Plastic Waste Recycling Process Simulation Using ASPEN Plus®

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การจำลองกระบวนการแปรสภาพขยะพลาสติกกลับมาใช้ใหม่โดยใช้โปรแกรม ASPEN Plus®

พิฆเนศ จันทรา

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Title	Plastic Waste Recycling Process Simulation Using ASPEN Plus®
By	Phikhanet Chantra
Field of Study	Petrochemical Engineering
Advisor	Assoc. Prof. Dr. Kriangsak Kraiwattanawong

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Abstract

This thesis provides plastic waste recycling process simulation using ASPEN Plus®. This work was done to study effects of operating parameters on products controlling which is recycled High Density Polyethylene for using as a guideline to construct plastic waste recycling process via simulation of catalyzed polymerization process and product separation for increasing in purity by using process simulation program which is ASPEN Plus® resulting in, plastic waste recycling can control properties of product by controlling of temperature, pressure, residence time and provide caution of the amount of hydrogen in the reactor.

This process simulation simulate the production of recycled HDPE by using 2 reactors and 2 separators which provide of 97.9%wt of product purity, molecular weight distribution between 125078-126175, more than 3.3 tons of rHDPE by temperature controlling of both of reactor to be between 200-400°C and 100-250°C respectively, have to control residence time of both of reactor to stay between 3-17 hours and 5-11 hours respectively, and still have to control the pressure of both of reactor to be higher than 12 atm and also have to beware of the amount of hydrogen in the 2nd reactor to be lower than 0.47kg together with get rid of heat from both of reactor around 58.093 kW. For separation section, temperature is controlled to stay at 160°C together with pressure controlling at 8 atm and 1 atm respectively, with the energy consumption around 79.933 kW.

Keywords: High Density Polyethylene, recycling process, Aspen plus simulation program, plastic waste.

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บทคัดย่อ

ปริญญานิพนธ์ฉบับนี้แสดงถึงการจำลองกระบวนการแปรสภาพขยะพลาสติกเพื่อนำกลับมาใช้ใหม่โดยใช้โปรแกรมจำลองกระบวนการ ASPEN Plus® เพื่อศึกษาผลกระทบของพารามิเตอร์ของหน่วยปฏิบัติการที่ทำงานในกระบวนการแปรสภาพขยะพลาสติกที่มีผลต่อการควบคุมผลิตภัณฑ์ซึ่งในที่นี้คือพอลิเอทิลีนความหนาแน่นสูง เพื่อเป็นแนวทางสำหรับการสร้างกระบวนการแปรสภาพขยะพลาสติกกลับมาใช้ใหม่ โดยผ่านการจำลองการเกิดปฏิกิริยาพอลิเมอร์ไรเซชันแบบใช้ตัวเร่งปฏิกิริยาและการจำลองการแยกผลิตภัณฑ์เพื่อเพิ่มความบริสุทธิ์โดยใช้โปรแกรมจำลองกระบวนการ ASPEN Plus® ซึ่งได้ผลลัพธ์ออกมาว่าในการแปรสภาพขยะพลาสติกกลับมาใช้ใหม่สามารถควบคุมคุณสมบัติของผลิตภัณฑ์โดยการควบคุม อุณหภูมิ, ความดัน, เวลาที่อยู่ในเครื่องปฏิกรณ์ และมีสิ่งที่ต้องระวังคือปริมาณของแก๊สไฮโดรเจนในเครื่องปฏิกรณ์

การจำลองกระบวนการนี้ได้จำลองการผลิตพอลิเอทิลีนความหนาแน่นสูงที่ผ่านการแปรสภาพโดยใช้เครื่องปฏิกรณ์จำนวน 2 เครื่องและหน่วยแยกสาร 2 หน่วย ซึ่งได้ผลิตภัณฑ์ที่ความบริสุทธิ์ร้อยละ 97.9 โดยมวล, มีการกระจายของมวลโมเลกุลอยู่ระหว่าง 125078-126175, ปริมาณมากกว่า 3.3 ตัน โดยควบคุมอุณหภูมิของเครื่องปฏิกรณ์ทั้งสองเครื่องให้อยู่ระหว่าง 200-400 องศาเซลเซียส และ 100-250 องศาเซลเซียส ตามลำดับ และควบคุมให้ทำปฏิกิริยาโดยใช้เวลาในเครื่องปฏิกรณ์ทั้งสองเครื่องให้อยู่ระหว่าง 3-17 ชั่วโมง และ 5-11 ชั่วโมง ตามลำดับ และยังต้องควบคุมให้ความดันภายในเครื่องปฏิกรณ์ทั้งสองมีค่าเกิน 12 บรรยากาศ และยังต้องระวังให้มีปริมาณแก๊สไฮโดรเจนในเครื่องปฏิกรณ์เครื่องที่สองน้อยเกินกว่า 0.47 กิโลกรัม พร้อมกับต้องดึงพลังงานออกจากเครื่องปฏิกรณ์ 58.093 กิโลวัตต์ สำหรับส่วนการแยกผลิตภัณฑ์ต้องควบคุมอุณหภูมิของหน่วยแยกสารให้อยู่ที่ 160 องศาเซลเซียส พร้อมกับควบคุมความดันให้อยู่ที่ 8 บรรยากาศ และ 1 บรรยากาศ ตามลำดับโดย พร้อมกับใช้พลังงานไปในส่วนการแยกสาร 79.933 กิโลวัตต์

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Phikhanet Chantra

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NOMENCLATURE

PVC	Polyvinylchloride
PET	Polyethyleneterephthalate
HDPE	High Density Polyethylene
PS	Polystyrene,
PP	Polypropylene
LDPE	Low Density Polyethylene
k_p	rate constant for propagation
ε_p	steric factor
σ_p	cross section of the collision
μ	reduced mass of the colliding pair
E_p	activation energy for propagation
R	gas constant
T	absolute temperature
M_R	mass of the propagating radical
M_M	mass of the propagating monomer
k_t	rate constant of chain termination
k_i	rate constant of initiating radicals
f	fraction of initiating radicals
[M]	concentration of monomer
[I]	concentration of initiating radicals
X_A	conversion of reactant (A)
T_c	ceiling temperature
ΔG	Gibbs-free energy change
ΔH	enthalpy change
ΔS	entropy change
n	degree of polymerization
$^{\Delta Hp^\circ}$	standard enthalpies of polymerization
$^{\Delta H_f^\circ}$	standard enthalpies of formation
ΔS_f°	standard entropies of polymerization
S°	absolute entropies
M	monomer

P_n	polymer
C_p	heat capacity of polymer under constant pressure
ΔQ	required heat quantity
m	mass
ΔT	temperature difference of any two states of polymer
C_v	heat capacity of polymer under constant volume
V	volume at that state
α	thermal expansion coefficient
T	temperature at that state
K_T	isothermal bulk modulus
PSW	plastic solid waste
Q_l	amount of latent heat
L	latent of fusion
$G^E{}_{EOS}$	excess Gibbs free energy from an EOS model
φ	mixture fugacity coefficient
φ_i	fugacity coefficient of component i in a mixture
γ_i	activity coefficient of component i in a mixture

CHAPTER I

INTRODUCTION

1.1 Background

Nowadays the world is facing against overwhelming waste issue which has an effect on human living and environment from plastic waste.

Plastic is the convenient material for many fields such as healthcare, technology, tourism, transportation, medical equipment and many more, this is few of many petrochemical products because of petrochemical can be produced to various type of products which support to a wide varieties of application and relatively inexpensive so that demand of plastic does not decrease, combine with difficult to replace it by other material and moreover plastic does not belong only in topography, river or ocean. Its product belong in our home, school, university and workspace. Plastic was usually used in two ways that are long terms use such as pipe, sport equipment, furniture, etc., which rapidly replace other materials for example wood, iron, glass, etc., so can say that nowadays plastic is an indispensable necessity and plastic that cause trouble that is single use plastic that has large quantity.[1,2]

Plastic was produced more than 300 million metric tons/year across the world affect to generate new trend of developed country which choose couple ways to eliminate plastic waste that are recycle and circular economy but recycle is better choice because it is conservation of origin resource and still get value from plastic by use it as raw material or create new product.[3,4]

Thailand is entering a plastic waste crisis point. plastic waste in Thailand can take place in two routes: "originating from the country" and "caused by importing garbage", which is due to China has announced that it will stop importing plastic waste as a result, there is a huge amount of waste flowing to Thailand which more than 81 countries sending garbage to Thailand and most of Thailand's plastic waste solutions are spot-on temporary solutions, does not really solve the root cause of the problem in combination with Thai law are still no measures to reduce environmental problems so the solution right now that looks good and most effective that is pushing for environmental laws and set out appropriate policies and the use of circular economy measures including other environmental measures that governments and businesses have to seriously support this matter because if there is no law to control and there are

no preventive measures to support plastic waste management then Thailand will certainly encounter more environmental problem more than now. Thailand currently has 2.7 million tons of plastic and foam waste which is an average of 7,000 tons per day, divided into 80 percent plastic bags or 5,300 tons per day or about 2 million tons. Fifty percent of all rubbish was found that was incorrectly eliminated. Plastic waste will take up three times more space than normal waste in landfills in the event that it is incinerated, it will affect the environment significantly including a lot of environmental residue because plastic bags are made from petroleum causing contamination of soil and water residues bring about the greenhouse gas emissions that causes of global warming. There are approximately 27 million tons of Thai waste, comprised of 13.5 million tons of improper disposal, 8 million tons of properly disposed of and 5 million tons of recycled waste.. So that if Thailand can recycle more plastic will be able to reduce more problems caused by plastic waste. [2,5]

Design of process often begins with laboratory scale then scale up to pilot plant which is the efficiency method if start with great hypothesis, comprehensive variables, steps of experiment otherwise waste of time and budget will be occurred. Trial and error in experimental will not be occurred with providing of process simulation to determine process possibility which offer more efficiency in experiment via possible hypothesis which can be provided by process simulator program. From these reason, resulting in the commercial process simulation program was used in this project.

This thesis will focuses on chemical recycling process for plastic waste which perform with process simulation program ASPEN Plus® for better estimation of process with raw materials base on plastic solid waste which is High Density Polyethylene (HDPE).

1.2 Objectives

1. To using simulation program to simulate plastic waste recycling process.
2. To reduce some steps of experimentation in bench-scale and pilot-scale.

1.3 Scopes of Work

1. Design recycling process with raw material is plastic solid waste which is High Density Polyethylene (HDPE).
2. Concepts of process design based on data from exist process, published journal article, and reliable sources.

1.4 Expected Outputs

1. Possible recycling process for plastic solid waste which can be adopt to characterize product by conditions changing of unit operation.
2. Useful as guideline for simple recycling process simulation.

CHAPTER II

LITERATURE REVIEW

2.1 Polymer

Polymer is the matter that consist of monomer recurring to be long chain which the number of monomer frequently has large number and uncertain, then wide range molecular weight of polymer occurred.[6]

2.1.1 Polymer classification

Polymer was divided by mechanical and thermal properties into 3 major types that are elastomer, thermoplastic polymer, and thermosetting polymer. Around 80% of plastic is thermoplastics, the rest 20% is thermosets and elastomers which have only thermoplastics that can be recycled.[6,7]

Table 2.1: Thermoplastics vs Elastomers vs Thermosets[6,8,9]

Thermoplastics	Elastomers	Thermosets
Linear structure	Cross-links network	Cross-links with 3D network
Processed by injection molding, extrusion, rotational molding, blow molding, and thermoforming	Processed by compression molding, injection molding, and extrusion	Processed by reaction injection molding and compression molding
Low tensile strength, brittleness, durability, rigidity, and stiffness	Properties obtained by chemicals, additives, and subsequent vulcanization conditions	High tensile strength, brittleness, durability, rigidity, and stiffness
Soluble in some organic solvent	Insoluble in organic solvent and chemicals	Insoluble in organic solvent

2.1.2 Type of recyclable thermoplastic

Although polymers have 3 major types but only thermoplastic that can be recycled and also have only 3 types of thermoplastic that be recycled such as Polyvinylchloride (PVC), Polyethylene terephthalate (PET), and High Density Polyethylene (HDPE). The other types such as Polystyrene (PS), Polypropylene (PP), and Low Density Polyethylene (LDPE) cannot be recycled because of they can be get stuck and cause damage to equipment. There are several types for recycling municipal plastic solid waste, i.e. mechanical recycling, biological recycling, thermal recycling, chemical recycling.[6,10] In this work will focus on chemical recycling process which mainly focus on reaction process and separation process.

