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PREDICTION OF CRACKING HYDROCARBON COMPOUNDS FROM PALM OIL WITH CHEMICAL EQUILIBRIA

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ระบบปฏิกิริยาการแตกตัวของแนฟทา ณ สมดุลเคมีแบ่งออกเป็นสองกลุ่มคือ กลุ่มปฏิกิริยาของสารประกอบไฮโดรคาร์บอนชนิดโซ่ตรงและกลุ่มปฏิกิริยาของสารประกอบไฮโดรคาร์บอนชนิดเป็นวง การพยากรณ์ผลผลิตของกลุ่มปฏิกิริยาทั้งสองต้องคำนวณแยกกันตามสัดส่วนขององค์ประกอบในแนฟทา ระบบปฏิกิริยาและการพยากรณ์ต้องถูกดัดแปลงไปใช้กับกรณีการแตกตัวสารประกอบไฮโดรคาร์บอนจากน้ำมันปาล์ม พบว่าผลิตภัณฑ์หลักคือเอทิลีนและโพรพิลีน และมีร้อยละการผลิตมากกว่าร้อยละ 50 และร้อยละ 25 ตามลำดับ ณ อุณหภูมิสูงกว่า 800 องศาเซลเซียส

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Cracking reactions for naphtha have been modeled with chemical equilibria. The reactions have been divided into two groups, reactions for paraffins and reactions for naphthenes and aromatics. Both groups have to be simulated separately with respect to the groups of composition in naphtha. The reaction system has been modified for cracking hydrocarbon compounds from palm oil. The results have demonstrated that both ethylene and propylene yields can be produced more than 50 % and 25 %, respectively at reaction temperature above 800 °C.

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A_k	total number of atoms of element k in the system
a_{ik}	number of atoms of element k in a molecule of chemical species i
$\hat{f}_i$	fugacity of chemical species i in a solution
$G_{T,P}$	total Gibbs free energy of the system at constant temperature and pressure
ΔG°_{fi}	Gibbs free energy of formation
n_i	number of moles of chemical species i in the system
y_i	vapor-phase mole fraction
λ_k	lagrangian multiplier of element k
μ_i	chemical potential
$\hat{\phi}_i$	fugacity coefficient

Subscripts

i	i^{th} species
k	k^{th} element
T	temperature
P	pressure

Superscripts

*	free radical
o	standard state

Chapter I

Introduction

Palm oil, a mixture of triglycerides of fatty acids, is an important agricultural product, cultivated in southern part of Thailand. It has been used as a raw material for food and soap industries [1]. In comparison with petroleum, it may be considered as an alternative source of hydrogen and carbon elements, which can be produced in relatively short period.

Although fats and oils have been used for a long time, their chemical nature just has been studied since the 18th century at the beginning of modern organic chemistry. The technology of fatty acids was developed with acceleration in the first half of the 20th century. Fatty acids became unattractive because of their simple molecular structure, chemical inactivity and difficulty in separation into individual fatty acid. Additionally, the chemistry of high molecular weight polymers had not been known [2].

Eighty percent of the world fat and oil comsumption are used as human food, six percent as animal feed, and the remainder fourteen percent as oleochemicals that are fatty acids and their derivatives [3]. The utilization of these oleochemicals is in many areas, for instance, surfactants, protective and decorative coatings, lubricants, cosmetics, pesticides, plasticizers, textile industries, paper industries, leather industries, pharmaceutical industries, and rubber industries [4,5]. In addition, some application of fatty acid derivatives, which were generated from palm oil, are listed in Table 1.1.

Due to the cost of natural gas and petroleum as well as the limitation of them, one application of palm oil is biodiesel. This application has been studied for more than 90 years in some countries that lacked petroleum [6,7]. If the engine is not modified, methyl esters of vegetable oils or animal fats are recommended, while the original oils or fats should be employed only in a modified engine such as the Elsbett engine produced in Germany [3].

In 1983, Alencar et al found that main products of pyrolysis of vegetable oil were paraffins and α-olefins [8]. This showed that it was possible to produce α-olefins, such as ethylene and propylene, from palm oil. Two years later, Lipinsky et al proved this idea with steam cracking and discussed that olefins had had a good trend [9].

Although, the exploration, which was carried out by Alencar et al, uses palm oil in the form of triglycide to produce olefins, it is more attractive to hydrolyze palm oil before cracking. The reason is that glycerol, a valuable product, is also obtained. The fat splitting proceeds in stages, from triglyceride to diglyceride, to monoglyceride, and finally fatty acid and glycerol are attained.

