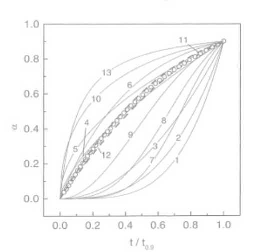
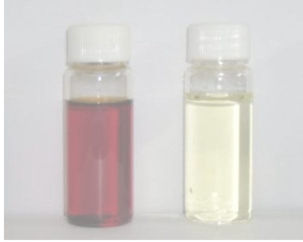
Polymer Pyrolysis





2014. 9. 23. SNU Presentation

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Pyrolysis Research Laboratory

Hallym University

Contents

1. Introduction

Introduction: Definition of pyrolysis

Pyrolysis = Pyro + Lysis

Thermal cracking of polymers into smaller molecules

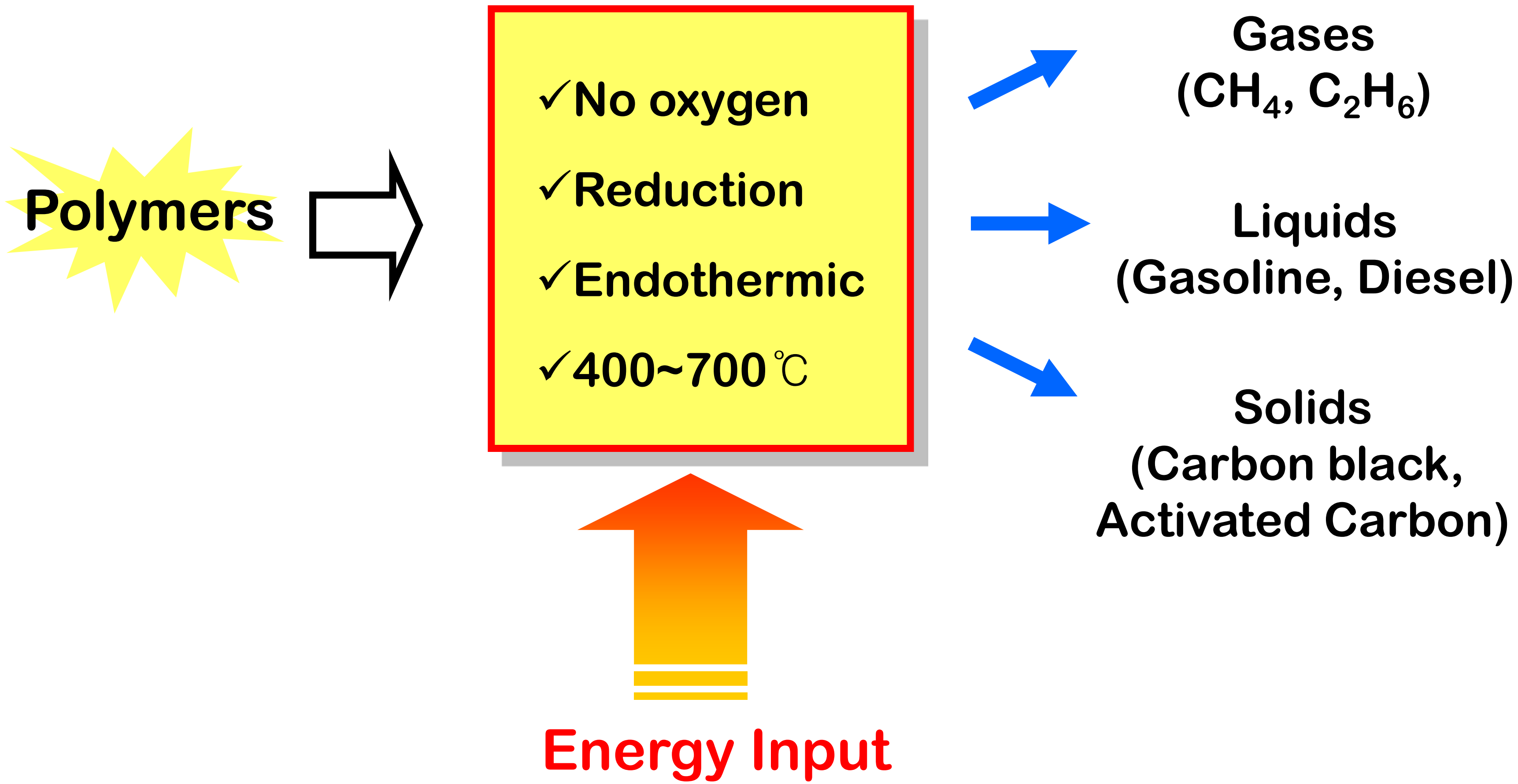
Reverse Reaction

Polymerization

Introduction: Basic Principles

- ❖ Attacking the weakest bond
  - ✓ Related to bond dissociation energy
    - C-C, C-H, C-O, C-Cl
- ❖ More thermal energy input yields lower molecular weight compounds
  - ✓ Crashing walnut with hammer!

Introduction: Conceptual Reaction



Polymers

- ✓No oxygen
- ✓Reduction
- ✓Endothermic
- ✓400~700℃

Energy Input

Gases
(CH_4, C_2H_6)

Liquids
(Gasoline, Diesel)

Solids
(Carbon black,
Activated Carbon)

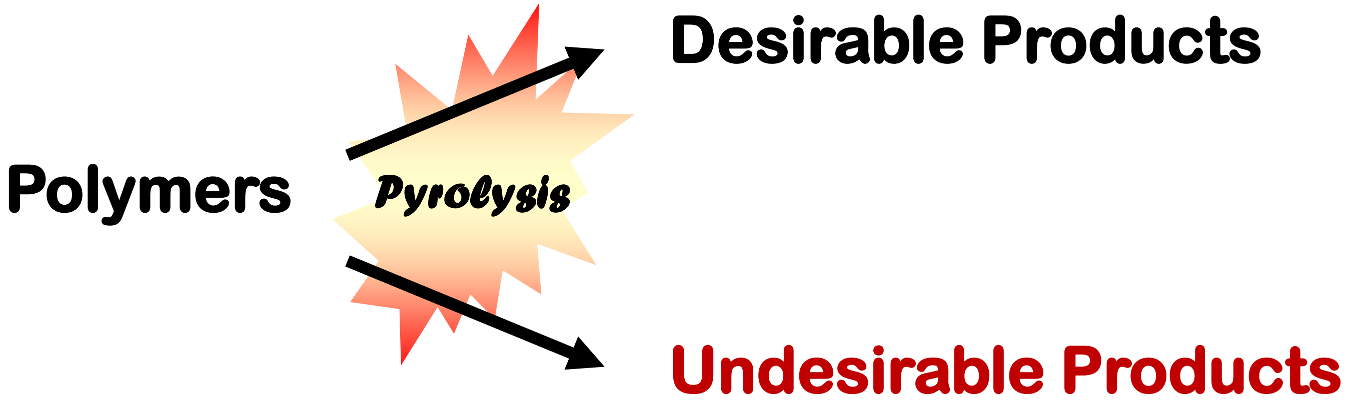
Design Target of Pyrolysis Reaction

- **Minimization of Energy Input**
- **Maximization of Valuable by-products**

2. Pyrolysis Mechanisms

Why pyrolysis mechanism is important?