2.2 Polymerization reaction

Polymerization reactions can be roughly classified into three types: condensation, addition, and ring-opening polymerizations but explicit classification is based on the general mechanistic pathways that are involved.[11] From three types of recyclable thermoplastic cause only one type of polymerization reaction was interested in this work that are Free-radical polymerization which is Chain-growth type polymerization.

2.2.1 Free-radical addition polymerization

Free-radical polymerization can be generally described by the scheme shown in reaction below[11]:

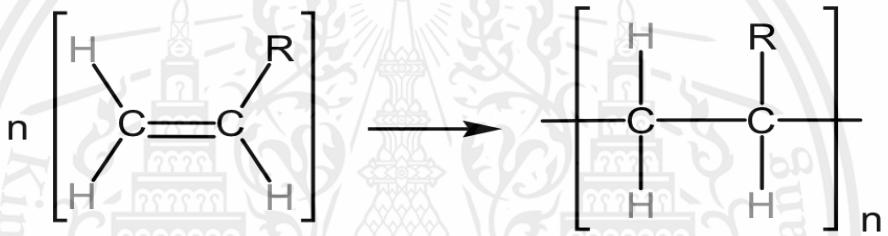


Figure 2.1: Addition reaction[11]

In free-radical addition reactions, the growing chain end bears an unpaired electron, so that addition of each monomer at the end of chain will be attack the other unsaturated monomer with the radical site, then the unpaired electron is transferred to the new chain end at each addition sequence.

Figure 2.2: Unpaired electron at the end of polymer chain[11]

2.2.1.1 Chain reactions

The regeneration of active site at the chain end occurred after the addition of a monomer molecule to an active chain end. In chain-reaction polymerization compose of four steps:

1. Chain initiation; a highly reactive molecules or active center are generated.
2. Chain propagation; the addition of monomer molecules to the active chain end, together with the regeneration of the terminal active site.
3. Chain transfer; the transfer of the active site to another molecule.
4. Chain termination; the active centers are demolished.

Table 2.2: Free-radical polymerization sequence[11]

$\text{Initiator} \rightarrow 2\text{R}'\cdot$	} Initiation
$\text{R}'\cdot + \text{M} \rightarrow \text{R}_i\cdot$	
$\text{R}_i\cdot + \text{M} \rightarrow \text{R}_2\cdot$	} Propagation
$\text{R}_n\cdot + \text{M} \rightarrow \text{R}_{n+1}\cdot$	
$\text{R}_n\cdot + \text{YZ} \rightarrow \text{R}_n\text{Y} + \text{Z}\cdot$	Chain transfer
$\text{R}_n\cdot + \text{R}_m\cdot \rightarrow \text{P}_{n+m}$	} Termination
$\text{R}_n\cdot + \text{R}_m\cdot \rightarrow \text{P}_n + \text{P}_m$	

2.2.1.2 Initiators for free-radical polymerization

Table 2.3: Free-radical initiators[11]

Initiator type	Example
Organic peroxides or hydroperoxides	Benzoyl peroxide
Redox agents	Persulfates + reducing agents
Azo compounds	Azobisisobutyronitrile
Organometallic reagents	Silver alkyls
Heat, light, UV, or high energy radiation	-
Electrolytic electron transfer	-

The first four types are compounds that associate into free radicals when heated or subjected to radiation. The last two categories are physical influences that generate free radicals from the monomer itself or the solvent.[11]

2.2.1.3 Kinetics of free-radical polymerization

A precise kinetic of free-radical polymerization, it is necessary to provide some assumptions and approximations: 1) **kinetic chain length:** the number of monomer molecules consumed in the chain initiation process is negligible compared with the number consumed in the chain propagation reactions, 2) **the direction of radical addition to the monomer:** head-to-tail addition is the sole type occurring, 3) **radical reactivity and size:** the reactivity of the propagating radicals is independent of the size or degree of polymerization of radical, 4) **the steady state approximation:** all of free radicals which involve all degrees of polymerization in the system are assumed to be at steady-state concentration. The result of assumption number 3 is that the rate constants for propagation in each step are all equal and according to collision theory, the rate constant for propagation can be written as[11]:

$$k_p = \varepsilon_p \sigma_p \left(\frac{RT}{\pi\mu}\right)^{1/2} e^{-E_p/RT} \qquad 2.1$$

Where; k_p is the rate constant for propagation
ε_p is the steric factor
σ_p is the cross section of the collision
μ is the reduced mass of the colliding pair
E_p is the activation energy for propagation
R is the gas constant, and
T is the absolute temperature

The reduced mass is defined as:

$$\mu = \frac{M_R M_M}{M_R + M_M} \qquad 2.2$$

Where; M_R is the mass of the propagating radical
M_M is the mass of the propagating monomer

The rate of free-radical polymerization is defined as decreasing of monomer and radical concentration, according to the assumption of long chains, the assumption about radical size, and steady state radical concentration can be expressed by following equation[11]:

$$r_p = \left(\frac{k_p^2}{2k_t}\right)^{1/2} r_i^{1/2}[\mathrm{M}] = \left(\frac{k_p^2}{2k_t}\right)^{1/2} (2fk_i)^{1/2}[\mathrm{I}]^{1/2}[\mathrm{M}] \qquad 2.3$$

Where; k_t is the rate constant of chain termination

k_i is the rate constant of initiating radicals

f is the fraction of initiating radicals

[M] is the concentration of monomer

[I] is the concentration of initiating radicals

Equation 2.3 predicts that the rate of polymerization at a given temperature should vary with the square root of the initiation rate or initiator concentration and with the first power of the monomer concentration.[11]

2.2.1.4 Conversion

Conversion can refer to amount of products are formed for every mole of reactant (A) consumed with knowing reaction together with stoichiometry

$$X_A = \frac{moles\ of\ A\ reacted}{moles\ of\ fed} \qquad 2.4$$

Where; X_A is conversion of reactant (A)

2.2.2 Polymerization and depolymerization of polymer

2.2.2.1 Monomer-polymer equilibria

At high temperatures, many polymer can depolymerize to monomer. This phenomenon can be inferred by following figure:

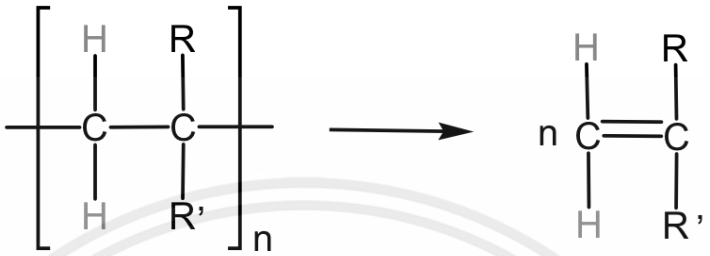


Figure 2.3: Simple depolymerization[11]

The monomers formed from these polymers cannot undergo α-hydrogen removal, so hydrogen abstractive side reactions do not compete with simple depolymerization to the monomers. Furthermore, some of monomers such as acetaldehyde, butyraldehyde, or acetone can be polymerized, the polymers depolymerize back to the monomer at moderate temperatures. For polymerization need high-pressure and low-temperature conditions, but depolymerization occurs at lower-pressure and warmer-temperature and depolymerization is process of several that are possible will happen when a polymer is heated up to high temperatures.[11]

2.2.2.2 Thermodynamic effects

First, the hypothetical series of compounds which extends from the monomer to the high polymer, it will be assumed that initially the lower oligomers in the series are cyclic and that the higher polymers are either cyclic or linear. From this assumptions, the series can be expressed as[11]:

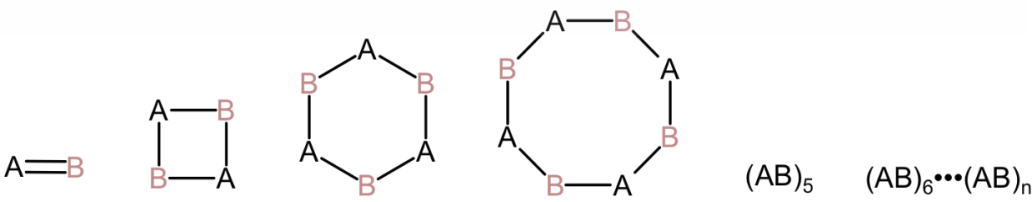


Figure 2.4: Hypothetical series of monomer extends to high polymer[11]

So every member of the series can coexist in the equilibrium only if each compound has a similar stability to the others at a given temperature and pressure.[11]

Ceiling temperature:

Ceiling temperature, T_c is temperature that the tendency of polymer to monomers reversion equal to the tendency of monomers to polymer conversion.

The thermodynamic expression:

$$\Delta G = \Delta H - T\Delta S \qquad 2.5$$

Can be used for understanding of the polymerization-depolymerization behavior. If the Gibbs free-energy change, ΔG is negative means polymerization is thermodynamic possible, but ΔG is positive then depolymerization will be favored.[11,12]

From previous expression can be conclude that any chemical species in the system that have lower in enthalpy or higher in entropy will shift the equilibrium to favor that species.

2.2.2.3 Standard enthalpies, entropies, and free energy

Standard enthalpies of polymerization can be obtained via calorimetric measurement of the amount of heat evolved when a known amount of monomer is converted to a known amount of polymer or determine by heats of combustion of monomer and polymer to give standard enthalpies of formation for monomer and polymer. The general process of polymerization may be described by the stoichiometric equation[11]:

$$M(l) \rightarrow \frac{1}{n} P_n(a) \qquad 2.6$$

This equation means 1 mol of monomer in liquid state becomes to 1/n mol of polymer with average degree of polymerization, n , in the amorphous or slightly crystalline state. Then the enthalpy of polymerization is obtained from 2.5, will get relationship as[11]:

$$\Delta H_P^\circ = \frac{1}{n} \Delta H_f^\circ(P_n) - \Delta H_f^\circ(M) \qquad 2.7$$

Where; $^{\Delta Hp^\circ}$ is the standard enthalpies of polymerization

$^{\Delta H_f{}^\circ}$ is the standard enthalpies of formation

And the standard entropies of polymerization are generally defined from the absolute entropies of the monomer and polymer[11]:

$$\Delta S_f^\circ = \frac{1}{n} S^\circ(P_n) - S^\circ(M) \qquad 2.8$$

The absolute entropies can be determined by heat capacities of monomer and polymer over wide range of temperature using the following equation[12]:

$$S^\circ(T) = \int_0^T \frac{C_P}{T} dT \qquad 2.9$$

Where; C_P is the heat capacity at constant pressure

T is the absolute temperature

And generally the integral is usually evaluated graphically from the experimental data. The standard free energies of polymerization, ΔG_P° are obtained by calculation by equation 2.4, once ΔH_P° and ΔS_P° are known.[11,12]

2.2.3 Heat capacity and Latent heat of Polymers

The heat capacity of a substance can be defined as the amount of heat required to change its temperature by one degree. A more useful quantity is specific heat capacity, which is the amount of heat required to change the temperature of one unit mass of a material by one degree. Heat capacity is a fundamental property of any material. It is a macroscopic parameter that can be linked to molecular structure and vibrational motions at microscopic level.[13]

Heat capacity under constant pressure (C_p) is defined as the heat quantity which is required to increase the temperature of the unit mass of a material by 1°C under constant pressure. It is given by the following equation:

$$C_p = \Delta Q / m\Delta T \qquad 2.10$$

Where; C_p is the heat capacity of polymer under constant pressure

ΔQ is the required heat quantity

m is the mass of the polymer

ΔT is the temperature difference of any two states of polymer

At constant volume, heat capacity can be defined as follows;

$$C_v = \Delta Q / m\Delta T \qquad 2.11$$

Where; C_v is the heat capacity of polymer under constant volume

The relationship between two heat capacities is

$$C_p - C_v = V\alpha^2 T / K_T \qquad 2.12$$

Where; V is the volume at that state

α is the thermal expansion coefficient

T is the absolute temperature at that state

K_T is the isothermal bulk modulus

Latent heat of polymer in this project will focus on Latent heat of fusion which can be expressed follow:

$$Q_l = mL \qquad 2.13$$

Where; Q_l is the amount of latent heat

L is the latent of fusion

2.3 Unit operation in process simulation

2.3.1 Batch Reactor

Batch reactor is often used in small-scales process for many proposes such as new process testing, expensive product manufacturing, and process that difficult for doing via continuous operating. Batch reactor provides high conversion when let the reactants stay in the reactor with a long period of time but batch reactor also has advantages in operating cost per batch, products deviation from batch to batch, and difficulty in large scale production.[15]

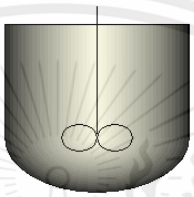


Figure 2.5: Batch reactor with agitator

For this work, both of reactors are batch reactor which have duty to provide occurring of reaction. These batch reactor are assumed to have constant volume and ignore how long of processing but also are considered about the effects of operating parameters on product and conversion.