Table 1.1 applications of fatty acids and their derivatives [10]

Metallic salt

Fatty acid	*metal*	*application*
Palmitic, stearic	Ca, Zn	mould release agent
Stearic	Ca, Mg	cosmetics for spreading and adherence. food and pharmaceuticals for emulsification, lubrication and binding, rubber chemical
Stearic	Al, Li	grease for gelling property, rubber chemical
Oleic	Zn, Pb	pigment grinding aid, medicinal ointments for antiseptic action
Oleic	Ba	anti-chalking agent

Fatty alcohols, monoglycerides and fatty aldehydes

Fatty molecule	*derivative*	*application*
C_{16} and C_{18} alcohol	sulphated	biodegradable detergents
C_{16} and C_{18} alcohol	esterified with higher saturated fatty acids	sperm oil replacer, carnouba wax substitute
C_{16}, C_{18} and $C_{18:1}$ alcohols		cosmetics
C_{16} and C_{18} alcohol	ethoxylation	non-ionic surface active compounds
Monoglycerides		food emulsifiers
Monoglycerides	ethoxylated, acetylated	cosmetics
C_{16} aldehyde		modifier in blending of perfumes

Table 1.1 applications of fatty acids and their derivatives (continued)

Fatty amine

Amine	*derivative*	*application*
Primary		
C_{16} and C_{18}	hydrochlorides and acetates	anticaking property for protecting inorganic compounds
C_{16} and C_{18}	ethoxylated	emulsifiers and anti-static agents, textile processing oils
C_{16} and C_{18}	guanidine ethoxylated	surface active compounds
Secondary		
C_{16} and C_{18}	ethoxylated	surface active compounds, corrosion inhibitors for petroleum industries
Ternary		
C_{16} and C_{18}	-	cationic surface active agents in a variety of applications form fabric softeners with bactericidal actively to dispersants and corrosive inhibitors in petroleum products

Fatty acid amide and derivative

Amide and derivative	*application*
Stearamide	anti-block agent for polymer, mould release agent for moulded rubber articles, durable textile water repellent
Oleamide	slip agent for polymer
Sulphated alkanolamide of palmitic, stearic and oleic acid	lime soap dispersing agents
Alkanolamides	chemical intermediates for textile auxiliaries, wetting agents, dyeing assistants, waxes, detergents, etc.

Oxygenated fatty acid

Oxygenated fatty acid	*derivative*	*application*
Epoxy stearic	octanol ester	sperm oil replacer
Epithio stearin	various mono and polyhydric alcohol esters	extreme pressure lubricants

Polyalkoxylated derivative

Fatty acid	*alkoxy*	*application*
Palmitic, stearic	ethylene oxide, propylene oxide	emulsification, detergency and related fields
Oleic acid dimer	ethylene oxide, propylene oxide	special non-ionic detergents for end uses

Table 1.1 applications of fatty acids and their derivatives (continued)

Ester

Fatty acid	*alcohol*	*application*
Palmitic	isopropanol	cosmetics for excellent skin absorption without oily film
Palmitic, stearic	butanol-octanol	plasticizers in rubber and polymer
Stearic, oleic	glycol, Propylene glycol, Sugar, etc.	food emulsifiers and cosmetics
Oleic	methanol-butanol	plasticizers in rubber and polymer
Oleic	oleyl alcohol	sperm oil replacer

Ester of dibasic acid

Acid	*derivative*	*application*
Azelaic	butanol and octanol esters	lubricant and plasticizer for plastics and rubbers
Azelaic	glycol esters	polymeric plasticizers for electrical insulations
Oleic acid dimer	butanol and octanol esters	lubricants

There are several processes manufacturing fatty acids [11,12,13,14]. The first process, alkali saponification, is the oldest. The sodium salt is neutralized with strong acids to recover fatty acids. Commercial scale of this process becomes no longer feasible since it requires a large amount of labour, energy, and chemicals.

The second one is an acid catalyzed hydrolysis, namely Twitchell. It is used on a relatively small scale. A mixture containing about 60 percent fat, 40 percent water, 0.5 percent sulfuric acid, and 1 percent Twitchell reagent, is boiled with open steam. The Twitchell reagent, i.e. sulfonated oleic and naphthenic acids, acts as a surface-active agent. This process is not important in commercial at present because of high energy comsumption, long cycle time, and poor product quality. However, it has low initial cost and simple equipment.