- Pyrolysis mechanism can elucidate **PATHWAY** to ***Valuable Products***



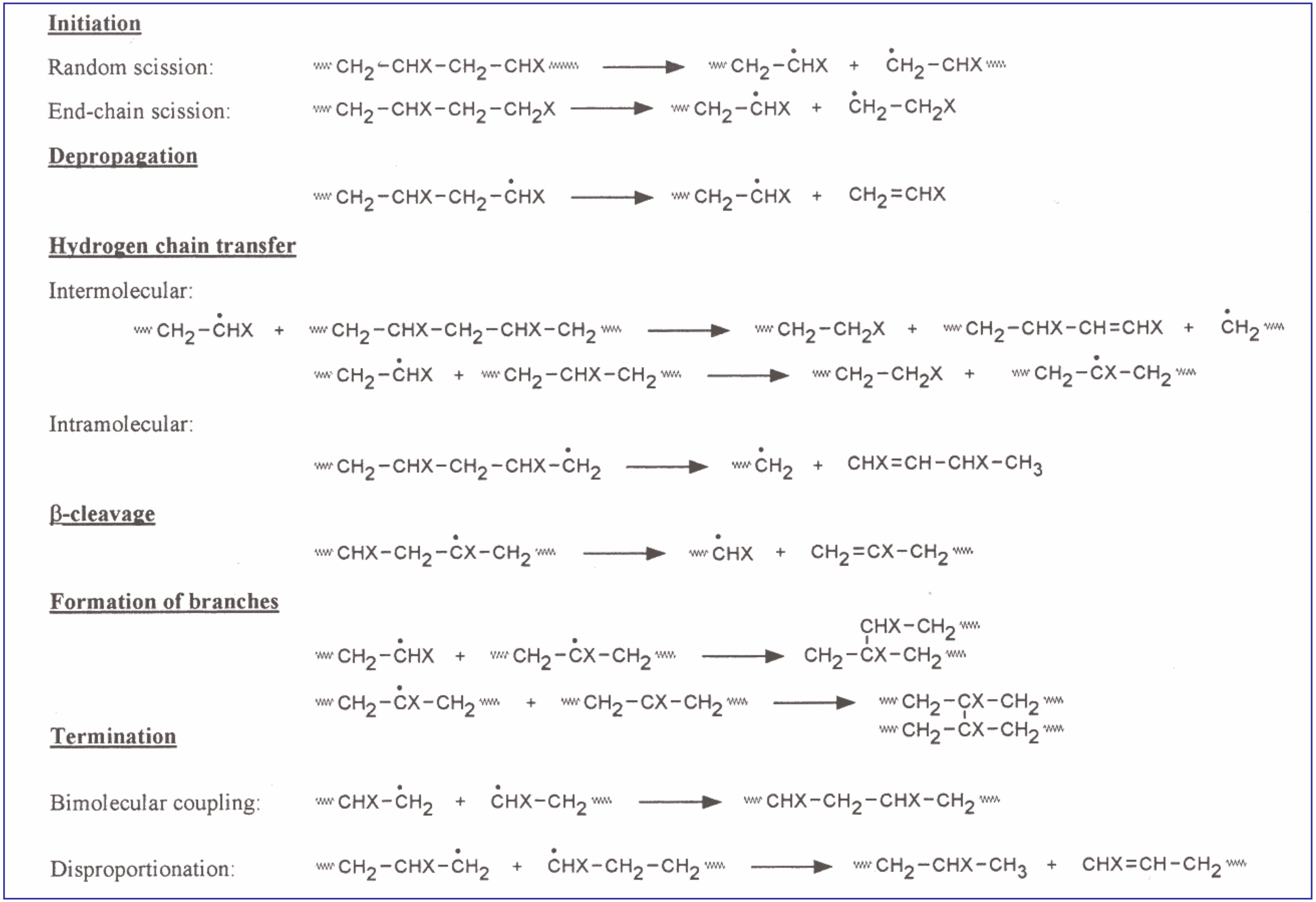
Polymers

Pyrolysis

Desirable Products

Undesirable Products

Why pyrolysis mechanism is important?



Initiation

Random scission: $\sim CH_2-CHX-CH_2-CHX\sim \longrightarrow \sim CH_2-\dot{C}HX + \dot{C}H_2-CHX\sim$

End-chain scission: $\sim CH_2-CHX-CH_2-CH_2X \longrightarrow \sim CH_2-\dot{C}HX + \dot{C}H_2-CH_2X$

Depropagation

$$\sim CH_2-CHX-CH_2-\dot{C}HX \longrightarrow \sim CH_2-\dot{C}HX + CH_2=CHX$$

Hydrogen chain transfer

Intermolecular:

$$\sim CH_2-\dot{C}HX + \sim CH_2-CHX-CH_2-CHX-CH_2\sim \longrightarrow \sim CH_2-CH_2X + \sim CH_2-CHX-CH=CHX + \dot{C}H_2\sim$$

$$\sim CH_2-\dot{C}HX + \sim CH_2-CHX-CH_2\sim \longrightarrow \sim CH_2-CH_2X + \sim CH_2-\dot{C}X-CH_2\sim$$

Intramolecular:

$$\sim CH_2-CHX-CH_2-CHX-\dot{C}H_2 \longrightarrow \sim \dot{C}H_2 + CHX=CH-CHX-CH_3$$

β-cleavage

$$\sim CHX-CH_2-\dot{C}X-CH_2\sim \longrightarrow \sim \dot{C}HX + CH_2=CX-CH_2\sim$$

Formation of branches

$$\sim CH_2-\dot{C}HX + \sim CH_2-\dot{C}X-CH_2\sim \longrightarrow \begin{array}{l} \quad\quad\ \ CHX-CH_2\sim \\ \quad\quad\ \ \ | \\ CH_2-CX-CH_2\sim \end{array}$$

$$\sim CH_2-\dot{C}X-CH_2\sim + \sim CH_2-CX-CH_2\sim \longrightarrow \begin{array}{l} \sim CH_2-CX-CH_2\sim \\ \quad\quad\quad\ \ | \\ \sim CH_2-CX-CH_2\sim \end{array}$$

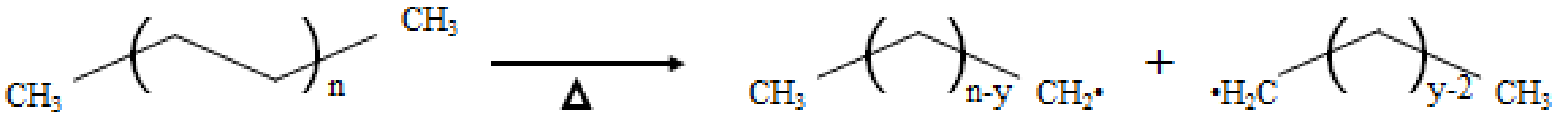
Termination

Bimolecular coupling: $\sim CHX-\dot{C}H_2 + \dot{C}HX-CH_2\sim \longrightarrow \sim CHX-CH_2-CHX-CH_2\sim$

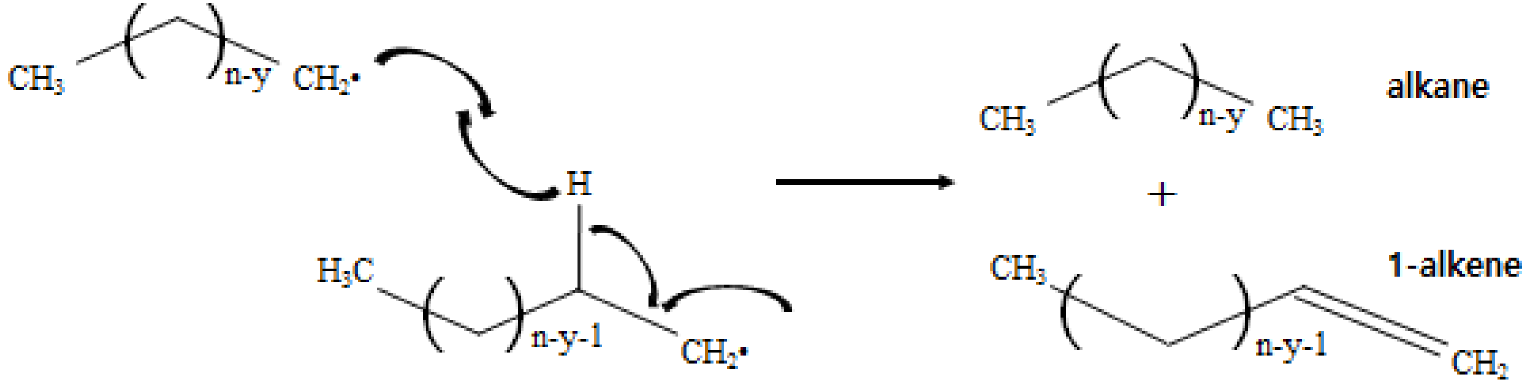
Disproportionation: $\sim CH_2-CHX-\dot{C}H_2 + \dot{C}HX-CH_2-CH_2\sim \longrightarrow \sim CH_2-CHX-CH_3 + CHX=CH-CH_2\sim$