2.3.1.2 Moles balance on batch reactor

Moles balance of batch reactor can be expressed as:

$$t = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{r_A V} \qquad 2.14$$

Where; t is the necessary time to reduce the number of moles of N_{A0} to N_{A1}

N_{A0} is the initial number of moles of reactants (A)

N_{A1} is the final desired number of moles of reactants (A)

r_A is the rate of reaction compare with A

V is the reactor volume

2.3.2 Flash separation

Figure 2.6: Flash drum

Flash drum is the vapor-liquid separator which base on fluid volatility via temperature, pressure control. The vapor phase favor substances will withdraw from the top and the liquid phase favor will stay at the bottom of the drum.[16] This unit is used to separate the product from others.

2.4 Plastic solid waste

Plastic waste in Bangkok has amount of 3440 tons/day which is contaminated wasted for 2780 tons/day and recyclable plastic waste around 660 tons /day.[17]

Plastic solid waste (PSW) at transfer station of Bangkok is composed of 57.4% of HDPE, 17.4% of LDPE, 7.3% of PP, and other which compose of 5.9% of PET, 5% of PC, 4.8% of PS, and 2.2% of PVC. In this work will focus only one recyclable plastic solid waste that are High Density Polyethylene (HDPE).[5]

From amount of recyclable plastic waste and ratio of plastic waste can be assumed that more than 400 tons/day of plastic waste is recyclable HDPE.

2.4.1 High Density Polyethylene

HDPE has low-weight, high amount ratio of strength to density so it can highly receive force compare with its small weight and also ignore against many solvent and corrosive materials so that it was often used in many application such as corrosion resistance container, pipes, bottles, etc., HDPE can be produced via slurry or solution and gas-phase polymerization to control the product properties i.e. Molecular weight distribution, density, and purity.[18,19] for this work focuses on production of HDPE via catalytic solution free-radical polymerization.

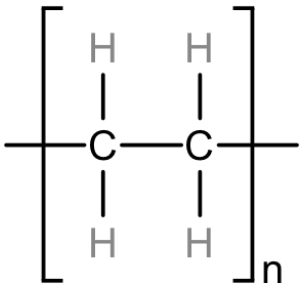


Figure 2.7: High Density Polyethylene (HDPE)

High Density Polyethylene (HDPE) is the popular thermoplastic which performed by ethylene molecules react to each other to form linear molecule without branch.[6,7] HDPE properties are showed at the table below:

Table 2.4: Properties of HDPE [19–25]

Properties	HDPE	
Chemical formula	$(C_2H_4)_n$	
Density	930-965 kg/m^3	
Molecular Weight Distribution	100,000-250,000	
Melting point	130.8 °C	
Ceiling temperature	610 °C	
Thermal conductivity	0.44 W/m·°C	
Insulation	Insulator	
Specific heat capacity	Solid phase	1.63 kJ/kg·°C
	Liquid phase	1.04 kJ/kg·°C
Latent heat of fusion	178.6 kJ/kg	

2.5 Simulation model and Assumption

This work use the commercial simulation program which is ASPEN Plus® with polymer Soave-Redlich-Kwong equation of state (SRK EOS) model of calculation for process simulation under the 4 assumptions;

1. Direction of radical addition occurs on only one ends (Head to Tail addition).
2. In chain propagation steps have no concern about chain length effects.
3. Propagating radicals reactivity is size independent.
4. The reaction mixture is perfectly mixed.
5. The system is assumed to be steady-state.

2.5.1 Soave-Redlich-Kwong equation of state model

Polymer Soave-Redlich-Kwong equation of state model, POLYSRK. POLYSRK is the extension of Soave-Redlich-Kwong cubic equation of state to mixture containing polymers. For mixture applications this model incorporates an excess energy term, based on activity coefficient models and also can be applied to both polar and non-polar fluid from low to high pressure. For mixture applications this model uses a Huron-Vidal-type mixing rule that incorporates an excess energy (Gibbs or Helmholtz) term.[26]

The excess Gibbs free energy can be written from an EOS using rigorous thermodynamics, and it can be equated to the same property from an activity coefficient model[26]:

$$\frac{G^E_{EOS}}{RT} = \ln\varphi - \sum_i x_i \ln\varphi_i \equiv \sum_i x_i \ln\gamma_i = \frac{G^E_\gamma}{RT} \qquad 2.15$$

Where; G^E_{EOS} is the excess Gibbs free energy from an EOS model

φ is the mixture fugacity coefficient

φ_i is the fugacity coefficient of component i in a mixture

γ_i is the activity coefficient of component i in a mixture

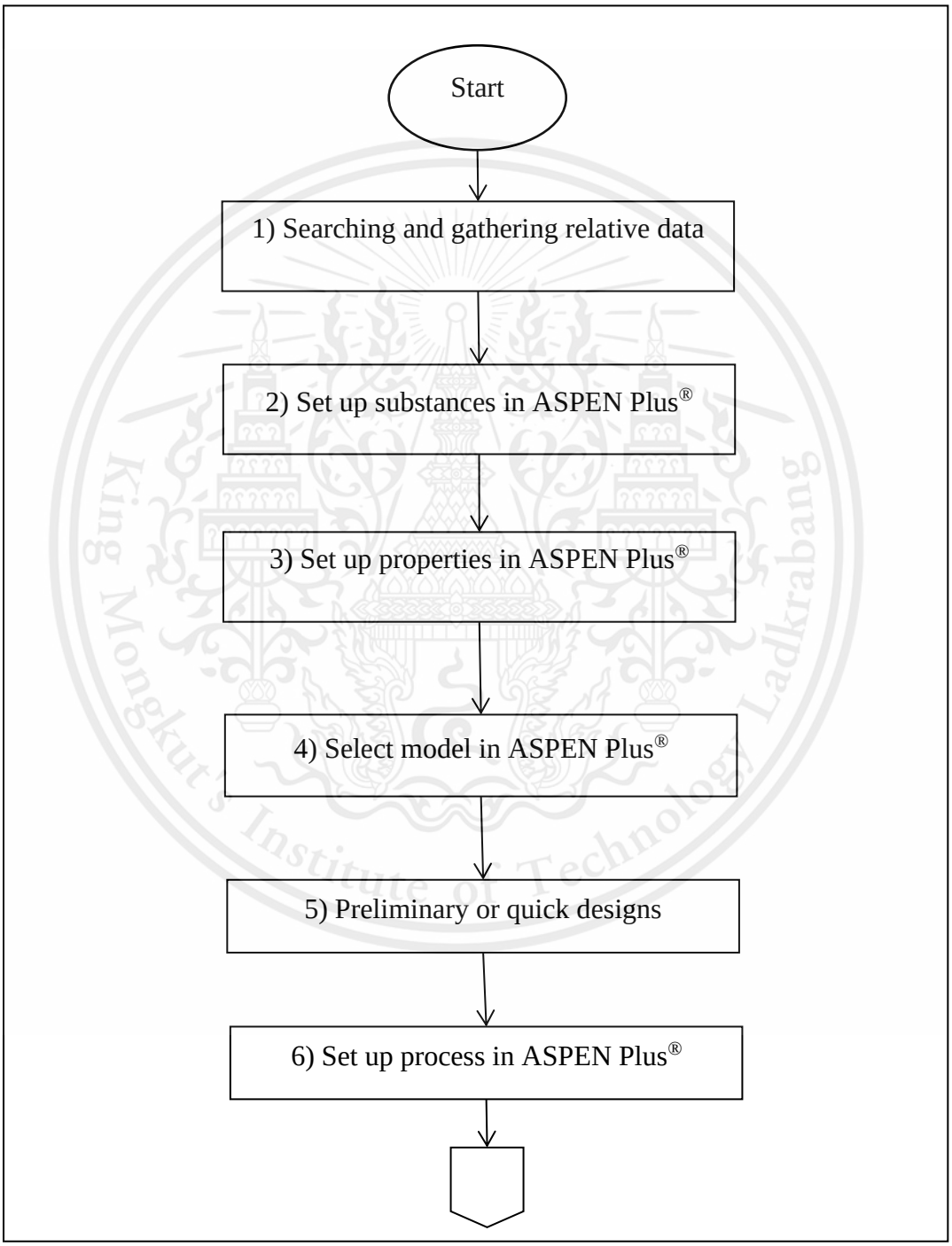
The above equality can only be written at a selected reference pressure. A reference for pressure is needed since the Gibbs free energy from an EOS is pressure dependent but the same term from an activity coefficient is not. Thus, an algebraically explicit equality can only be established at a single reference pressure.[26]

CHAPTER III

RESEARCH METHODOLOGY

3.1 Method

3.1.1 Sequences of project



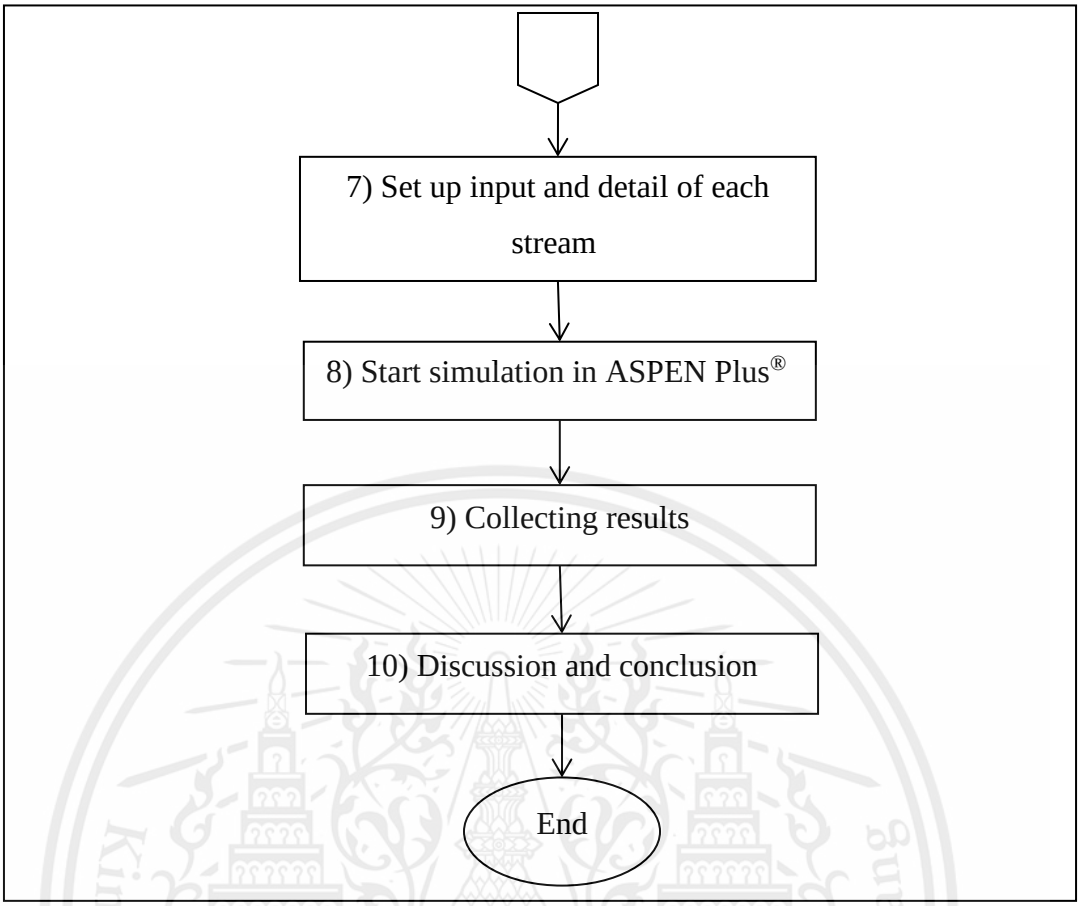


Figure 3.1: Flowchart of project procedure

This project begin with the idea that want to eliminate plastic waste problems by recycling, the first steps of this work is to search and collect relative data about recycling process, process unit for plastic recycling, polymer, and others such polymerization reaction, process design, simulation program etc.,. after that, is the steps of simulation that is data set up on simulation program which compose of substance with its properties, prediction model. Next, the process was constructed in the program with streams and unit data specification. The last section is the simulation to observe the effects of unit operation parameters on product.

