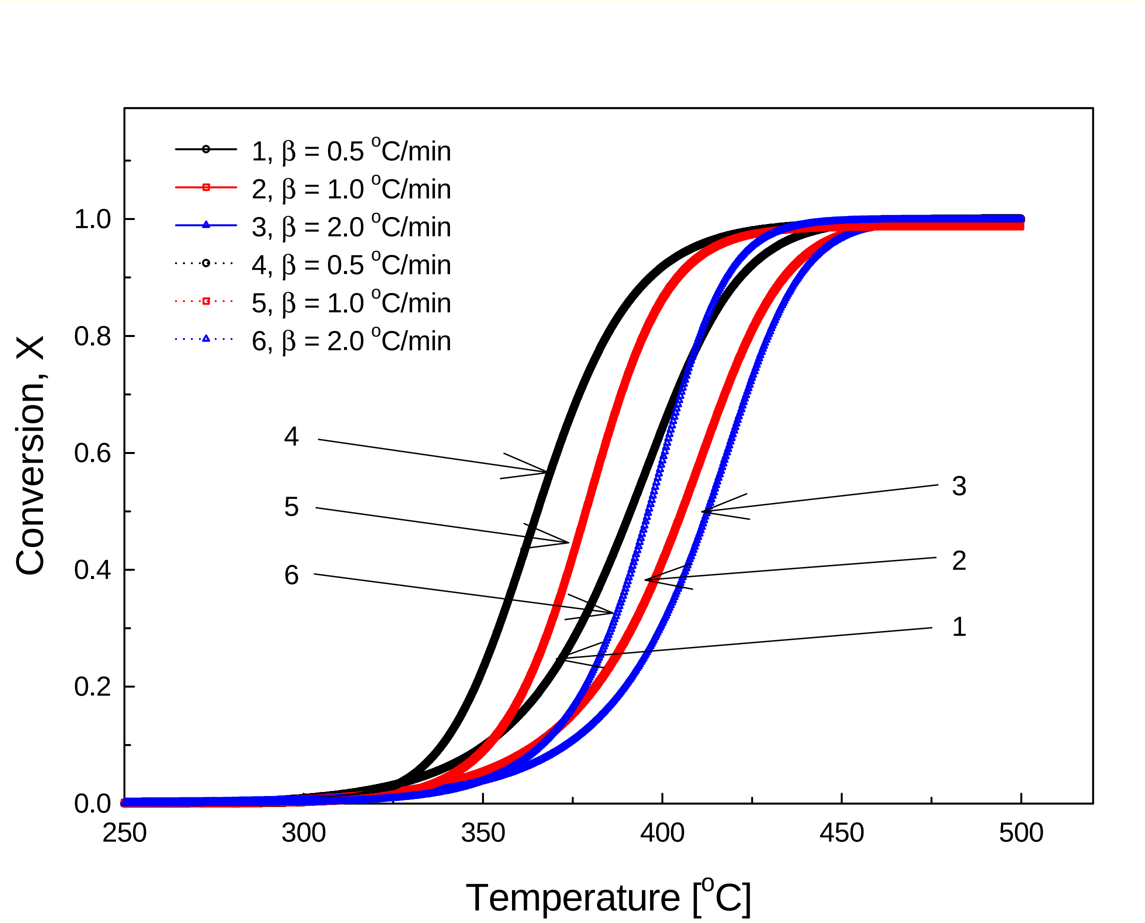
(a) Initial fast rate



(b) Slow rate



TGA curves : FFN and WFN



1; FFN; β = 0.5°C/min,

2; FFN; β = 1.0°C/min,