Batch autoclave process, the third one, is always used in laboratories. Fat and water amounting to about 30-60 percent of the fat are mixed together with catalysts such as zinc oxide or without them. Steam is added to prevent oxidation and to heat the mixture to the desired temperature (240 °C). The pressure is in the range of 1.03-3.45 M Pa (150-500 psig). The 92-95 percent conversion is achieved.

The Colgate-Emery process is the most efficient in fat splitting. The continuous countercurrent is used to shift the equilibrium of hydrolysis reaction. The conversion is always 98-98.5 percent. The pressure is about 4.5 M Pa (700psig). The high operating temperature (250-260 °C) is specified to raise the solubility of water in oil. The cost of fatty acids produced by this process is usually less than the cost of the original fat because the glycerol credit pays for labour, overhead, and energy required.

The last one, the enzymetic fat splitting is carried out in Japan to minimize energy cost, which is high in this country. Fatty acids from these processes are transformed into hydrocarbon compounds by decarboxylation. The decarboxylation of fatty acids without catalyst was investigated by many researchers, for instance, Lueck et al in 1967 [15], and Mitskevich et al in 1968 [16]. In 1948, Enkvist et al showed that this reaction can be accelerated by metallic iron catalyst [17]. Published in the same year, Ishikawa et al explored this reaction with Fe filings [18]. In 1968, Mitskevich et al examined the use of cobalt acetate as a catalyst [16]. The experiment using DBU (1,8-diazabicyclo-7-undecene) and Cu_2Br_2 was conducted in 1986 by Hori et al with 70-80 percent yield [19]. A block diagram of a process converting palm oil into hydrocarbon compounds is shown in Figure 1.1.

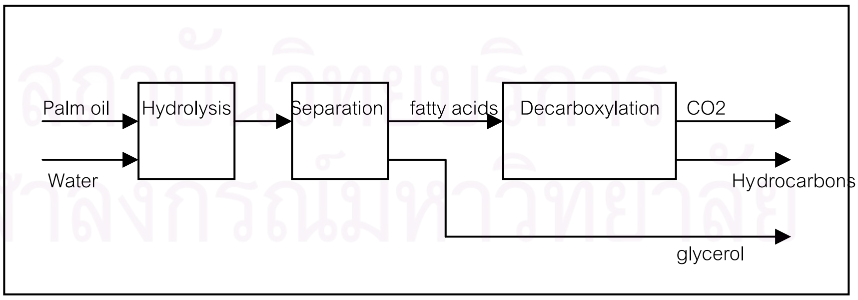


Figure 1.1 block diagram of a process converting palm oil into hydrocarbon compounds

Simulation of a process involving multiple reactions can be made by two approaches. The first one, kinetics approach, has been used to design reactor. Some difficulty for multiple reactions is actual chemical reactions and kinetic parameters of each reaction.

The other, equilibrium approach, has been used to find whether the reaction has a tendency to proceed. Furthermore, it can be used to search suitable operating conditions, especially operating temperature. In contradistinction to the kinetics approach, the kinetic rates of reactions become unnecessary and product distribution can be calculated from operating conditions.

Hydrocarbon cracking is operated at high temperature to produce ethylene and propylene. A larger number of reactions will be concerned in this process. The number of reactions tend to increase exponentially with the number of carbon atom in hydrocarbon compounds. Consequently, the kinetics approach becomes much more complicated. In addition, the rates of reactions become very fast at high temperature, the chemical equilibrium can be achieved within the order of few seconds. Thus the equilibrium approach is chosen for this investigation.

Since the experiment exploring pyrolysis of hydrocarbon compounds from palm oil has not been set up, the reaction model is developed by using data from naphtha cracking. Naphtha is selected because it is a multicomponent mixture containing mainly straight chain hydrocarbons, which are similar to paraffins and olefins derived from palm fatty acids. In comparison with naphtha, the mixture from palm oil comprises not only well-defined compounds but also the small number of them. Therefore, the reaction model for naphtha should be extended to the mixture of hydrocarbon compounds from palm oil.

Objectives

(1) To model equilibrium reactor for multiple reactions.

(2) To study the effect of temperature on product distribution of cracking hydrocarbon compounds from palm oil.

(3) To study the effect of steam ratio on product distribution of cracking hydrocarbon compounds from palm oil.

Chapter II

Pyrolysis of Hydrocarbon Compounds

2.1 Pyrolysis of Methane

Methane is the major component of natural gas. There is much attention in finding processes to change methane directly to valuable products. Ordinarily, methane has not been an interesting feedstock for pyrolysis because of very high operating temperature and low yield of useful products until 1990 [20].