Pyrolytic Degradation Pathways of Polyethylene

1. Initiation

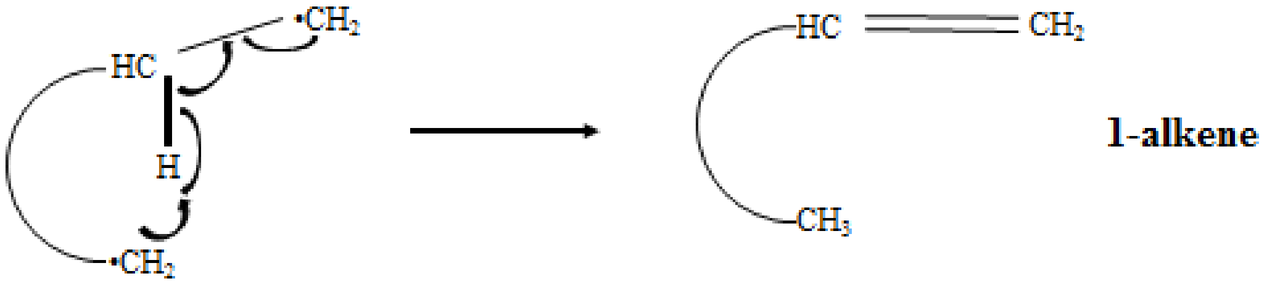


2A. Propagation : Intermolecular reaction



Pyrolytic Degradation Pathways of Polyethylene

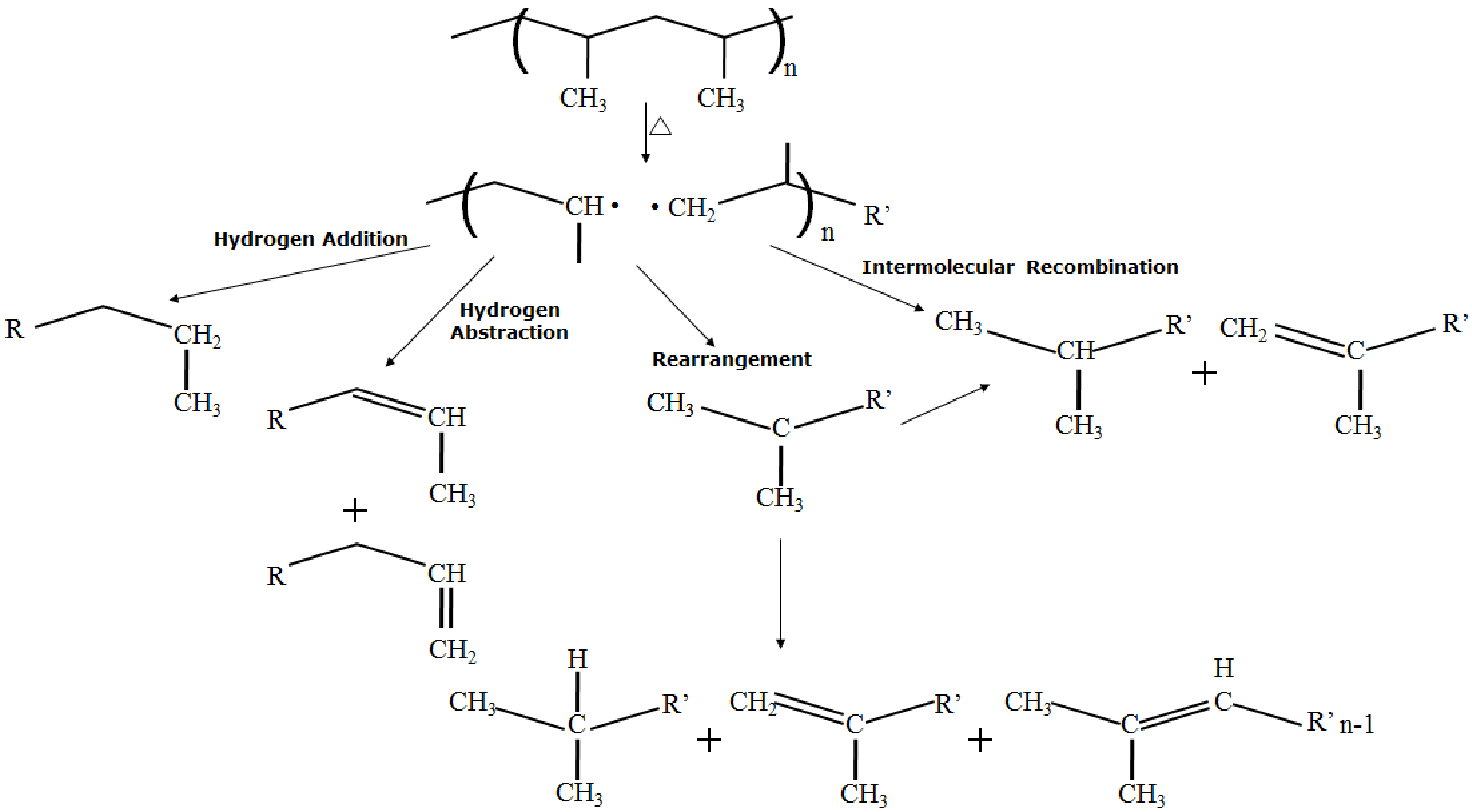
2B. Propagation : Intramolecular reaction



3. Termination

$$R\cdot + \cdot R' \longrightarrow R - R'$$

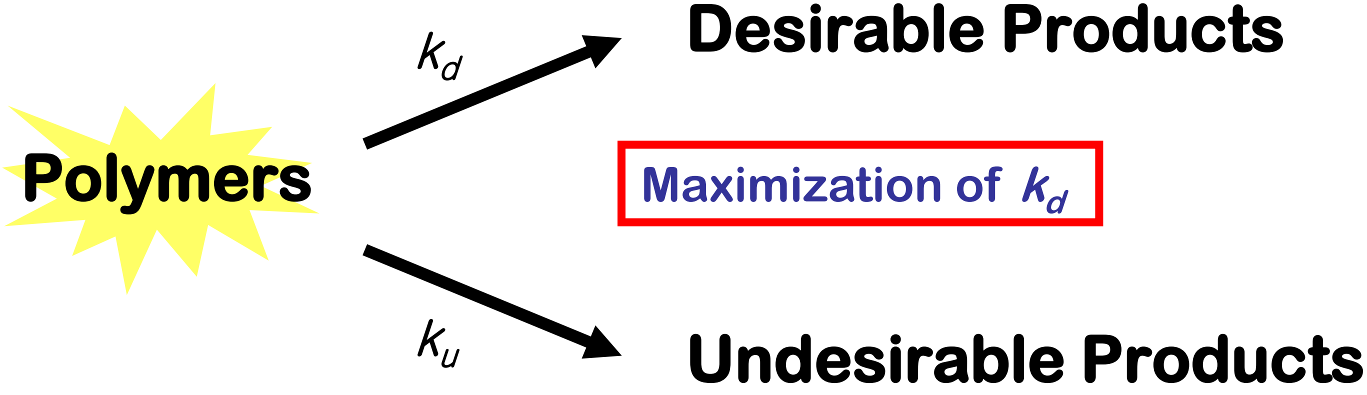
Pyrolytic Degradation Pathways of Polypropylene



3. Pyrolysis Kinetics

Why pyrolysis kinetics is important?

- Pyrolysis kinetics can elucidate 1) how fast the reaction is completed and 2) how the production rate of desirable products can be increased