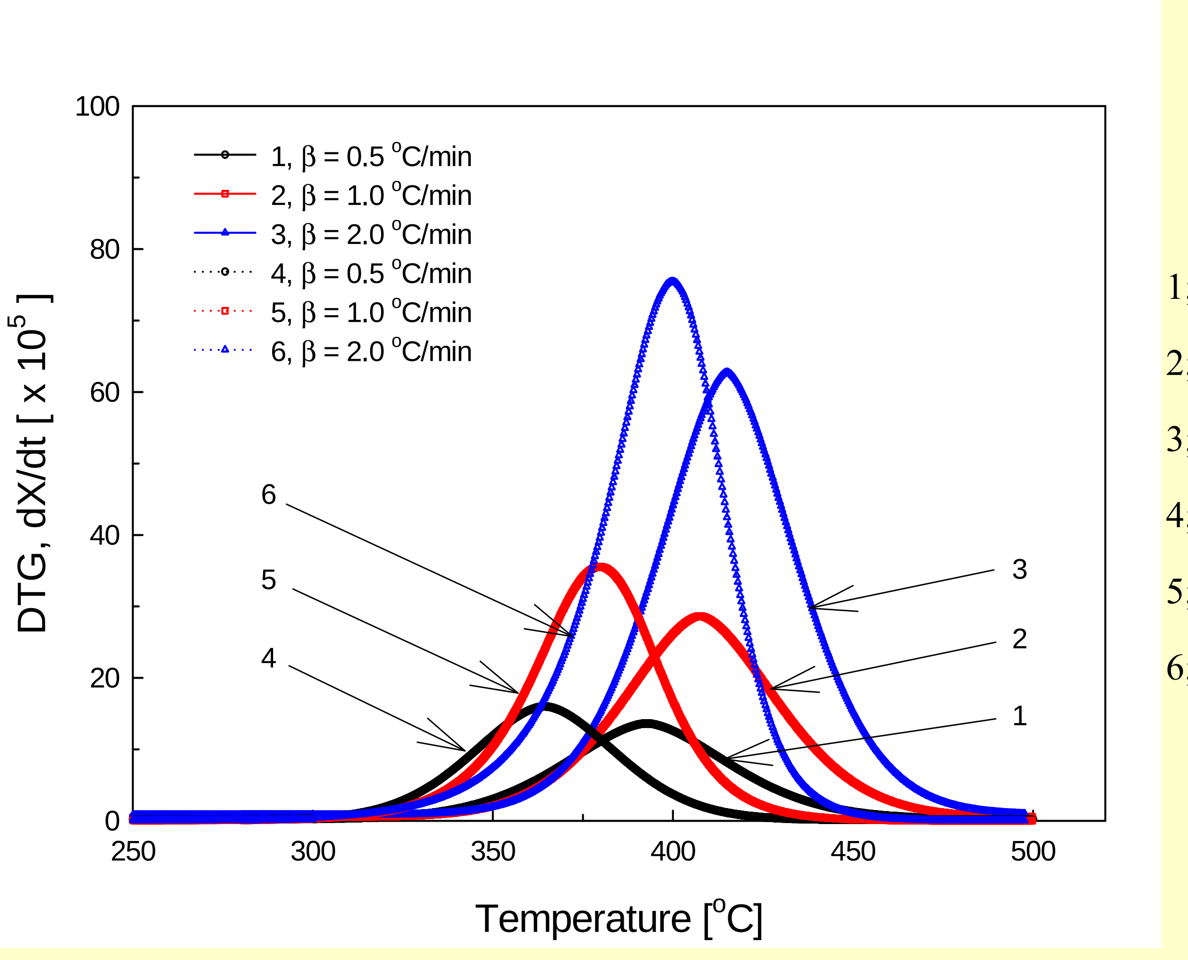
3; FFN; β = 2.0°C/min,

4; WFN; β = 0.5°C/min,

5; WFN; β = 1.0°C/min,

6; WFN; β = 2.0°C/min.