3.2 Chemical Recycling Process Simulation

3.2.1 Data set up

This work begins with an idea that want to simulate product (HDPE) distribution of Chemical Recycling Process (CRP) of plastic solid waste which begin with information gathering and set up raw materials data in Aspen Plus® :

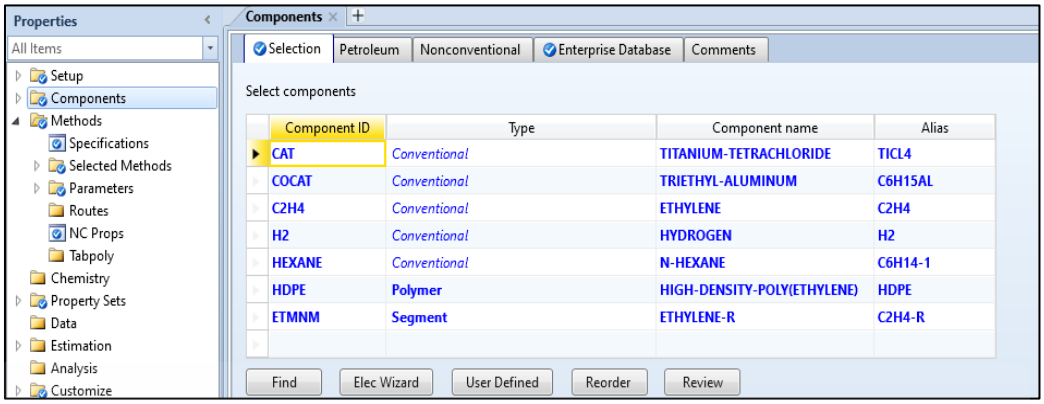


Figure 3.2: Setting up of raw materials in Aspen Plus® for CRP

All of raw materials in process is established in the program which compose of catalyst (Titanium tetrachloride, $TiCl_4$), co-catalyst (Triethylaluminium, $C_6H_{15}Al$), monomer (Ethylene, C_2H_4), hydrogen donor (Hydrogen, H_2), solvent (Hexane, C_6H_{14}), polymer (High Density Polyethylene, HDPE).

→ After that, set up the properties of every substances then select the model. For this work POLYSRK model is chosen:

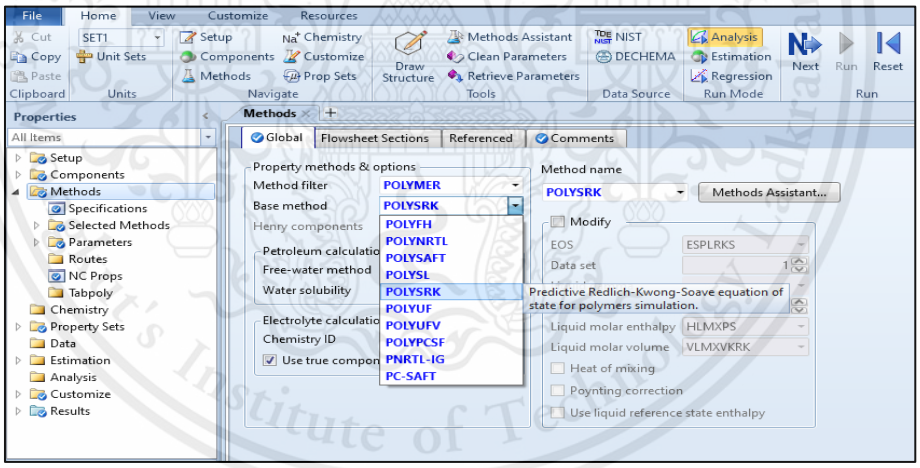


Figure 3.3: Selection of model

→ Next, make a quick design to get draft process for chemical process that include main unit operation as block flow diagram:

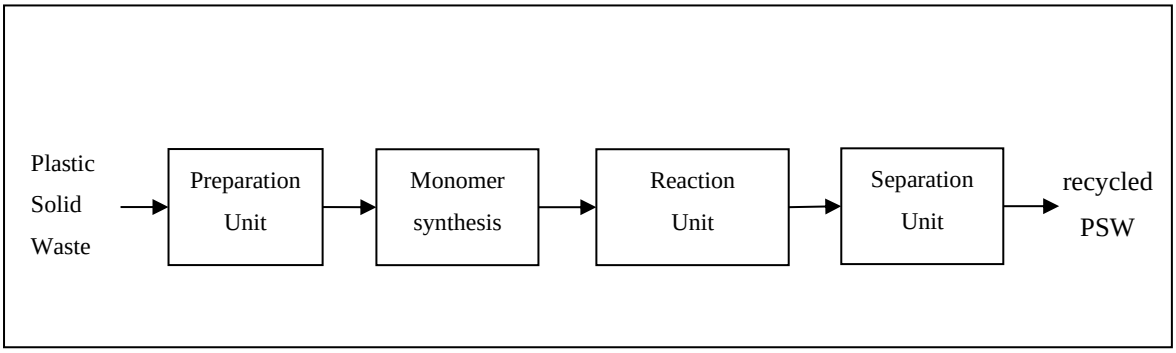


Figure 3.4: Preliminary block flow diagram of chemical recycling process

For chemical recycling process, plastic waste is sent to the preparation unit like the mechanical process after that, melted plastic is sent to monomer synthesis section to create monomer for reaction unit to produce polymer then the polymer product is purified by separation unit but this work will focus only on reaction unit and separation unit.

→ After that, constructing Chemical Recycling Process on ASPEN Plus® which compose of reaction unit and separation unit:

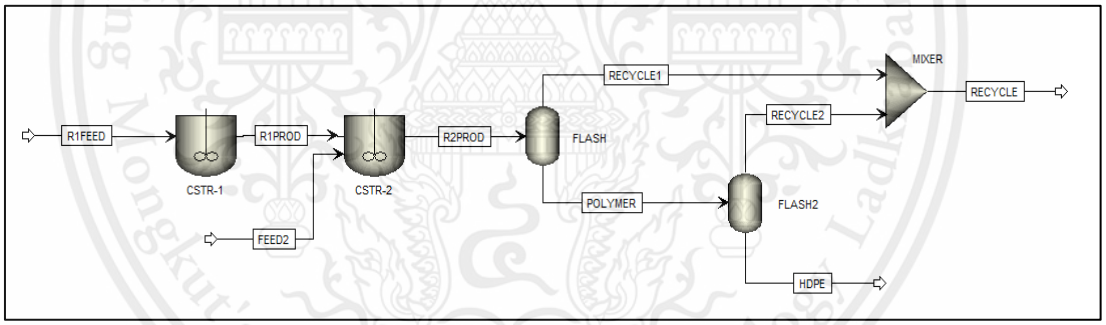


Figure 3.5: Chemical recycling process of plastic solid waste (HDPE)

For chemical recycling process, FEED1 stream which had already synthesized to be monomer is fed to the first reactor to produce HDPE then the product stream (R1PROD) is loaded to react with FEED2 stream in the second reactor to increase conversion, after that the product stream (R2PROD) is sent to separation unit which is flash drum to purified the product stream to get high purity of HDPE and both of RECYCLE1 and RECYCLE2 stream is mixed together as a recycle stream to use as a solvent again.

→ Input desired and necessary values to both of streams and unit operations for this work want to recycle Polyethylene monomer 4000 kg/day :.

Table 3.1: Conditions and mass fraction of each stream

Stream	Conditions			Mass faction[27]				
	Temperature	Pressure	Flow rate	Catalyst	Co-cat.	H_2	C_2H_4	Hexane
R1FEED	70 °C	1 atm	20000 kg/day	1e-4	15e-5	5e-6	0.1	0.899
FEED2	70 °C	1 atm	10000 kg/day	1e-4	15e-5	-	0.2002	0.799

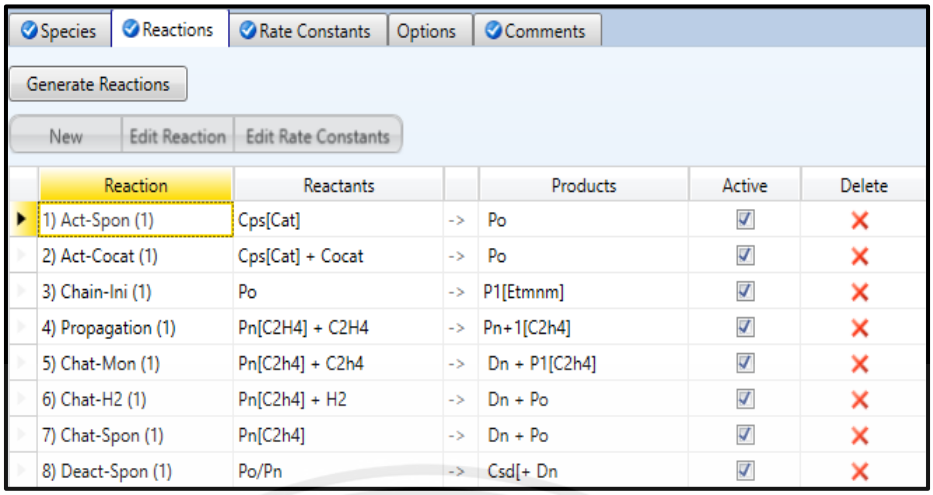
Table 3.2: Operating condition of each unit operation

Unit operation	Operating parameters[21,27]			
	Temperature	Pressure	Valid-phase	Residence time
R-1	160 °C	40 atm	Liquid-only	42.1 hr
R-2	160 °C	40 atm	Liquid-only	28.2 hr
FLASH	160 °C	8 atm	Vapor-Liquid	-
FLASH2	160 °C	1 atm	Vapor-Liquid	-

→ Set up reactions, this section is compose of 8 reactions and rate constant that are followed the table below:

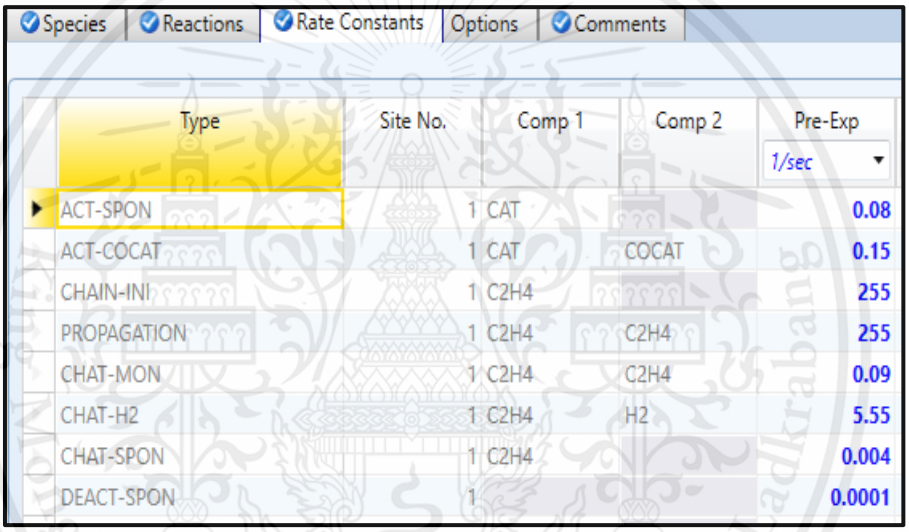
Table 3.3: Reactions and rate constant

Reactions	Rate constant (1/sec) @ 273K[27,28]
spontaneous site activation	0.08
site activation by co-catalyst	0.15
chain initiation	255
chain propagation	255
chain transfer to monomer	0.09
chain transfer to hydrogen (H_2)	5.55
spontaneous chain transfer	0.004
spontaneous site deactivation	0.0001