k_d

Desirable Products

Polymers

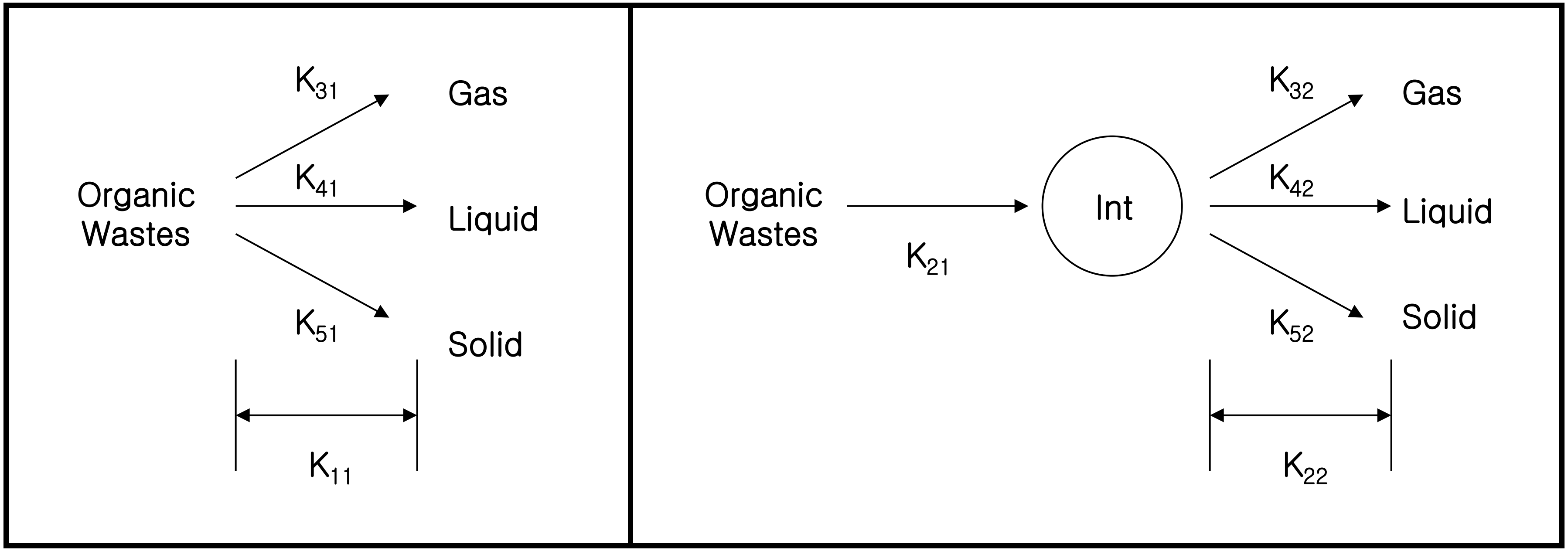
Maximization of k_d

k_u

Undesirable Products

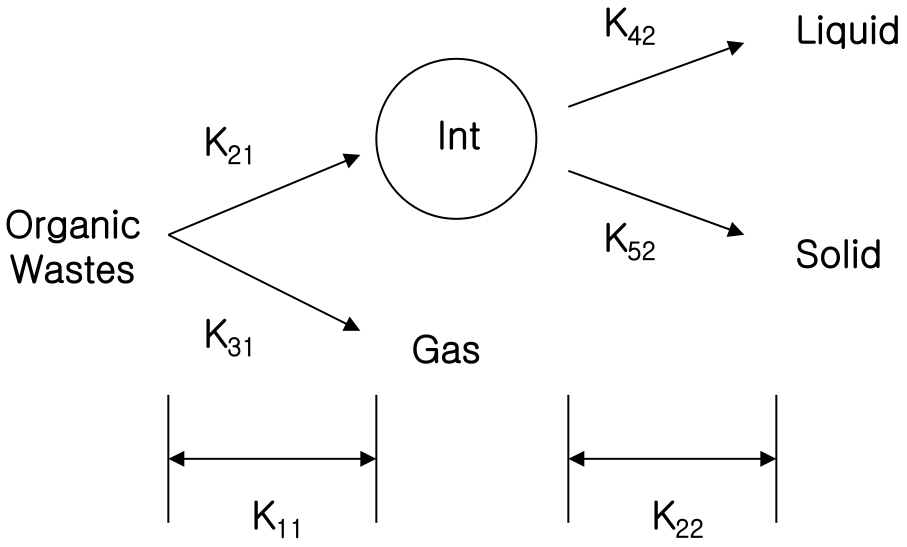
Pyrolysis Kinetic Models

MODEL I **MODEL II**



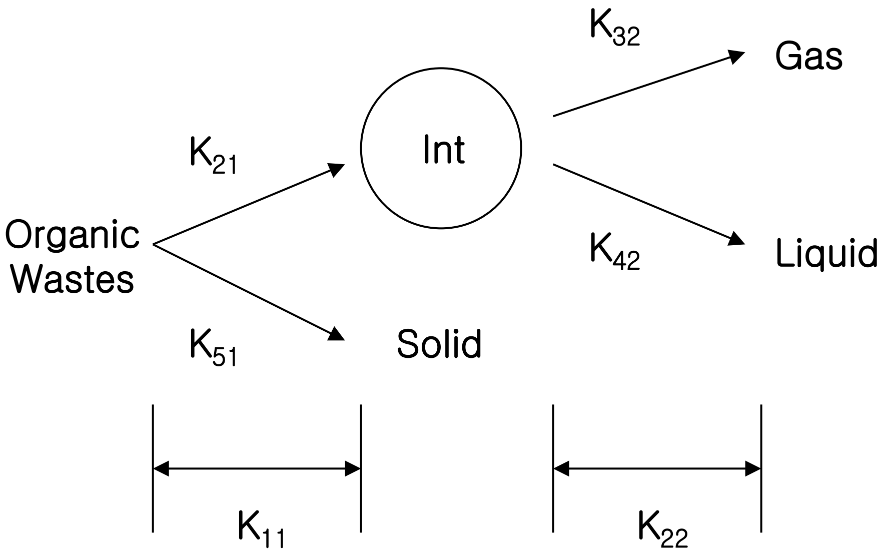
Pyrolysis Kinetic Models

MODEL III



Pyrolysis Kinetic Models

MODEL IV



K_{32}

Gas

Int

K_{21}

Organic Wastes

K_{42}

Liquid

K_{51}

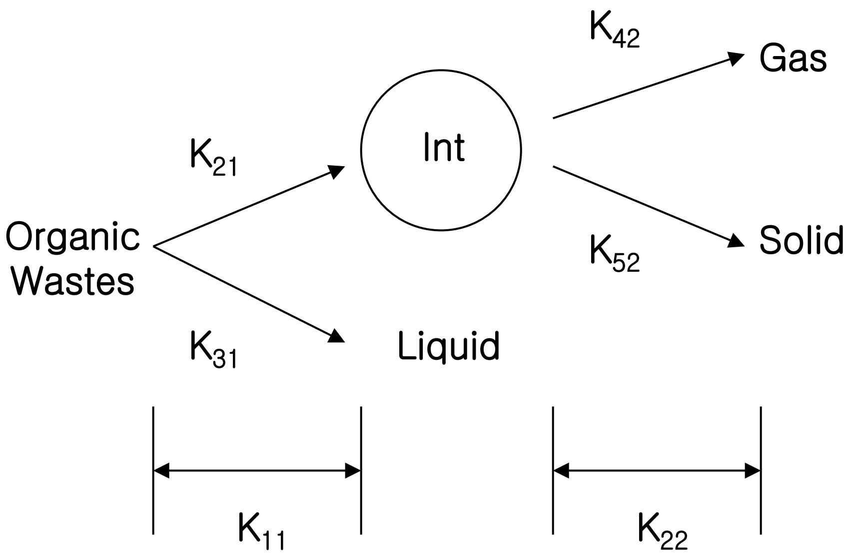
Solid

K_{11}

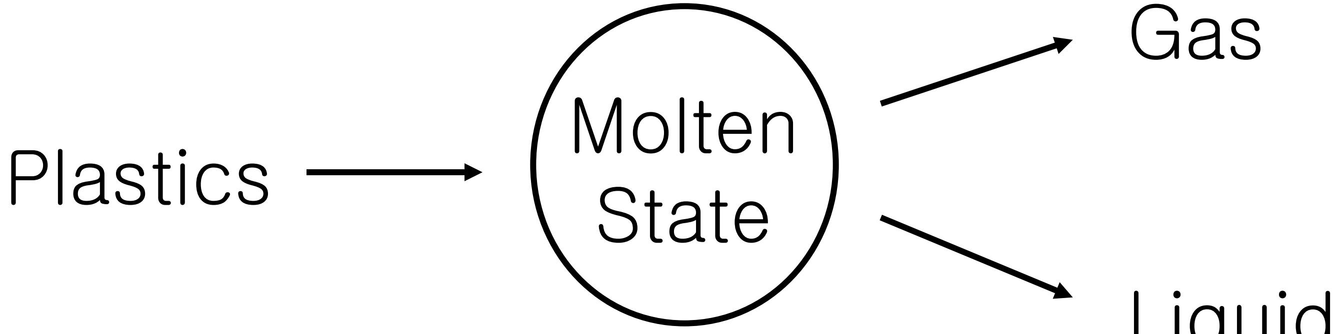
K_{22}

Pyrolysis Kinetic Models

MODEL V



Pyrolysis Kinetic Model of Thermoplastics



Pyrolysis Kinetic Equation

$$\frac{d\alpha}{dt} = k(T) f(\alpha)$$

Arrhenius Parameters

Kinetic Triplet

$$k(T) = A\exp(-E/RT)$$

Pyrolysis Kinetic Equation

A Unique Thermal Reaction can be characterized by ***one set of Kinetic Triplet***

Incorrect reaction model can mislead the Arrhenius Parameters as well

Example: Polypropylene

What is the reaction model commonly used for the pyrolysis of Polypropylene?

$$f(\alpha)=(1-\alpha)^n$$

Question

- Is Reaction Order Function appropriate for representing the pyrolysis reaction model of Polypropylene?

Evidences

- Discrepancy of Activation Energy Values between Model-fitting and Model-free method

- The reaction order function is usually applicable for homogeneous gas-phase kinetics, but the thermal degradation of polymers is accounted for by heterogeneous solid state mechanisms

Activation Energy Values derived from model-fitting and model-free Methods

Methods		n	E (kJ. mol-1)
Model-fitting Methods	**Freeman-Carroll**		
	at 5 K/min	1.57	338.15
	at 10 K/min	1.69	346.63
	at 20 K/min	1.38	290.13
	average	1.55	324.97
	Catterjee-Conrad		
	at 5 K/min		340.90
	at 10 K/min		351.16
	at 20 K/min		293.65
	average		328.57
	Coats-Redfern		
	at 5 K/min		316.71
	at 10 K/min		315.62
	at 20 K/min		321.02
	average		317.78
Model-free Methods	**Friedman**		189.18
	Kissinger		183.62
	Ozawa		186.75