Ethylene, acetylene, benzene and hydrogen were expected to be main products from pyrolysis of methane if carbon formation is excluded. This idea is supported by chemical equilibrium calculation and the experiment was carried out by Rodstad et al [21]. The reaction kinetics was investigated in a tubular flow reactor in the temperature range from 1000 to 1200 $^{\circ}$C at atmospheric pressure. The feed was diluted with helium or hydrogen to reduce coke formation. The main products were ethylene, acetylene, benzene, hydrogen, and carbon. Other products,which are observed in small amount, were ethane, propane, propylene, propyne, propadiene, butenes, butadiene, and toluene.

While the formation of liquid hydrocarbon and coke is not clearly understood, the formation of C_1-C_4 hydrocarbons has been generally explained by the following reactions [22].

$$2CH_4 \longrightarrow H_2 + C_2H_6$$

$$C_2H_6 \longrightarrow H_2 + C_2H_4$$

$$C_2H_4 \longrightarrow H_2 + C_2H_2$$

$$CH_4 + C_2H_4 \longrightarrow H_2 + C_3H_6$$

$$CH_4 + C_2H_2 \longrightarrow H_2 + C_3H_4 \text{ (propyne)}$$

$$C_3H_6 \longrightarrow H_2 + C_3H_4 \text{ (propadiene)}$$

$$CH_4 + C_3H_6 \longrightarrow H_2 + C_4H_8$$

The formation of benzene was proposed by Rodstad et al [21], as follows.

$$3C_2H_2 \longrightarrow C_6H_6$$

It has been believed that carbon is formed from polyaromatic hydrocarbons, the important intermediate in thermal conversion of methane. The polyaromatic hydrocarbons may be produced through both Diels-Alder reaction and polymerization reaction of 1,3-butadiene. Nevertheless, the mechanism of 1,3-butadiene formation is in some doubt [20].

The micro pilot plant for methane pyrolysis is constructed by Broutin et al [22]. The operating conditions and selectivity are shown in Table 2.1. With an advance in furnace technology, it will be able to manufacture ethylene or acetylene from natural gas at competitive costs.

Table 2.1 operating conditions and selectivity of methane pyrolysis

Operating conditions		Selectivity (in % of CH_4 converted)	
Temperature (°C)	1200	C_2H_2	32
Residence time (ms)	200	C_2H_4	23
Diluent gas	H_2	C_6H_6	15
Percent of diluent (% by vol)	50	C_3-C_5	4
Conversion (%)	31	C_7-C_{12}	8
		Heavy ends + coke	18

2.2 Pyrolysis of Ethane

Ethane is a major reactant for ethylene production in the United States due to its availability in large quantities near the Gulf Coast. Furthermore, ethylene production from ethane is simplest comparing to other feedstocks. Its capital investment is also lowest because of the size of production plant. Using ethane as a feedstock, the production contains the lowest yield of byproducts. As a result, the size of separation units are minimized. However, ethane is the most refractory feedstock, requiring the highest temperature to crack [23].

Although, ethane cracking mechanism is simplest among several feedstocks, it is still very complex. The mechanisms of main reactions have been proposed as follows [24].

Initiation

$$C_2H_6 \longrightarrow 2CH_3^*$$

Propagation

$$CH_3^* + C_2H_6 \longrightarrow C_2H_4 + H^*$$

$$C_2H_5^* \longrightarrow C_2H_4 + H^*$$

$$H^* + C_2H_6 \longrightarrow H_2 + C_2H_5^*$$

Termination

$$H^* + H^* \longrightarrow H_2$$

$$CH_3^* + H^* \longrightarrow CH_4$$

$$C_2H_5^* + H^* \longrightarrow C_2H_6$$

$$C_2H_5^* + CH_3^* \longrightarrow C_3H_8$$

$$C_2H_5^* + C_2H_5^* \longrightarrow C_4H_{10}$$

Other mechanisms of such reactions have also been proposed, see example below:

$$C_2H_4 + C_2H_4 \longrightarrow C_2H_3^* + C_2H_5^*$$

$$C_2H_4 + H^* \longrightarrow C_2H_3^* + H_2$$

$$C_2H_3^* \longrightarrow C_2H_2 + H^*$$

The product distribution of ethane cracking is summarized in Table 2.2 [25].