Reaction	Reactants		Products	Active	Delete
1) Act-Spon (1)	Cps[Cat]	->	Po	☑	✕
2) Act-Cocat (1)	Cps[Cat] + Cocat	->	Po	☑	✕
3) Chain-Ini (1)	Po	->	P1[Etmnm]	☑	✕
4) Propagation (1)	Pn[C2H4] + C2H4	->	Pn+1[C2h4]	☑	✕
5) Chat-Mon (1)	Pn[C2h4] + C2h4	->	Dn + P1[C2h4]	☑	✕
6) Chat-H2 (1)	Pn[C2h4] + H2	->	Dn + Po	☑	✕
7) Chat-Spon (1)	Pn[C2h4]	->	Dn + Po	☑	✕
8) Deact-Spon (1)	Po/Pn	->	Csd[+ Dn	☑	✕

Figure 3.6: Reactions set up



Type	Site No.	Comp 1	Comp 2	Pre-Exp 1/sec
ACT-SPON	1	CAT		0.08
ACT-COCAT	1	CAT	COCAT	0.15
CHAIN-INI	1	C2H4		255
PROPAGATION	1	C2H4	C2H4	255
CHAT-MON	1	C2H4	C2H4	0.09
CHAT-H2	1	C2H4	H2	5.55
CHAT-SPON	1	C2H4		0.004
DEACT-SPON	1			0.0001

Figure 3.7: Rate constant set up

→ After all value and properties are identified then, simulation program is ready to start simulation of the process

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Results

4.1.1 Material Balance and Energy Balance

The results of material balance showed that, this process provides purity of recycled HDPE product about 97.95 %wt. the results of energy balance showed that, the enthalpy flow of the product stream is higher than feed stream's enthalpy flow which occurred by heat releasing from the reaction (exothermic).

The results of material balance which compose of each components flowrate are showed as same as the results of energy balance which is enthalpy flow of each streams at the table below:

Table 4.1: Material Balance and Energy Balance of Chemical Recycling Process

Material Balance							
Streams	Components flowrate (kg/day)						
	Total	Catalyst	Co-catalyst	Monomer	H_2	Solvent	HDPE
R1FEED	20000	2	3	2000	0.1	17994.9	0
R1PROD	20000	2	3	252.892	0.082	17994.9	1747.13
FEED2	10000	1	1.5	2002	0	7995.5	0
R2PROD	30000	3	4.5	641.191	0.0756	25990.4	3360.83
RECYCLE1	25861.4	1.12e-10	0	639.455	0.0756	25221.9	0
POLYMER	4138.56	3	4.5	1.73599	2.7865e-5	768.49	3360.83
RECYCLE2	707.288	1.95e-11	0	1.72376	2.78415e-5	705.564	0
HDPE	3431.27	3	4.5	0.01223	2.35347e-8	62.926	3360.83

Energy Balance	
Streams	Enthalpy flow (kW)
R1FEED	-420.078
R1PROD	-437.697
FEED2	-165.11
R2PROD	-643.282
RECYCLE1	-478.735
POLYMER	-86.811
RECYCLE2	-13.6363
HDPE	-70.9774

4.1.2 Unit operation results

The results of unit operation is compose of net heat duty of reactor, volume of reactor, and net heat duty of flash drum. Net heat duty of Reactor-1 and Reactor-2 are minus value that mean heat have to be released from the reactor around 17.62 kW for Reactor-1 and around 40.474 kW for Reactor-2 because exothermic reaction was occurred in the reactor. Volume of Reactor-1 and Reactor-2 are around 64.5 m^3 and 64.4 m^3 respectively which is suitable for the system at given conditions. Net heat duty of Flash-1 and Flash-2 are 77.736 kW and 2.197 kW respectively that mean supplying of energy to flash drum is necessary.

The results of process unit are showed at the table below:

Table 4.2: Results summary of process unit

Units	Results	
	Net heat duty	Volume
Reactor-1	-17.619 kW	64.537 m^3
Reactor-2	-40.474 kW	64.453 m^3
Flash-1	77.736 kW	-
Flash-2	2.197 kW	-

4.1.3 Sensitivity analysis

For the sensitivity analysis, this part provide the effect of operating parameters such as residence time, temperature, and pressure on the character of product which is molecular weight distribution, the conversion of the reaction unit for reaction section, and purity of recycled HDPE product in term of mass fraction for separation section.

4.1.3.1 Sensitivity results of Reactor-1

Effect of residence time on the product and conversion

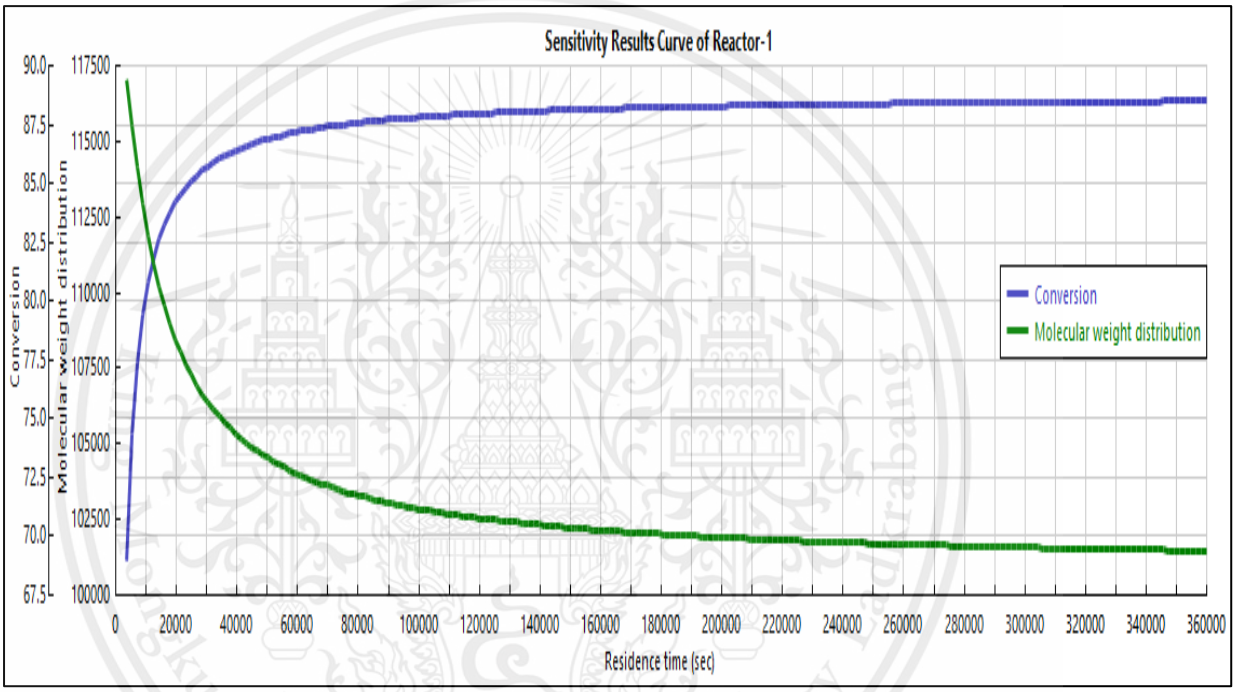


Figure 4.1: Graph show the effect of residence time in Reactor-1

From the results of residence time variation showed that, increasing in the residence time of reactor-1 from 1-100 hours affect to increase conversion from 68.93% to 88.49% and decrease molecular weight distribution of HDPE from 117028 to 101460 due to higher residence time provide more time for reaction therefore, monomers can become more polymer but if provide residence time too much will resulting in many polymer occurred in the system which provide better chain transfer to monomer, chain transfer to hydrogen, and spontaneous chain transfer steps which is chain termination that means chain length will be shorter and molecular weight distribution of HDPE will becomes lower until it reach to the equilibrium then, the steady of Molecular weight distribution decreasing rate will be occurred.

Effect of temperature on the product and conversion

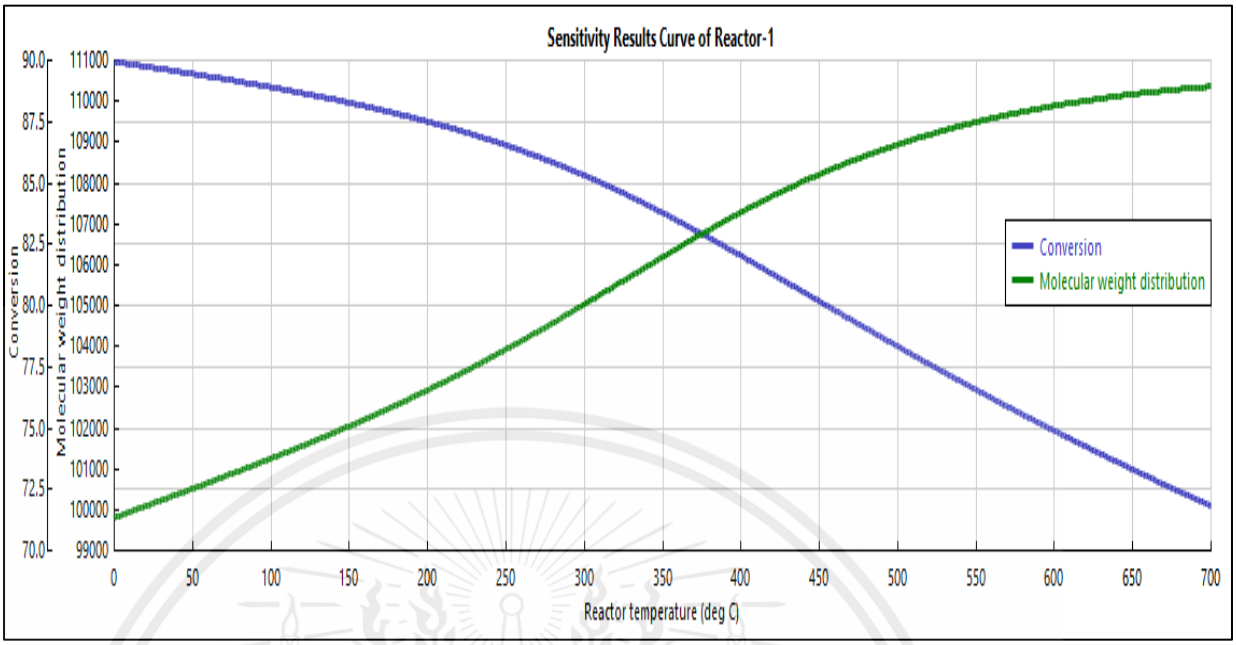


Figure 4.2: Graph show the effect of reactor temperature in Reactor-1

From the results of temperature variation showed that, if temperature increase from 0-700 °C, conversion will decrease from 89.94% to 71.82% and molecular weight distribution increase from 99802.3-110360. Because of, the reaction in this system which is catalyzed free-radical polymerization is exothermic reaction so that conversion will be decreasing when reactor temperature is increased. Increasing in molecular weight distribution can be occurred via molecules of polymer were excited by heat which provide more probability of reactant will react to other reactant.