Discrepancy of E values

How to identify Kinetic Triplet

How to Identify the Pyrolysis Reaction Model of PP and its Arrhenius Parameters

Kinetic Triplet

How to identify Kinetic Triplet

Procedures Estimating Kinetic Triplet

1st Stage

Determining Reaction Model → $f(\alpha)$

2nd Stage

Determining Reaction Constants at various isothermal temperatures → $k(T_i)$

3rd Stage

Estimating Arrhenius Parameters

Derivation of $g(\alpha)$

Kinetic equation

$$\frac{d\alpha}{dt} = k \cdot f(\alpha)$$

Integrating the kinetic equation

$$\frac{d\alpha}{f(\alpha)} = kdt$$

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_o^{t} kdt$$

$$g(\alpha) = kt$$

where $g(\alpha) = \int_0^{\alpha} [f(\alpha)]^{-1} d\alpha$

Theoretical 13 models of RTPs

Reaction Models

$$g(\alpha)=\int_{0}^{\alpha}\left[f(\alpha)\right]^{-1}d\alpha$$

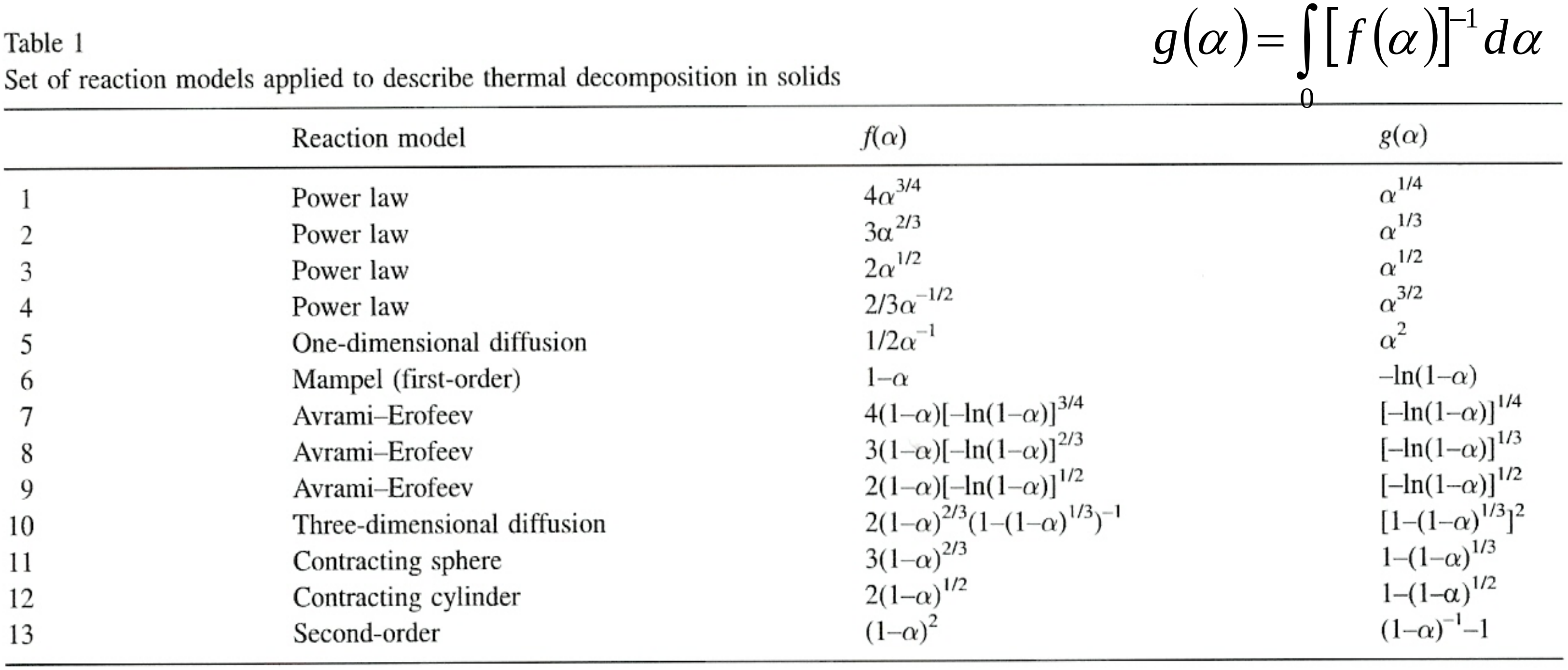


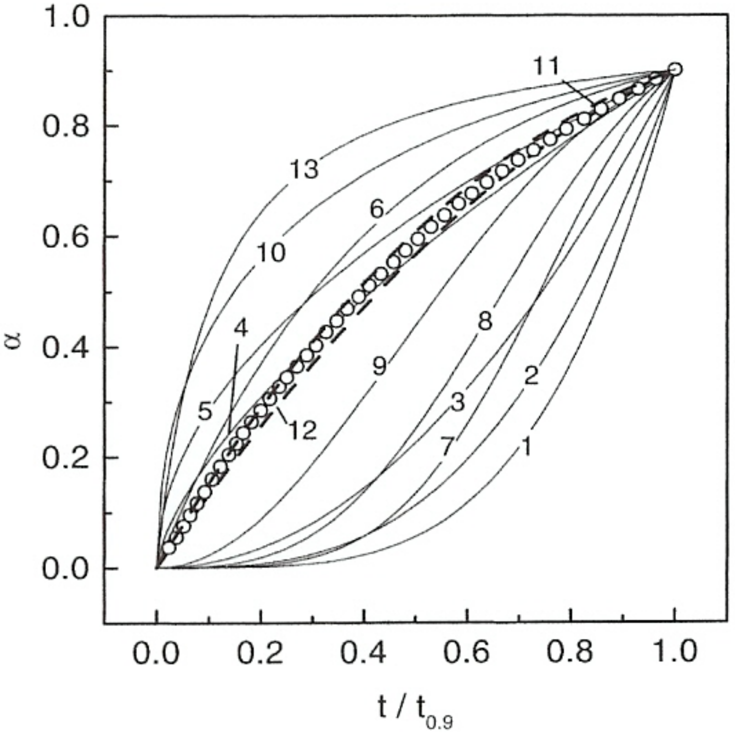
Table 1

Set of reaction models applied to describe thermal decomposition in solids

	Reaction model	$f(\alpha)$	$g(\alpha)$
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	$1/2\alpha^{-1}$	α^{2}
6	Mampel (first-order)	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami–Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$	$[1-(1-\alpha)^{1/3}]^{2}$
11	Contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	Second-order	$(1-\alpha)^{2}$	$(1-\alpha)^{-1}-1$

Procedures deriving Theoretical RTPs for 13 models

Procedures deriving Reduced Time Plots



1. Developing the following Relationship

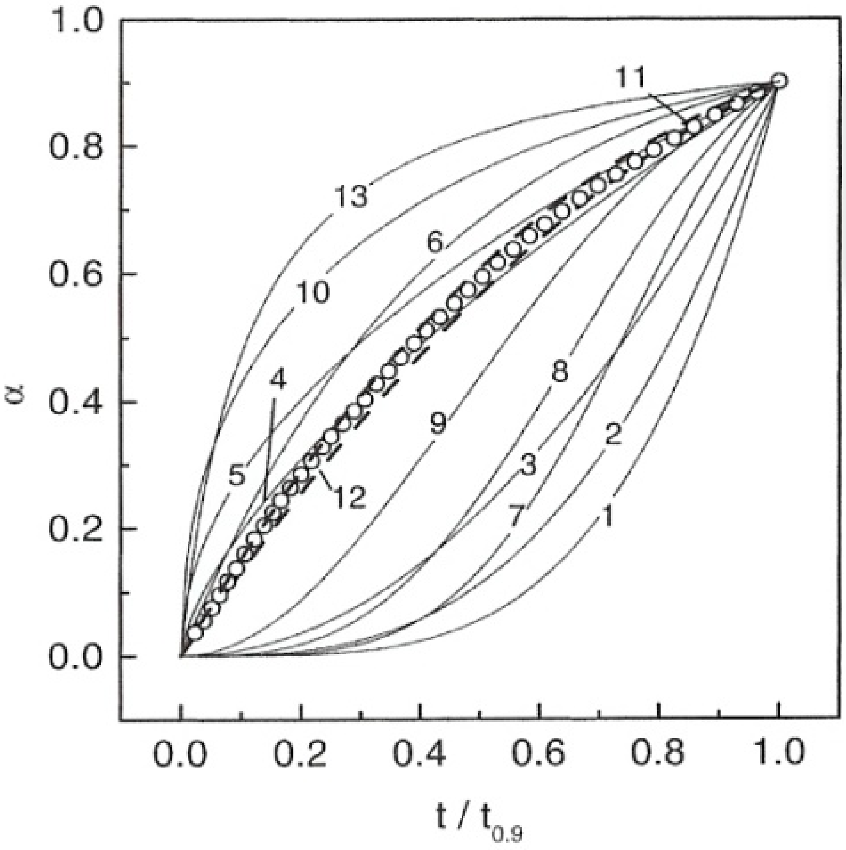
$$\frac{g_j(\alpha)}{g_j(0.9)} = \frac{t}{t_{\alpha=0.9}}$$