DGT curves : FFN and WFN



1; FFN; β = 0.5°C/min,

2; FFN; β = 1.0°C/min,

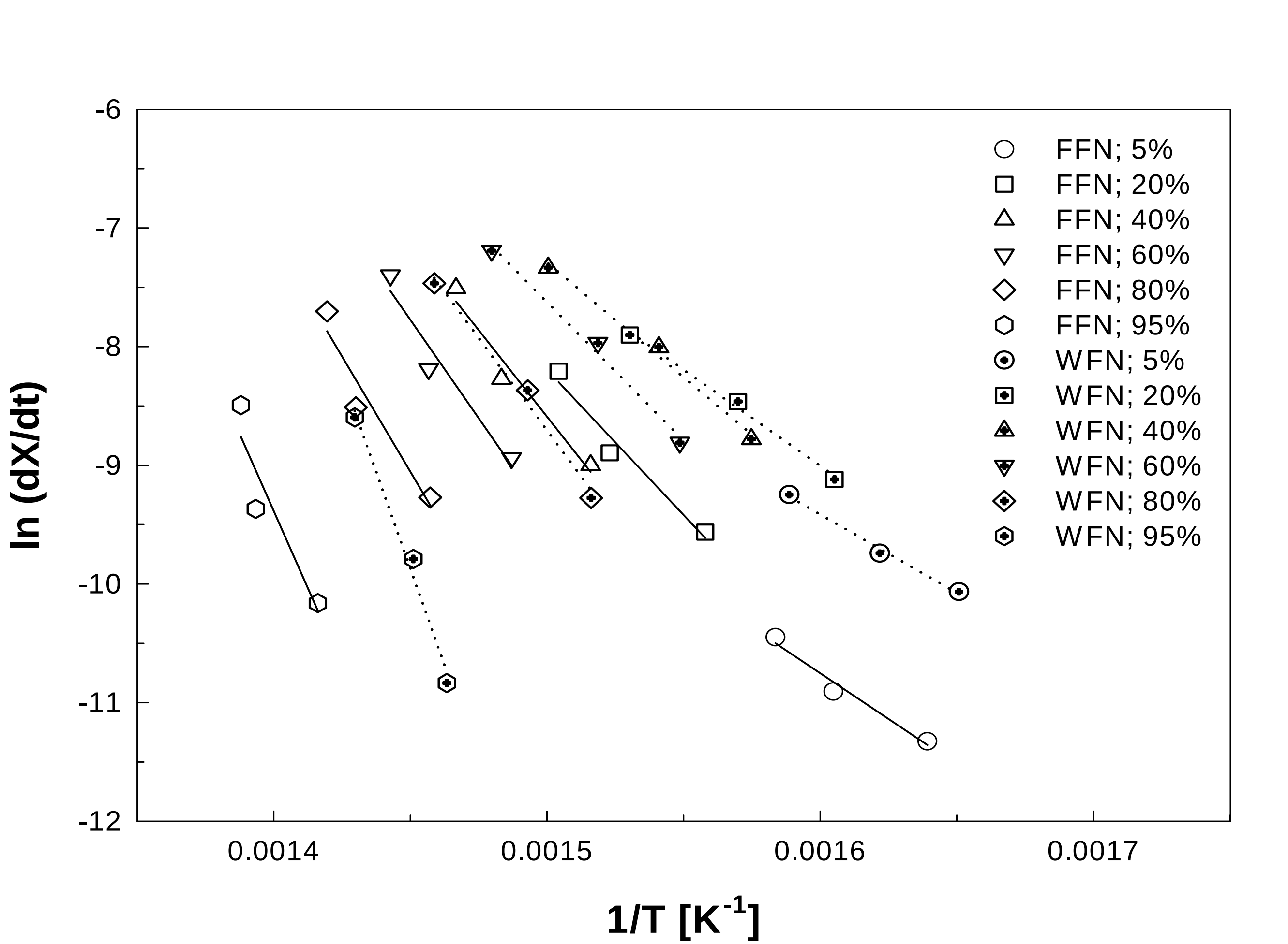