Effect of pressure on the product and conversion

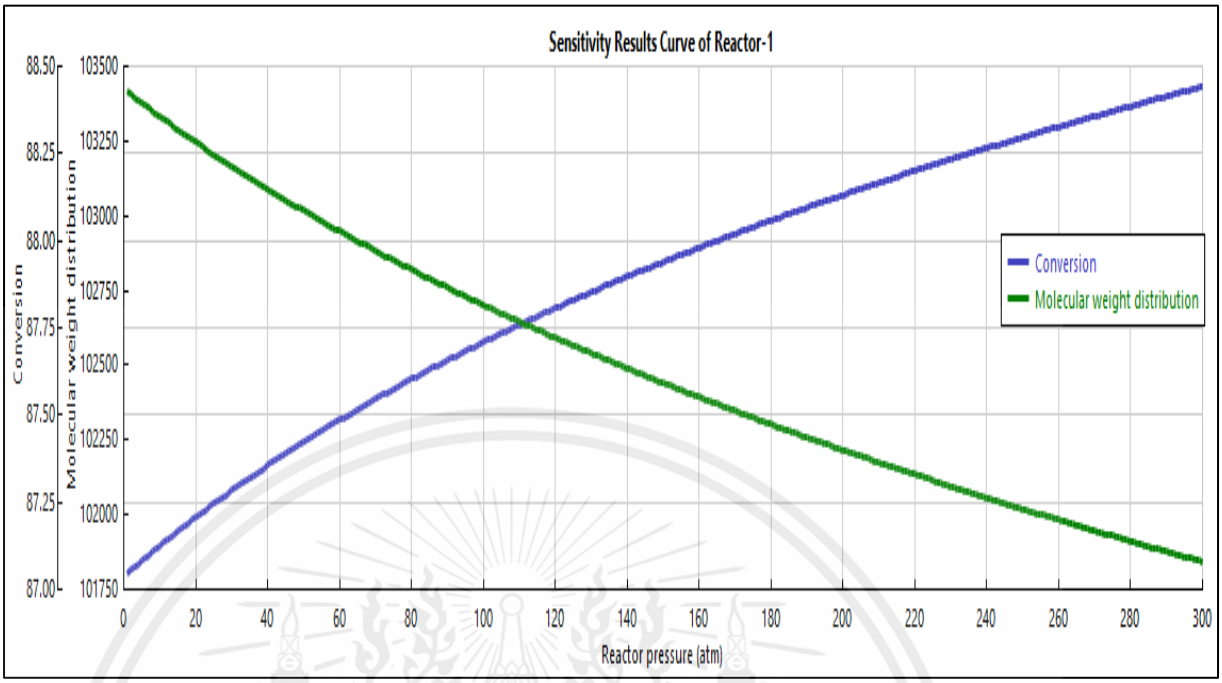


Figure 4.3: Graph show the effect of pressure in Reactor-1

From the results of pressure variation showed that, if pressure rise from 1-300 atm, conversion change from 87.05% to 88.44% (around 1%) and molecular weight distribution change from 103415 to 101843 (only 1.5%). Because of, this system is solution polymerization which occur in liquid phase so pressure has no effect on this system.

4.1.3.2 Sensitivity results of Reactor-2

Effect of hydrogen flow rate on the product and conversion

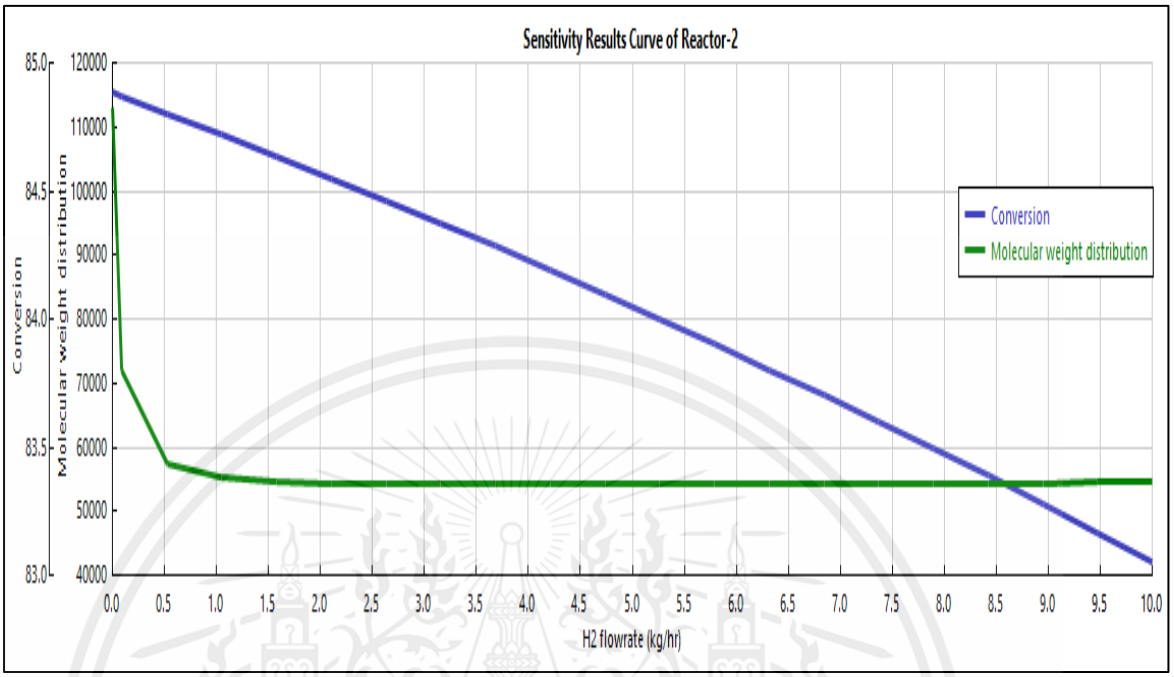


Figure 4.4: Graph show the effect of hydrogen flow rate in Reactor-2

From the results of hydrogen flow rate variation showed that, the flow rate of hydrogen in reactor-2 has slightly effect on conversion but it provide serious effect on molecular weight distribution. If amount of hydrogen in the reactor is higher than 0.02 kg/hr or 0.47kg/day, molecular weight distribution of recycled HDPE will be lower than 100000. Because of large amount of hydrogen will affect to better chain transfer to hydrogen which cause stopping of chain propagation steps then chain length of HDPE will be short that means molecular weight distribution value will be lower than the typical molecular weight distribution of HDPE.

Effect of residence time on the product and conversion

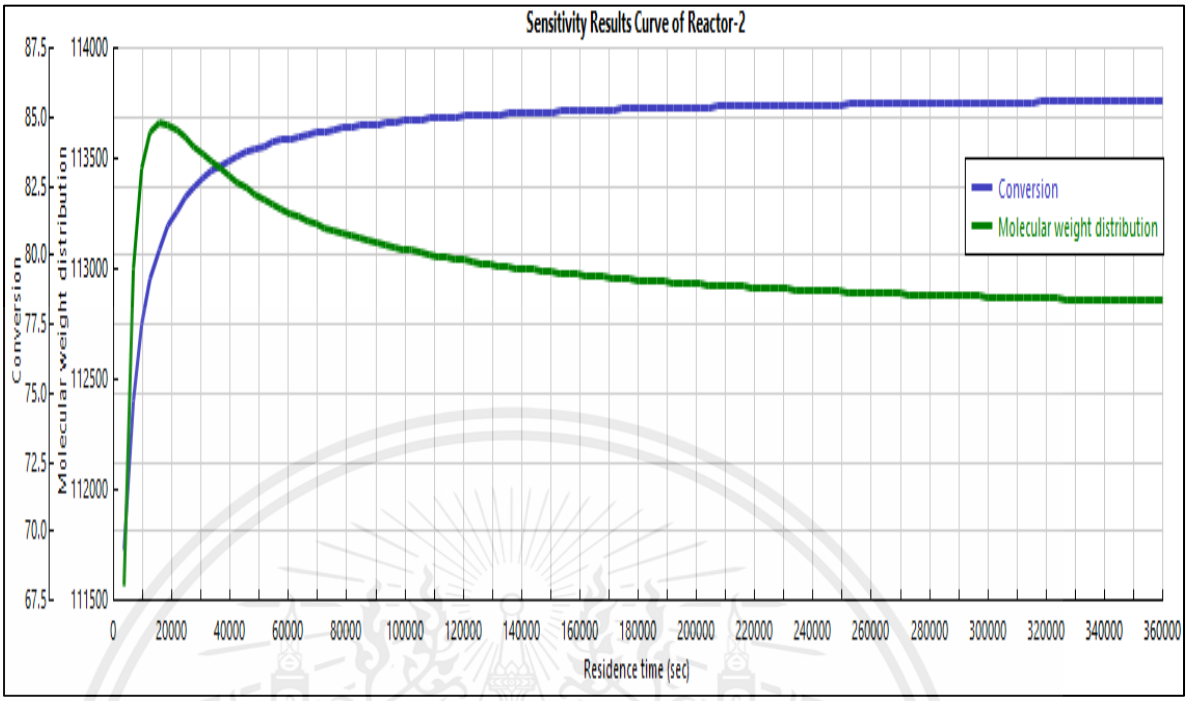


Figure 4.5: Graph show the effect of residence time in Reactor-2

From the results of residence time variation showed that, conversion rapidly increase with the residence time at the initial state of the process because of at the initial state has large amount of reactants so the reactant can convert to the product very quickly and the conversion increasing rate becomes slower residence time is higher than 60000 seconds or around 17 hours due to the effect of chain length that provide obstacle to the reaction combine with low amount of the remaining reactants.

Molecular weight distribution rapidly increase at the initial state then becomes lower at residence time around 15000 seconds or 4 hours which may be occurred from at the initial of state almost of the reaction that occurred in the system is of chain initiation and chain propagation which have large amount of rate constant value so polymer chain rapidly grow and decreasing of molecular weight distribution can be occurred from large amount of polymer product occurred in the system which have effect on the chain transfer reaction which is the chain termination steps of polymerization so that the molecular weight distribution becomes lower until steady when the equilibrium of the reaction occurred.

Effect of pressure on the product and conversion

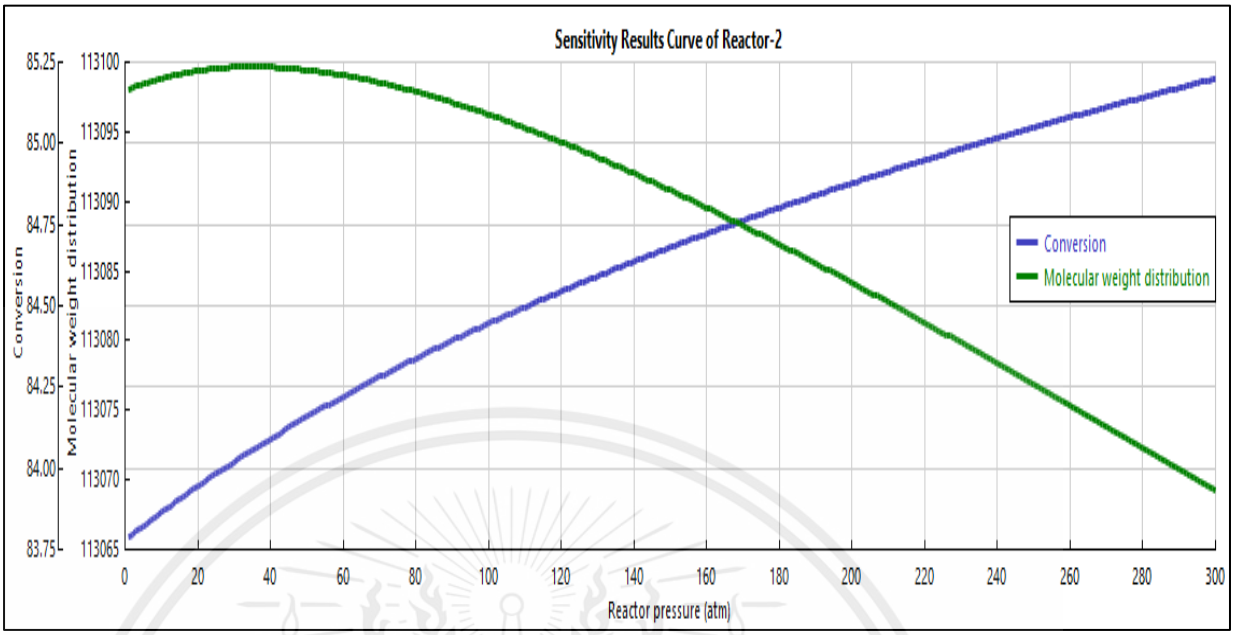


Figure 4.6: Graph show the effect of pressure in Reactor-2

From the results of pressure variation showed that, if pressure rise from 1-300 atm, conversion change from 83.68% to 85.23% (around 1.5%) and molecular weight distribution change from 113415 to 113061 (only 0.3%). Because of, this system is solution polymerization which occur in liquid phase so pressure has no effect on this system.