2. Substituting serial numbers(0.1, 0.2 etc) into α in the model equations and then determining $g_j(\alpha)$
3. Determining the reduced time from

$$\frac{g_j(\alpha)}{g_j(0.9)}$$

4. Developing the reduced time vs. α

How to determine pyrolysis reaction model of polymers



Fitting practices of experimental RTP to theoretical RTPs

Best-fit of an experimental RTP to a theoretical RTP

Estimation of Arrhenius Parameters

Determination of Arrhenius Parameters

1. **Estimating the reaction constants at various isothermal conditions**

$$g_j(\alpha) = k_j(T_i)t$$

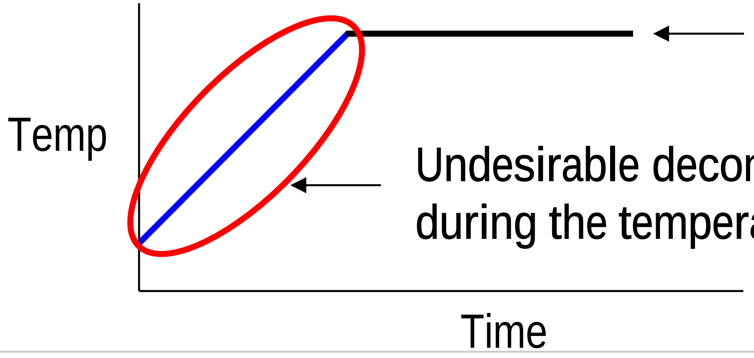
2. **Estimating A and E from Arrhenius Plot**

$$\ln k_j(T_i) = \ln A_j - \left(\frac{E_j}{R}\right)\frac{1}{T_i}$$

How to obtain Isothermal Kinetic Data

RTP requires decomposition pattern of polymers with time under isothermal conditions

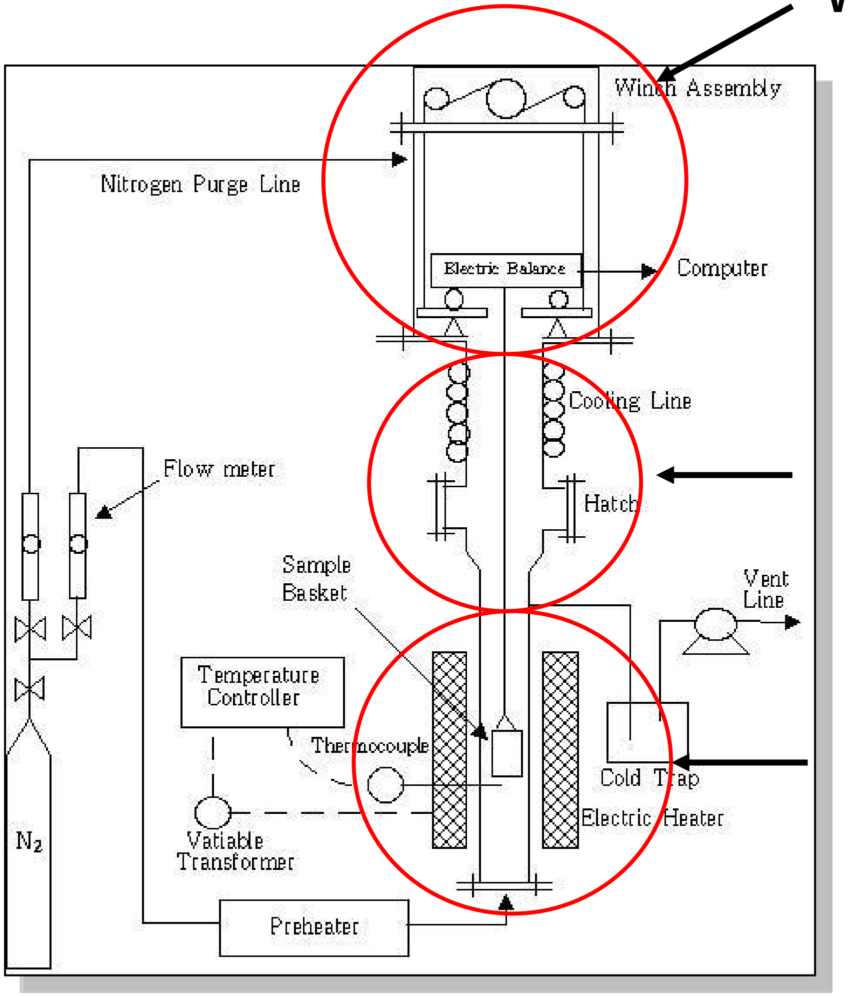
Most previous studies have used commercial TGA that allowed thermal decomposition that occurred during the course of the temperature rise to the target temperatures



Target Temperature

Undesirable decomposition happens during the temperature rise

Thermobalance operated under pure static conditions



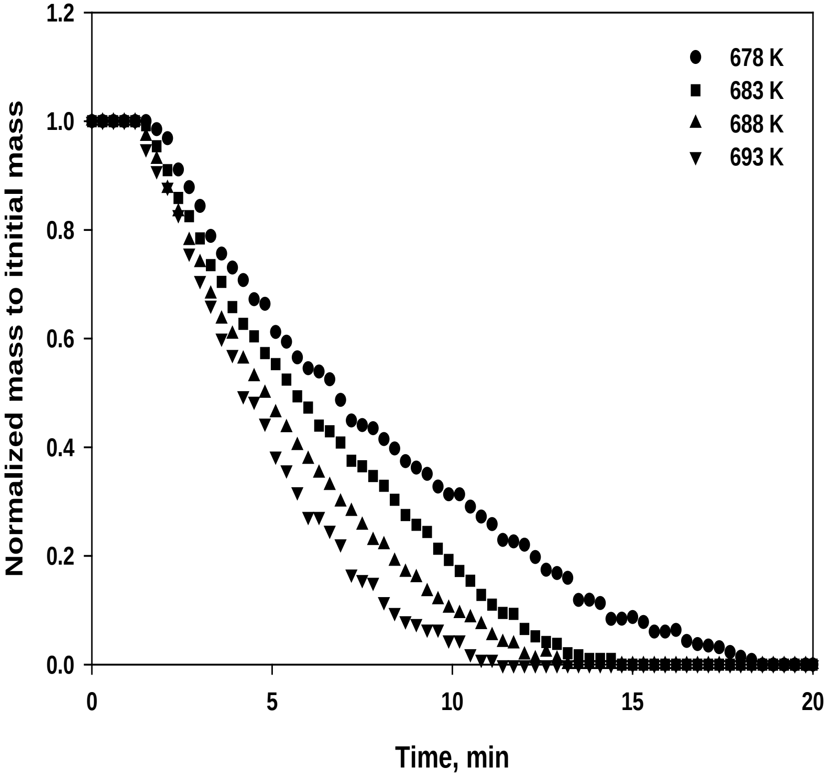
Weight Detection Part

Sample Loading Part

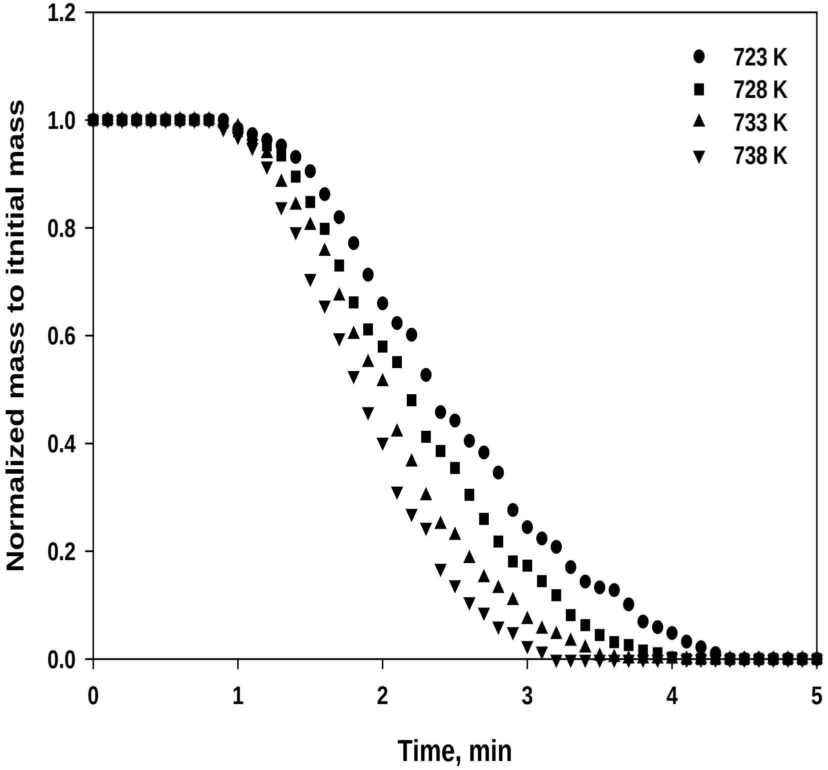
Pyrolysis Reactor

Pyroltic Decomposition of PP under Dynamic Conditions(678~738K)