3; FFN; β = 2.0°C/min,

4; WFN; β = 0.5°C/min,

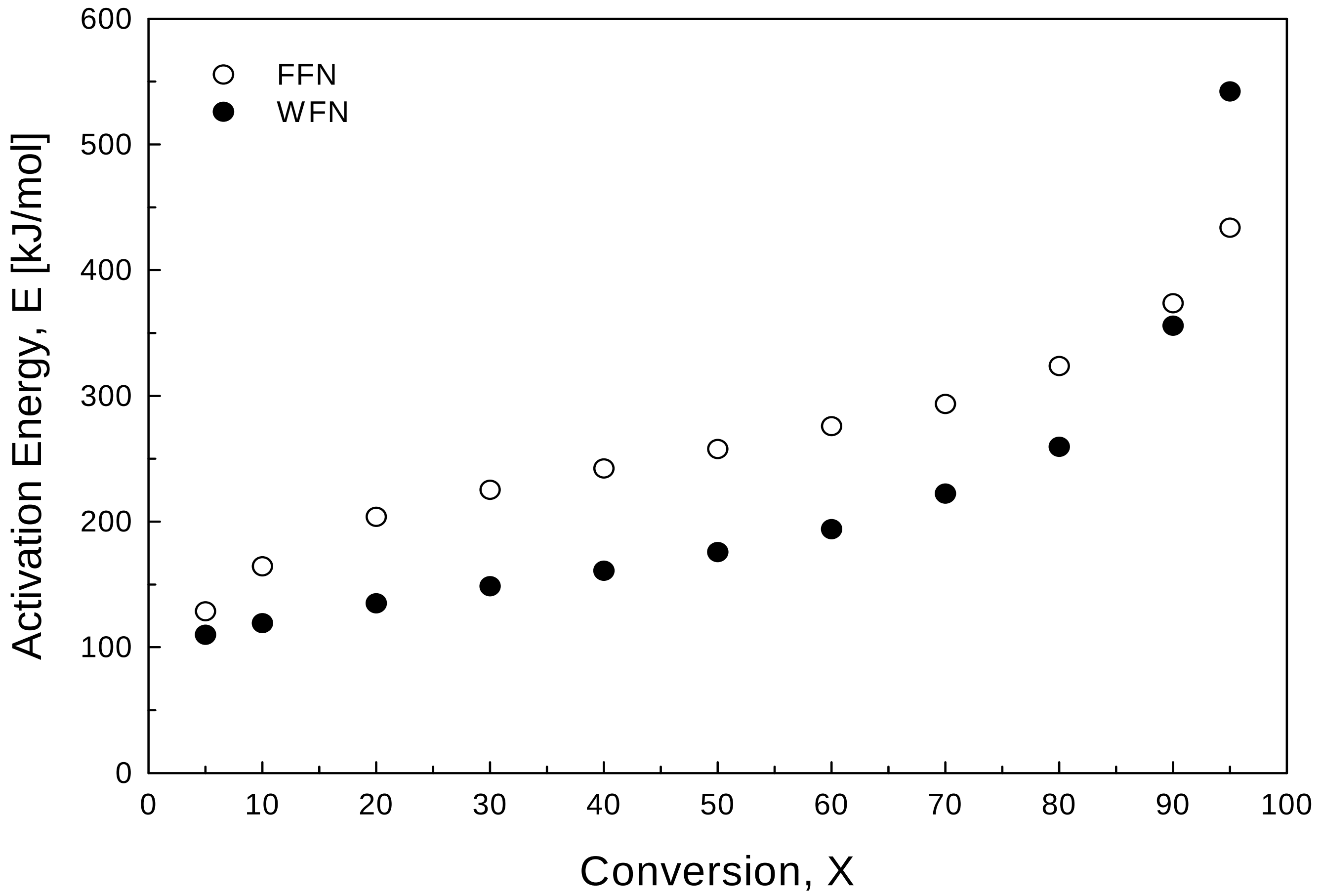
5; WFN; β = 1.0°C/min,

6; WFN; β = 2.0°C/min.