Effect of temperature on the product and conversion

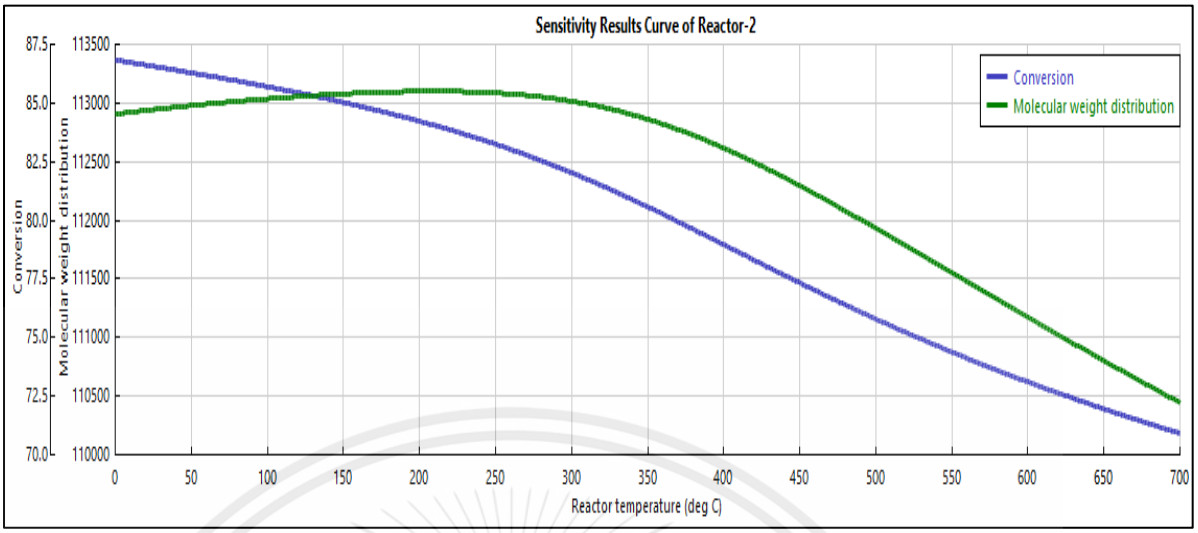


Figure 4.7: Graph show the effect of temperature in Reactor-2

From the results of temperature variation showed that, when temperature was increased from 0-700 °C, conversion will decreased from 86.98% to 68.66% and molecular weight distribution will slightly increase before rapidly decrease. Because of the high amount of conversion from reactor-1 that produce polymer product at high conversion and large amount of molecular weight distribution that means when the reactants is filled to reactor 2 with the product of reactor-1, the chain length effects will affect to harder in reaction occurring so the conversion and molecular weight distribution will be decrease and decrease faster when temperature is nearly to ceiling temperature.

4.1.3.3 Sensitivity results of separation unit

Effect of temperature on the product purity at constant pressure, 8 atm

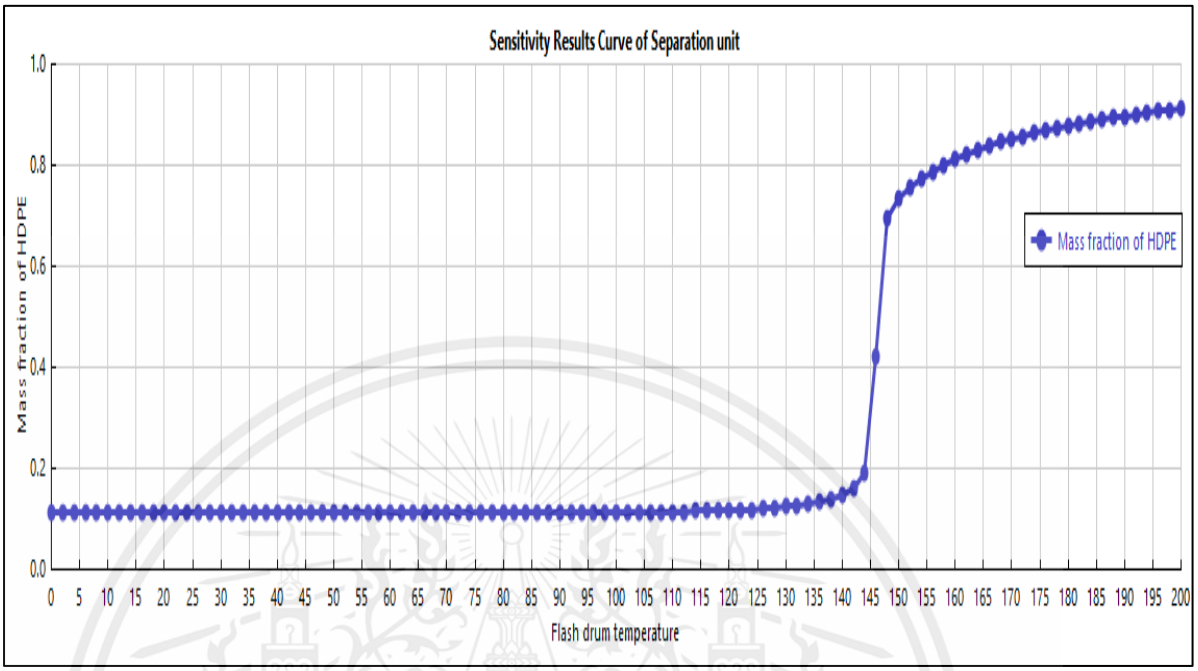


Figure 4.8: Graph show the effect of temperature on mass fraction of HDPE

From the result of temperature variation showed that, the suitable temperature is higher than 150 °C which is nearly with the reactor temperature so that the HDPE can be separated from the product streams by pressure reduction (temperature change is not necessary).

Effect of pressure on the product purity at constant temperature, 160 °C

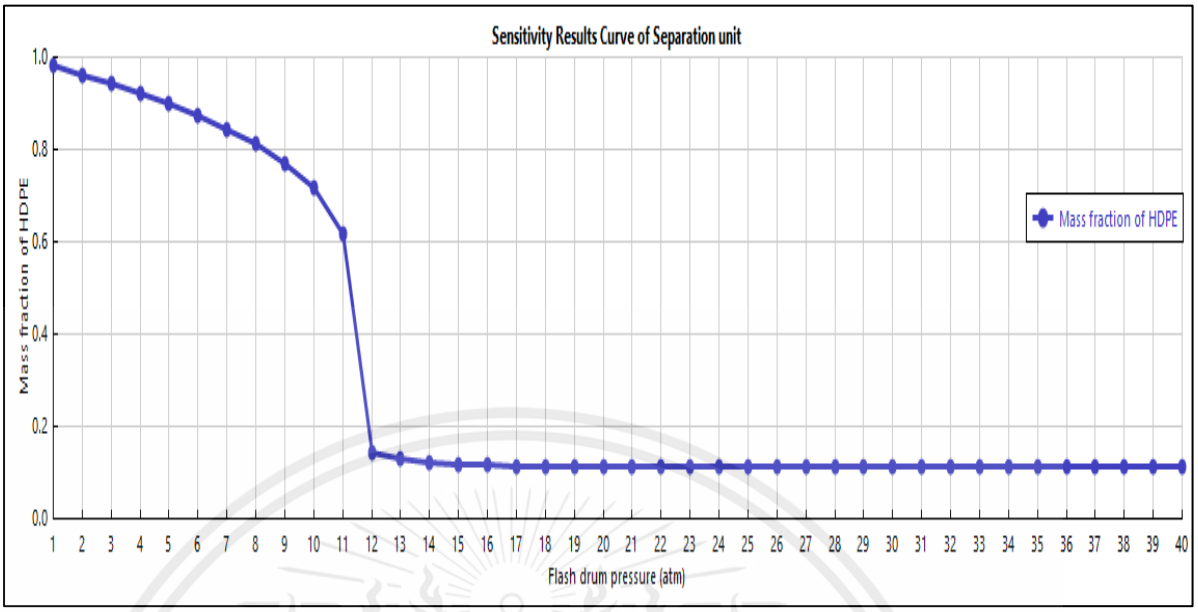


Figure 4.9: Graph show the effect of pressure on mass fraction of HDPE

From the results of pressure variation confirmed that, HDPE can be separated from the product streams at the pressure is lower than 11 atm.

From this results provide the suitable reactor pressure must higher than 12 atm to prevent vaporization of solvent.

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4.1.3.4 Molecular weight distribution of product

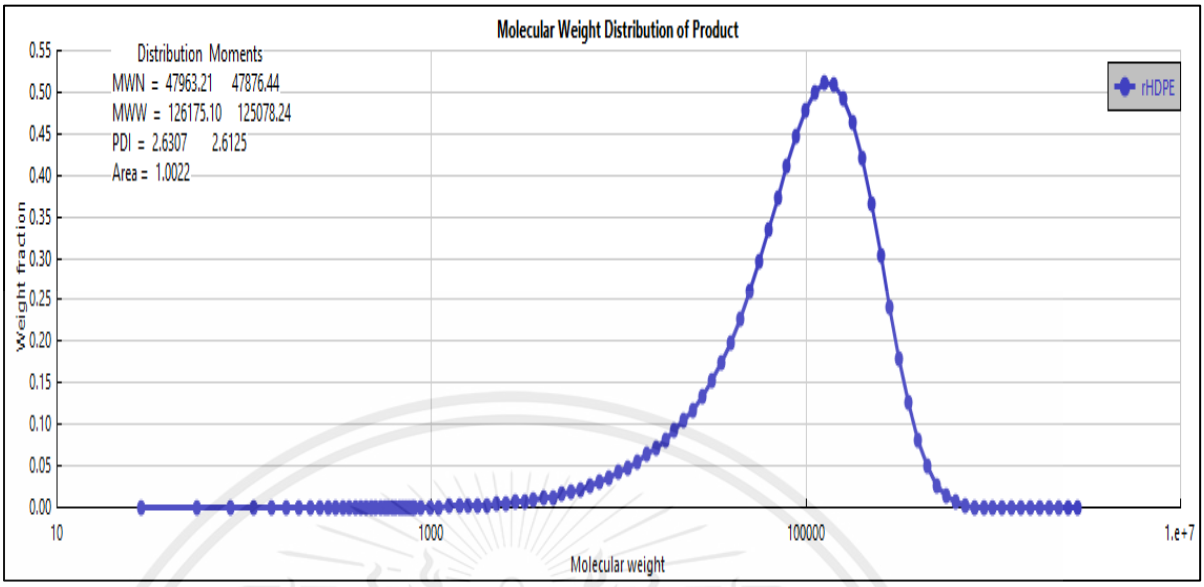

Figure 4.10: Graph show the molecular weight distribution of HDPE

From the results of molecular weight distribution of the product showed that, the product which is recycled HDPE is between 125078.24-126175.1 which is in the range of typical HDPE molecular weight distribution.

CHAPTER V

CONCLUSION

5.1 Conclusion

The simulation recycling process can simulate the occurring of reaction for the recycling process and available for optimization when stream conditions or process units conditions in the process is needed to change.

From doing this project, resulting in simulation process which can be applied to chemical recycling process. This work can be used as a guideline for simulation of plastic waste recycling process.

From the results of simulation can be concluded that, the suitable operating parameters for the first reactor which compose of residence time, temperature, and pressure are between 3-17 hours, 200-400°C, and more than 12 atm respectively, heat have to be eliminated from the reactor for 17.619 kW.