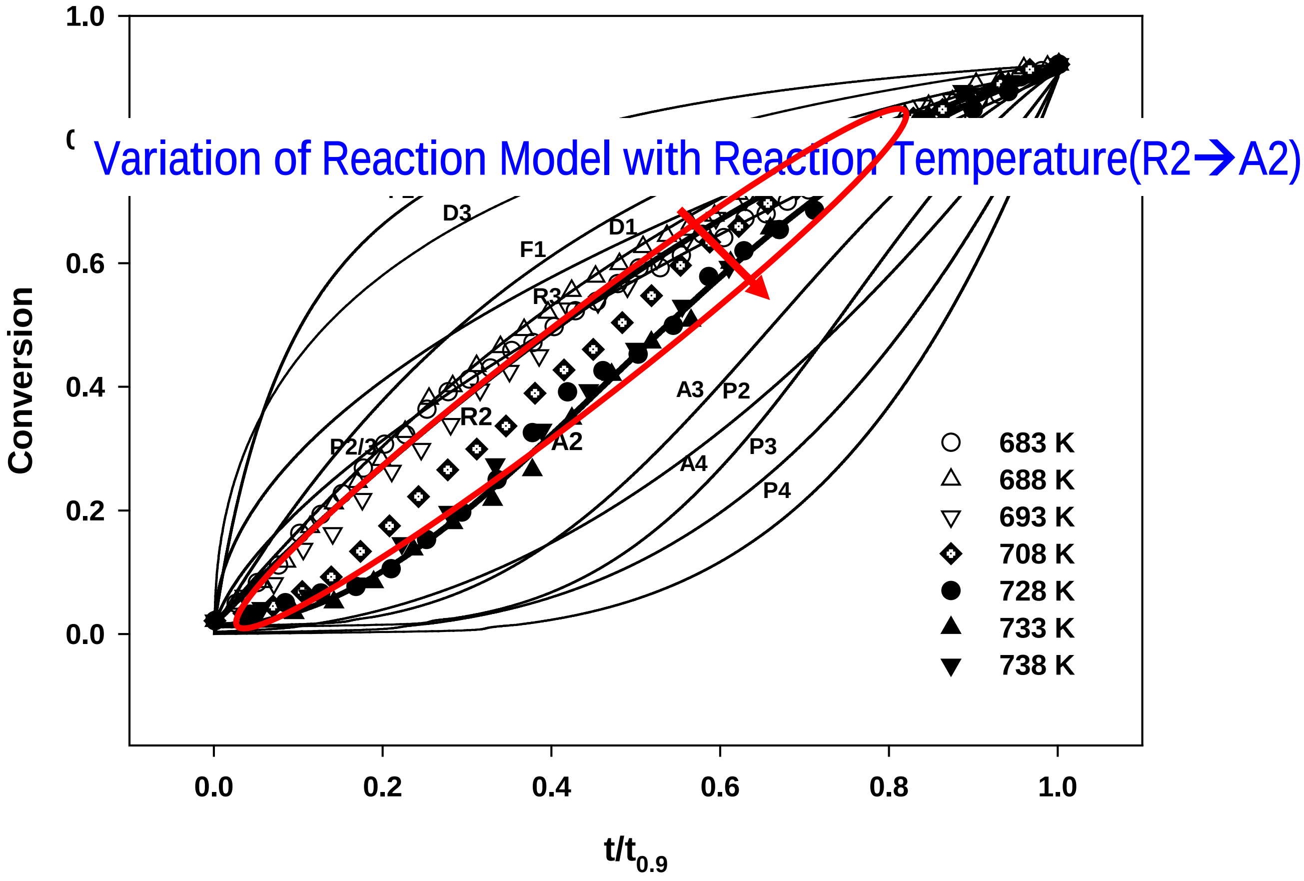
Lower Temperatures



Higher Temperatures



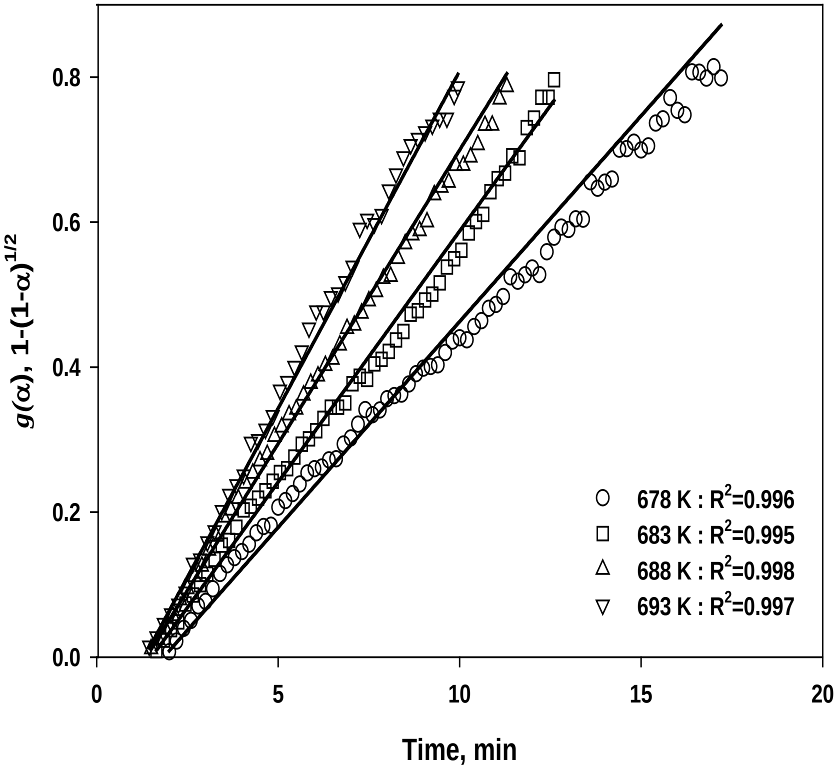
Reaction model of PP



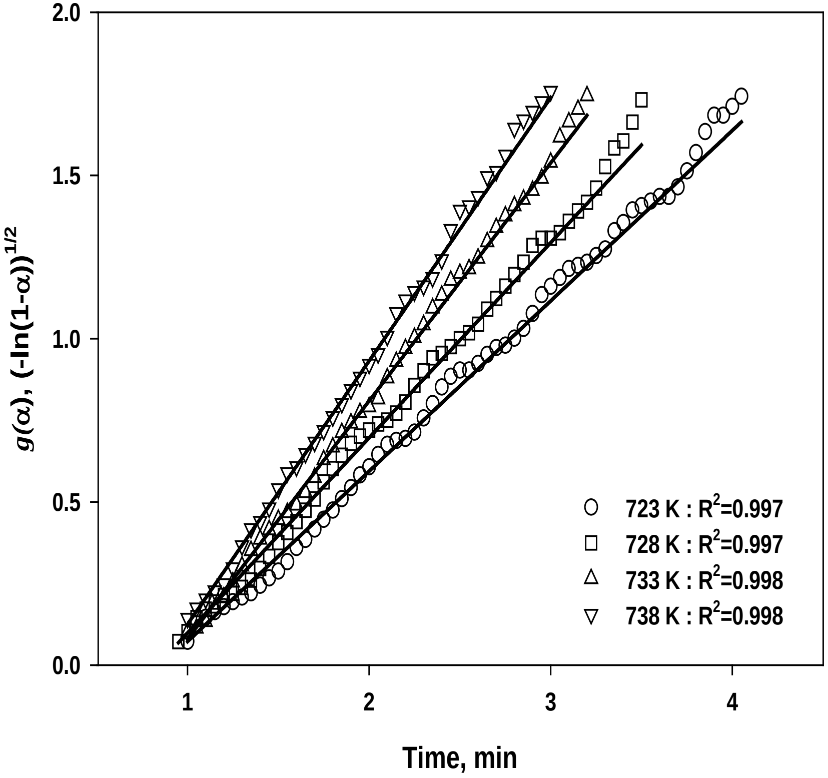
Variation of Reaction Model with Reaction Temperature(R2→A2)

Estimation of Reaction Constant (k): PP

Lower Temperatures



Higher Temperatures



Pyrolysis Reaction Model of PP

❖Lower Temperature Zones (650~700K)

- ✓Contracting Cylinder Model
- ✓E = 155 kJ/mol, lnA = 24.6 (A: min^{-1})

❖Higher Temperature Zones (>700K)

- ✓Avrami-Erofeev Model
- ✓E = 115 kJ/mol, lnA = 19.4 (A: min^{-1})

Verification

- ❖ **Model-free methods**
  - ✓ Isothermal data
  - ✓ Non-isothermal data

- ❖ **Model-fitting methods**
  - ✓ Differential
  - ✓ Integral

Model-free method using isothermal data

1. Compiling kinetic data at various isothermal operating temperatures
2. Developing a set of isoconversional data (α=0.1, 0.2, 0.3, ...)
3. Determining activation energy from the slope of the following equation:

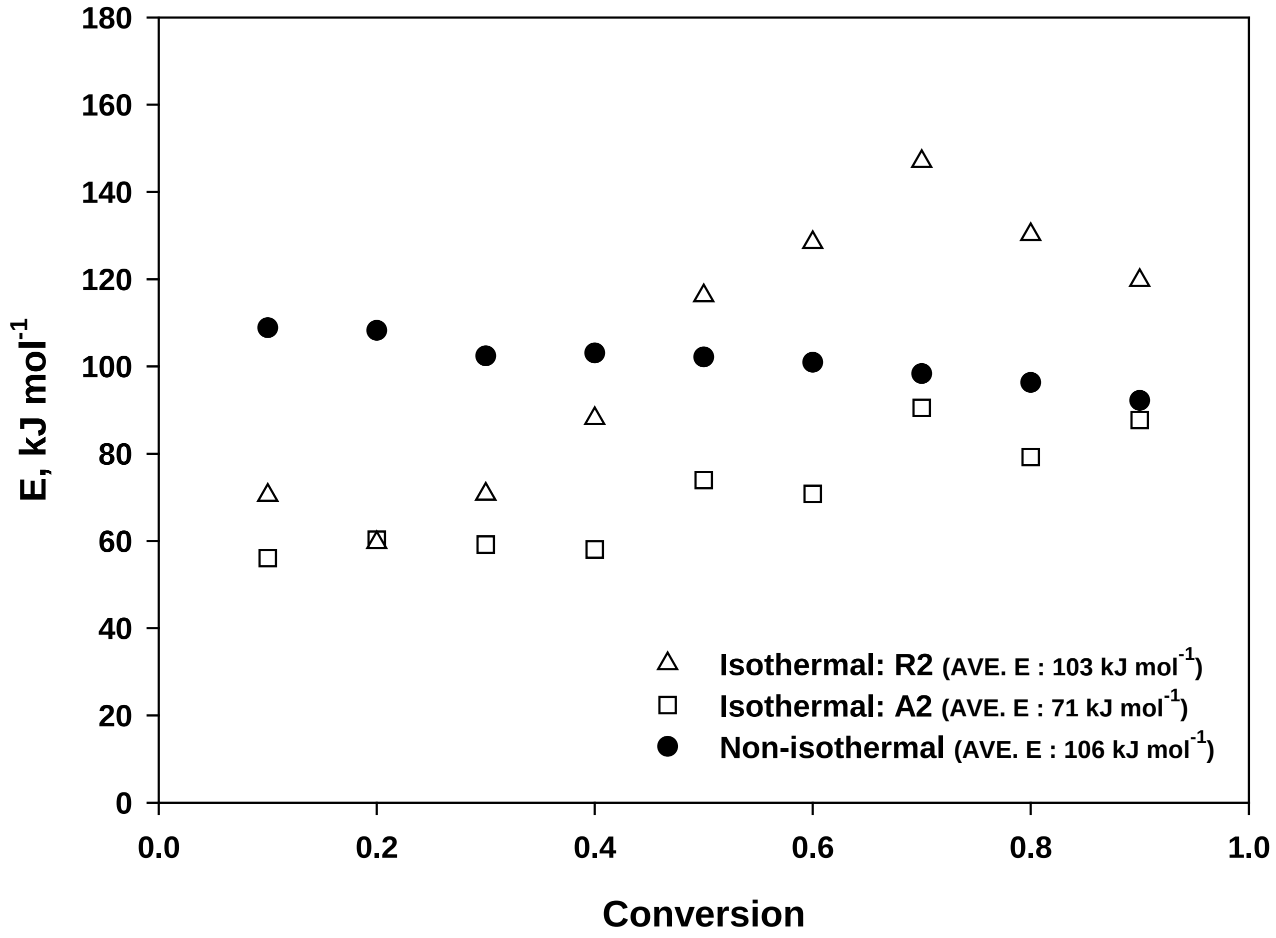
Model-free methods using non-isothermal data

- Friedman method
- Kissinger method
- Ozawa method
- Revised Ozawa method

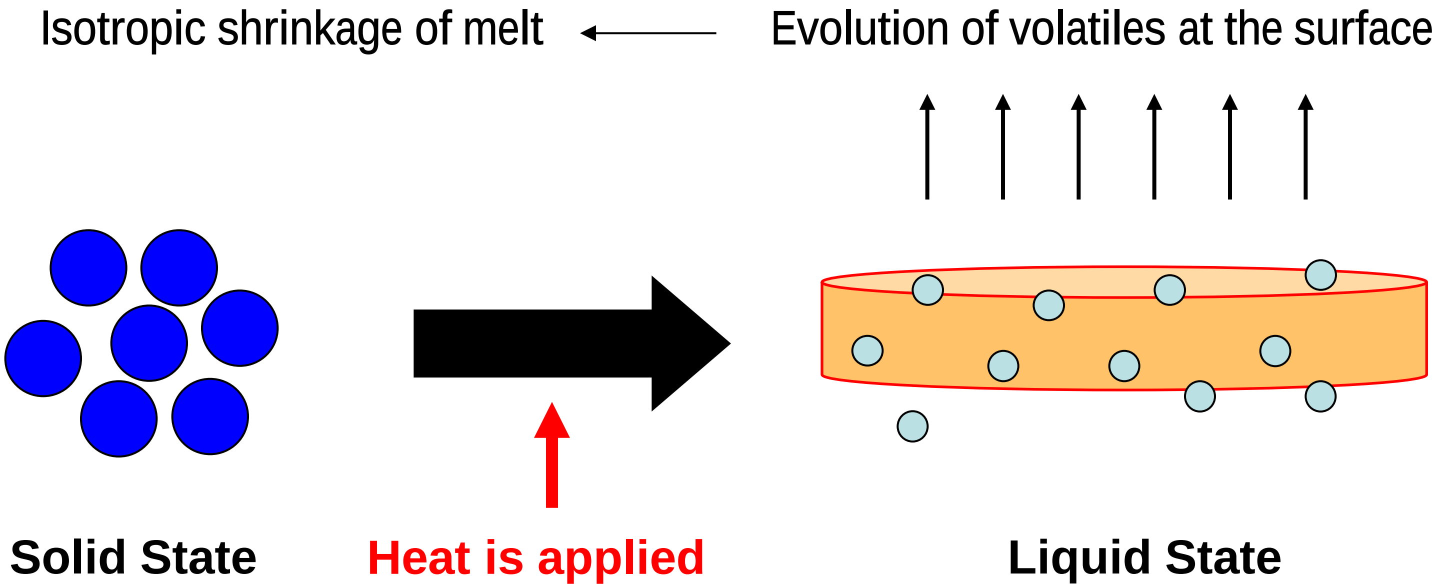
Activation energy(KJ/mol) values of PP

	Lower temperature regions	Higher temperature regions
Model-fitting method using Isothermal Data (This study)	**140**	**112**
Model-free method using Isothermal Data	**103**	**71**
Model-free method using Non-isothermal Data	**118**	
Model-fitting method using Non-isothermal Data	Lower conversion regions	Higher conversion regions
	112	**83**

Activation energy(KJ/mol) values of PP



Low Temeratures: Contracting-cylinder model



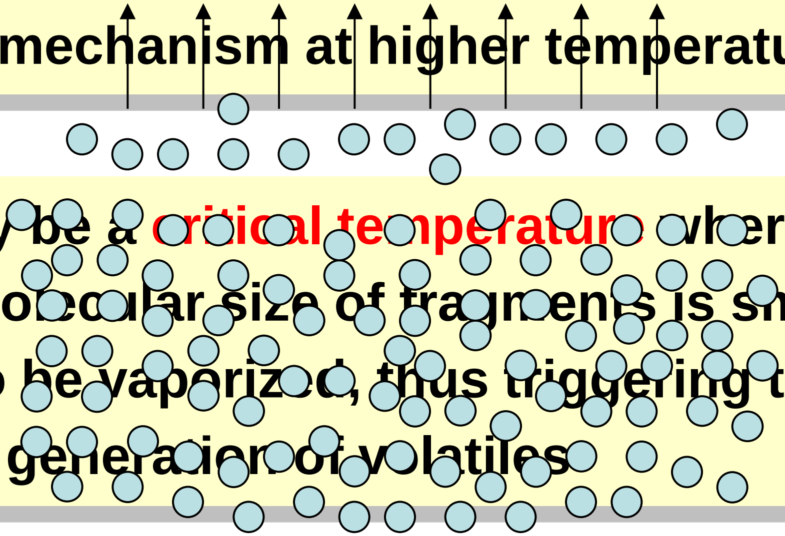
Isotropic shrinkage of melt ← Evolution of volatiles at the surface

Solid State

Heat is applied

Liquid State

Higher Temperatures: Avrami-Erofeev model



Bubble Nucleation is responsible for a major pyrolysis mechanism at higher temperatures

There may be a critical temperature where the highest molecular size of fragments is small enough to be vaporized, thus triggering the explosive generation of volatiles

At the critical concentration of volatiles, bubbles may begin to nucleate

Implication

Rate of bubble nucleation appears to be limited by the kinetics of heat, momentum or mass transfer and thermodynamic properties of melt

4. Pyrolysis Reactor Design

Step for Effective Reactor Design

1) **Investigating Pyrolysis Mechanism**
    - ✓Determining REACTION PATHWAY
2) **Estimating Pyrolysis Kinetic Model and Kinetics (Chemical Kinetics)**
    - ✓Determining REACTION TIME
    - ✓Controlling REACTION PARAMTERS
3) **Determining Scale-up Factors**
4) **Determining Temperature and Pressure Profiles of Reactor**
5) **Determining Reaction Rate and Time**

Thank You !