Application of equation 5 : 0.5~2.0 °C/min



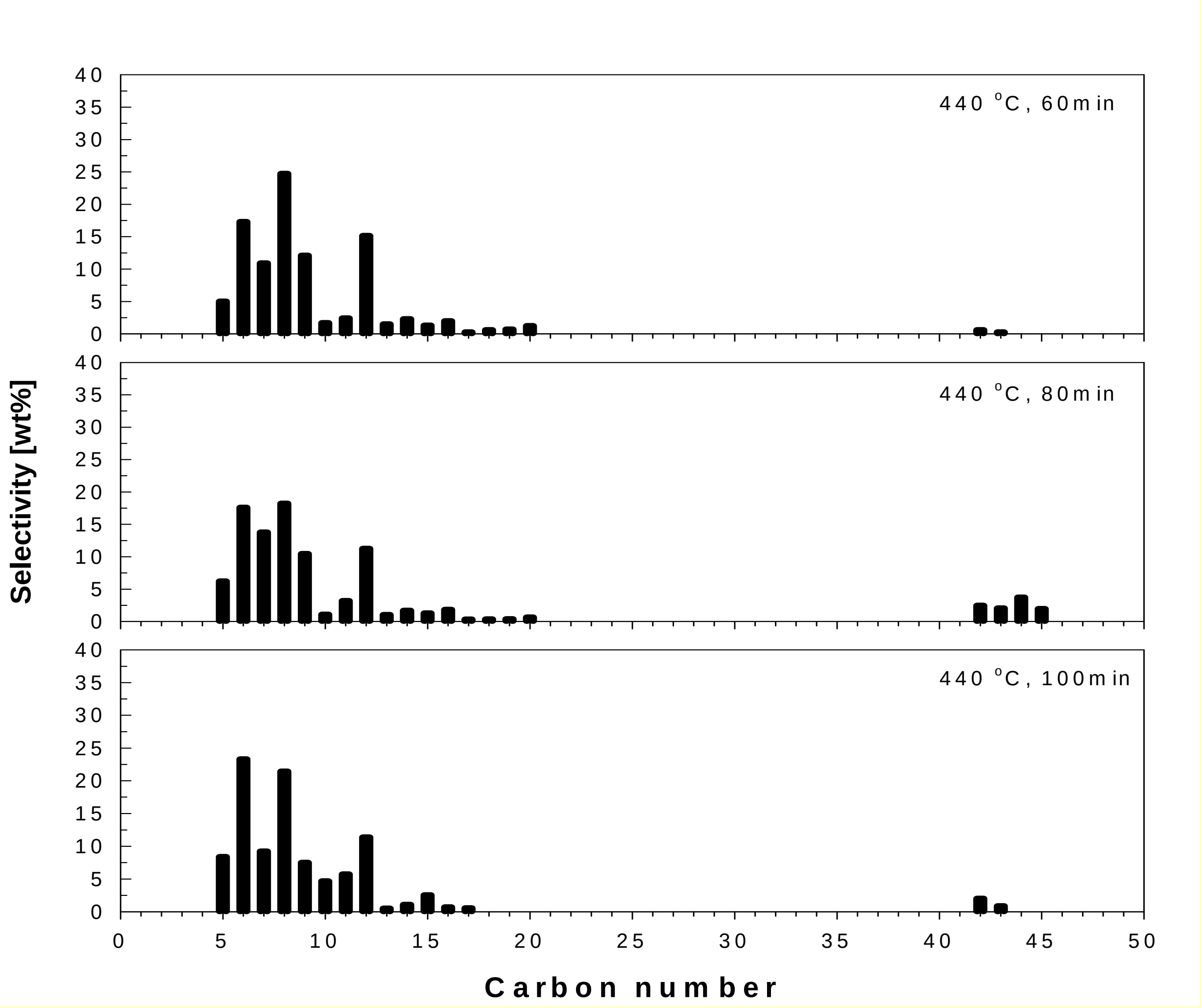
Calculated activation energies



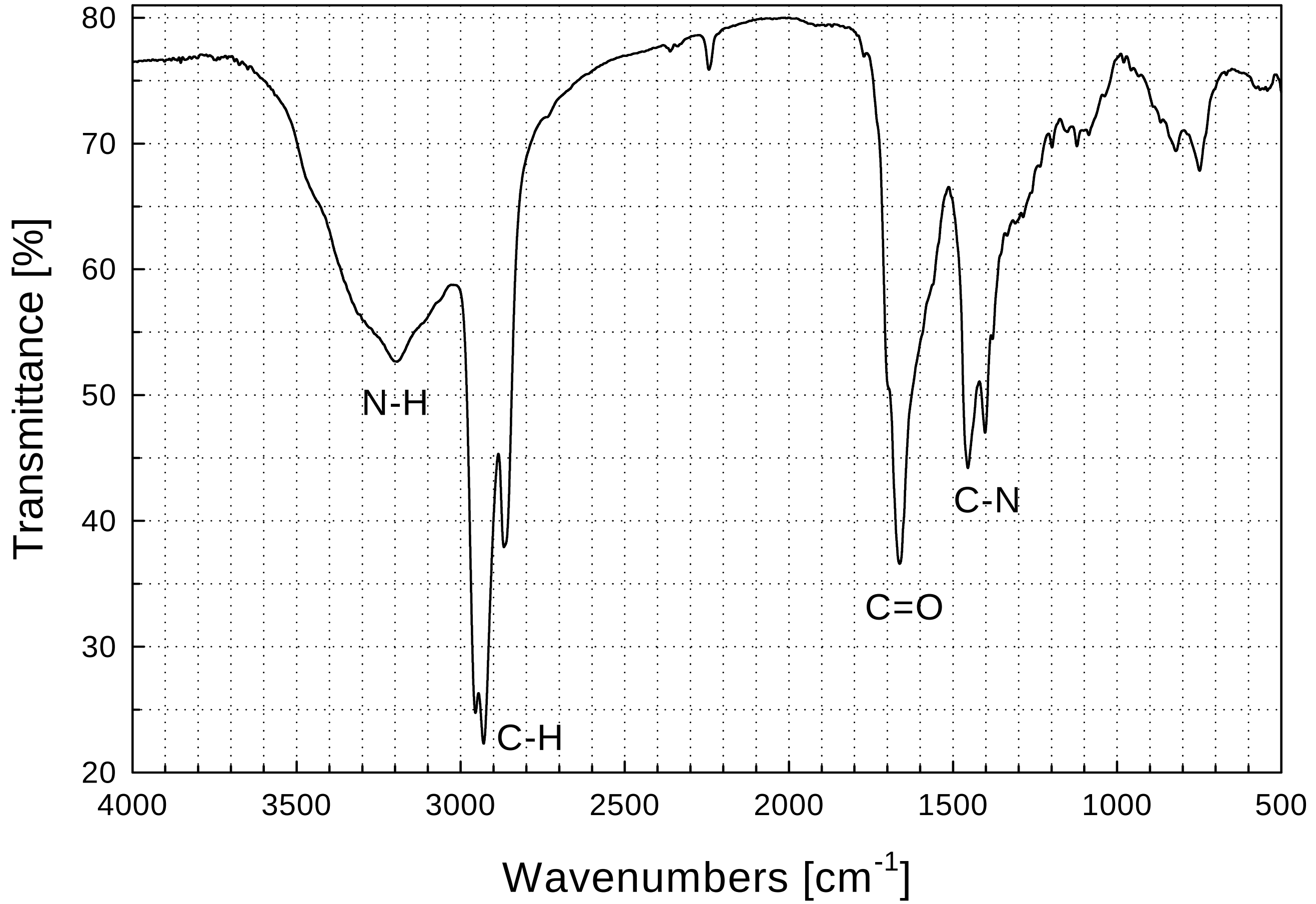
Application of Eq. (7) to calculate pre -exponential factor

		Conversion [%]										
		5	10	20	30	40	50	60	70	80	90	95
FFN	0th	1.17×10^{6}	1.57×10^{6}	2.45×10^{12}	1.06×10^{14}	1.78×10^{15}	2.03×10^{16}	3.23×10^{17}	4.15×10^{18}	3.74×10^{20}	5.95×10^{23}	4.38×10^{27}
	1st	1.23×10^{6}	1.75×10^{6}	3.07×10^{12}	1.52×10^{14}	2.96×10^{15}	4.06×10^{16}	8.07×10^{17}	1.38×10^{19}	1.87×10^{21}	5.95×10^{24}	8.76×10^{28}
WFN	0th	1.23×10^{5}	9.61×10^{5}	2.25×10^{7}	2.88×10^{8}	2.67×10^{9}	3.49×10^{10}	7.58×10^{11}	8.35×10^{13}	3.44×10^{16}	5.39×10^{23}	5.84×10^{36}
	1st	1.29×10^{5}	1.07×10^{6}	2.82×10^{7}	4.12×10^{8}	4.46×10^{9}	6.98×10^{10}	1.90×10^{12}	2.78×10^{14}	1.72×10^{17}	2.39×10^{24}	1.17×10^{38}

Carbon number distribution : 440℃, 60~100 min



IR -spectra for FFN : 440°C , 100 min



Conclusion

- The apparent activation energies increased with an increase of conversion. The average activation energy for **FFN was 266 kJ mol^{-1}**, while that of **WFN was 220 kJ mol^{-1}**.
- Pre-exponential factor was **between 10^{12} and 10^{21} sec^{-1}** when the slope of thermogravimetric curves was almost linear.
- The carbon number of C_6 like caprolactam was slightly increased with the increase of reaction time, but the selectivity of specific hydrocarbons was not observed from the pyrolyzed oil.