The suitable operating parameters for the second reactor which compose of residence time, temperature, and pressure are between 5-11 hours, 100-250°C, and more than 12 atm respectively. In additional, amount of hydrogen have to be control to lower than 0.47 kg/day, and heat have to be eliminated from the reactor for -40.474 kW.

The suitable operating parameters for both of separation unit is the same as temperature of reactor which is 160°C and pressure have to be reduce from 40 atm to 8 atm and 1 atm respectively with total energy consumption is 79.933 kW to produce 97.9%wt of recycled HDPE.

This project presents about how to perform plastic waste recycling process by using process simulation program which is ASPEN Plus®. From the results can be concluded that, the simulation program meet the needs of constructing of the process and achieving objective of this project.

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APPENDIX

Appendix A: Data table

Table A-1: Typical Commercial Chain-Growth Polymers

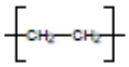
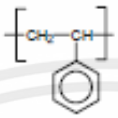
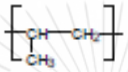
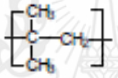
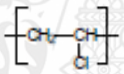
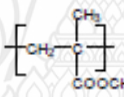
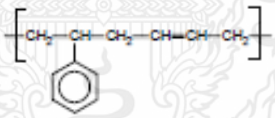
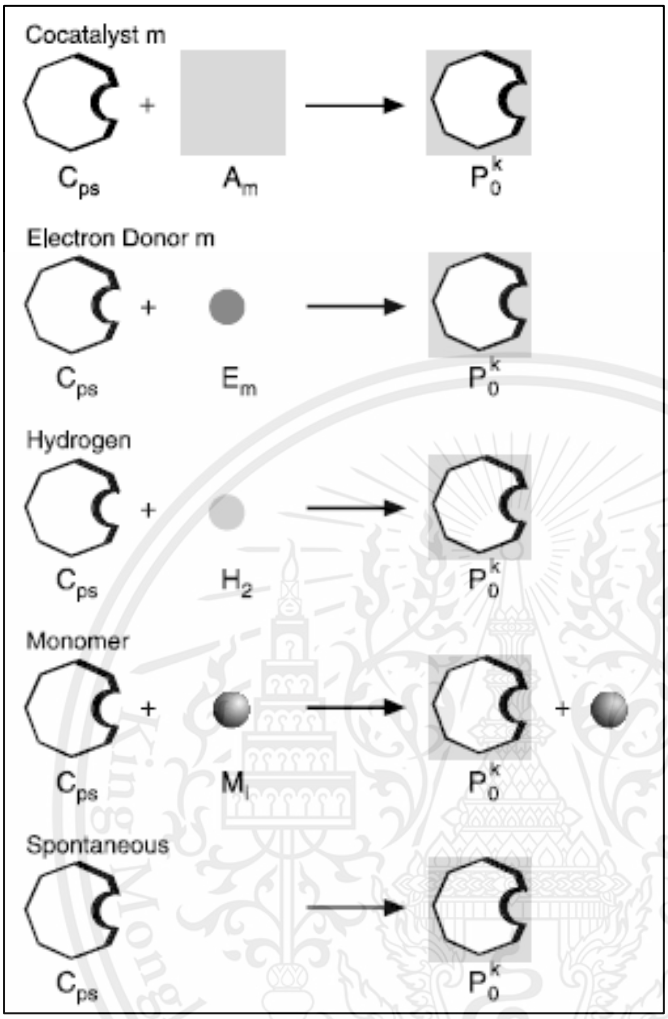
Polymer	Monomers	Repeat Unit	Reaction Types	Applications
Polyethylene	Ethylene		Bulk/solution (free-radical) Coordination complex (Ziegler-Natta)	Film, packaging
Polystyrene	Styrene		Bulk/solution/ suspension (free-radical)	Containers, packaging, insulation
Polypropylene	Propylene		Coordination complex (Ziegler-Natta)	Films, packaging, autoparts, sealants
Polyisobutylene	Isobutylene		Ionic	Films, plastic tubing
Polyvinyl chloride	Vinyl chloride		Bulk/solution/ suspension (free-radical)	Floor coverings, pipes
Polymethalmethacrylate	Methyl Methacrylate		Bulk/solution (free-radical)	Lenses, plastics
Styrene butadiene rubber	Styrene Butadiene		Emulsion (free-radical)	Tires, belting, shoe soles

Table A-2: Polymers Plus Polymerization Reaction Models

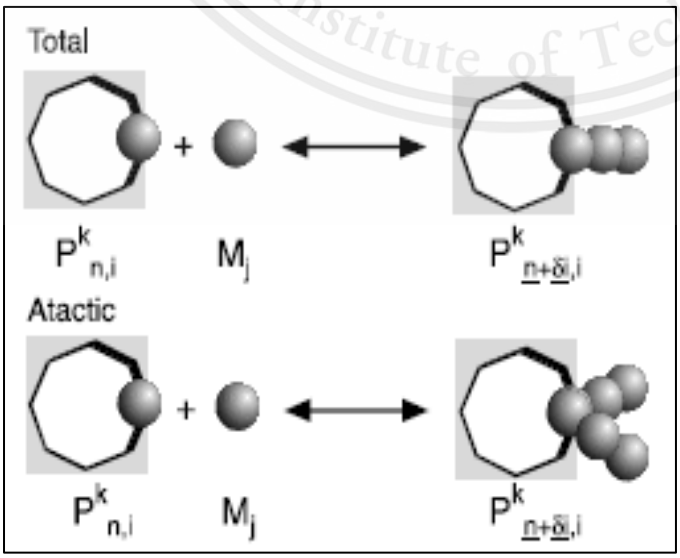
Model Name	Chemistry	Processes	Polymers
Step-growth			
STEP-GROWTH	Condensation	Melt phase	PC, PBT, PET, Nylons
Chain-growth			
FREE-RAD	Free-radical	Bulk, solution	PS, PVAC, SAN, PMMA
EMULSION	Free-radical	Emulsion	SBR, SBA
ZIEGLER-NAT	Ziegler-Natta / metallocene coordination complex	Bulk, solution	HDPE, PP, LLDPE
IONIC	Anionic/Cationic group transfer	Solution	PIB, SBR, PEO
Generic			
SEGMENT-BAS	Standard power-law	N/A	PVA from PVAC

Appendix B: Ziegler-Natta catalysts kinetic scheme

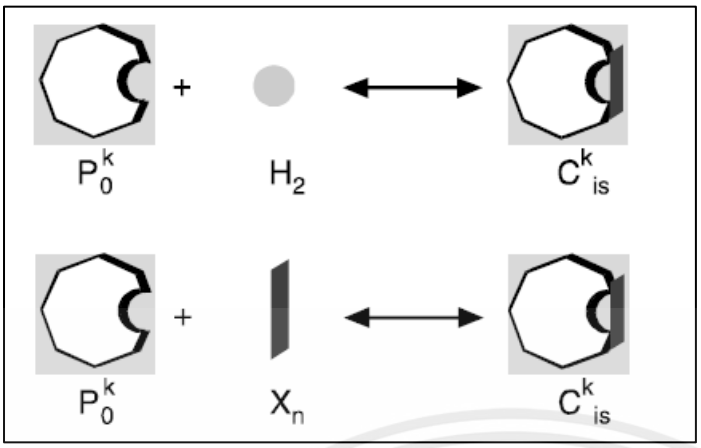
Site activation reactions



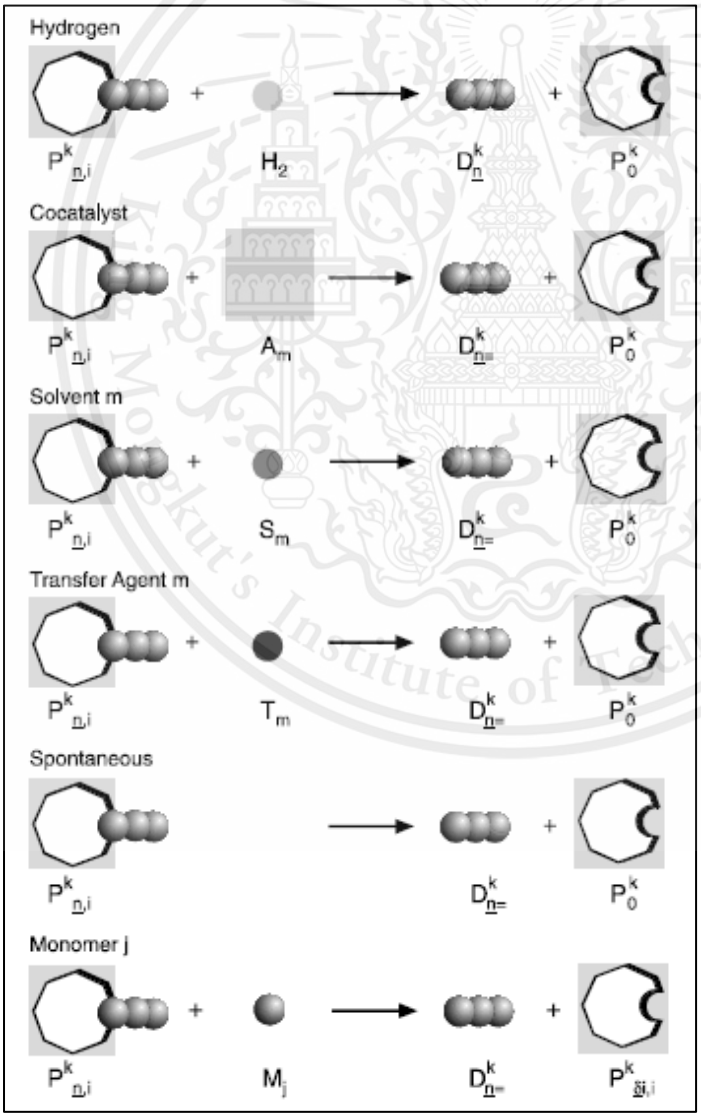
Chain propagation reactions



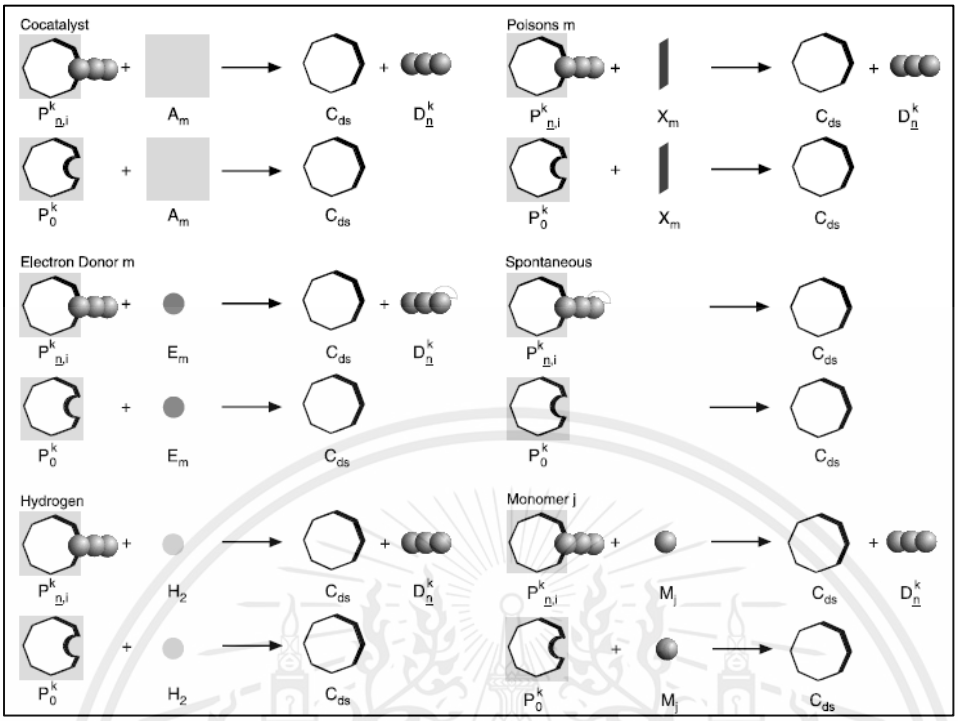
Chain inhibition reactions



Chain transfer reaction



Site deactivation reactions



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