Table 2.2 product distribution of ethane pyrolysis

Feed (wt%)	
C_2H_4	0.75
C_2H_6	99.25
Operating conditions	
Residence time (s)	0.79
Hydrocarbon partial pressure out (atm)	1.24
Coil outlet temperature (°C)	838
Yields (wt%)	
H_2	4.06
CH_4	5.0
C_2H_2	0.37
C_2H_4	50.05
C_2H_6	34.42
C_3H_4+C_3H_6	1.30
C_3H_8	0.17
C_4H_6	1.32
C_4H_8+C_4H_{10}	1.02
C_{5+}	2.25
C in (CO+CO_2)	0.04
total	100.00

2.3 Pyrolysis of Propane

Pyrolysis of propane is normally constructed in the United States like that of ethane. Propane is able to be cracked more easily than ethane. When the molecular weight of a feedstock increases, it can be cracked more easily than the lower one at a given condition such as temperture and residence time. Table 2.3 summarizes reaction conditions designed for a plant using various feedstocks [23].

Reaction mechanism for pyrolysis of propane has been proposed [26], as follows.

Table 2.3 reaction conditions for various feedstocks

	LPG	Light naphtha	Heavy naphtha	Gas oil
Residence time (s)	0.3	0.3	0.3	0.3
Steam ratio (by wt)	0.3	0.5	0.7	0.9
Coil outlet temperature (°F)	1550	1540	1520	1480-1500

Initiation

$C_3H_8 \longrightarrow CH_3^* + C_2H_5^*$

Propagation

$CH_3^* + C_3H_8 \longrightarrow CH_4 + C_3H_7^*$

$C_2H_5^* + C_3H_8 \longrightarrow C_2H_6 + C_3H_7^*$

$C_2H_5^* \longrightarrow C_2H_4 + H^*$

$CH_3^* + H_2 \longrightarrow CH_4 + H^*$

$H^* + CH_4 \longrightarrow H_2 + CH_3^*$

$C_2H_5^* + H_2 \longrightarrow C_2H_6 + H^*$

$C_2H_5^* + C_2H_4 \longrightarrow C_3H_6 + CH_3^*$

$H^* + C_2H_4 \longrightarrow C_2H_5^*$

$C_2H_6 \longrightarrow 2CH_3^*$

$CH_3^* + C_2H_6 \longrightarrow CH_4 + C_2H_5^*$

$CH_3^* + C_2H_4 \longrightarrow C_3H_7^*$

$CH_3^* + C_2H_6 \longrightarrow C_3H_8 + C_2H_5^*$

$H^* + C_2H_6 \longrightarrow H_2 + C_2H_5^*$

$H^* + C_3H_6 \longrightarrow C_3H_7^*$

$C_3H_7^* \longrightarrow C_2H_4 + CH_3^*$

$C_3H_7^* \longrightarrow C_3H_6 + H^*$

$C_3H_7^* + H_2 \longrightarrow C_3H_8 + H^*$

$C_3H_7^* + CH_4 \longrightarrow C_3H_8 + CH_3^*$

$H^* + C_3H_8 \longrightarrow H_2 + C_3H_7^*$

$CH_3^* + C_3H_6 \longrightarrow C_4H_9^*$

$C_4H_9^* \longrightarrow C_4H_8 + H^*$

$C_4H_9^* + H_2 \longrightarrow C_4H_{10} + H^*$

$C_4H_9^* \longrightarrow C_3H_6 + CH_3^*$

$C_4H_9^* \longrightarrow C_2H_4 + C_2H_5^*$

$C_2H_5^* + C_4H_{10} \longrightarrow C_2H_6 + C_4H_9^*$

$C_4H_{10} \longrightarrow CH_3^* + C_3H_7^*$

$C_4H_{10} \longrightarrow 2C_2H_5^*$

$H^* + C_4H_{10} \longrightarrow H_2 + C_4H_9^*$

$CH_3^* + C_4H_{10} \longrightarrow CH_{10} + C_4H_9^*$

Termination

$2H^* \longrightarrow H_2$

$H^* + CH_3^* \longrightarrow CH_4$

$H^* + C_2H_5^* \longrightarrow C_2H_6$

$H^* + C_3H_7^* \longrightarrow C_3H_8$

$2CH_3^* \longrightarrow C_2H_6$

$CH_3^* + C_2H_5^* \longrightarrow C_3H_8$

$2C_2H_5^* \longrightarrow C_2H_4 + C_2H_6$

$2C_2H_5^* \longrightarrow C_4H_{10}$

$CH_3^* + C_3H_7^* \longrightarrow CH_4 + C_3H_6$

The product distribution of propane pyrolysis is summarized in Table 2.4 [25].

2.4 Pyrolysis of Butane

Butanes are obtained from natural gasolines and refinery waste gases [24]. Generally normal butane is not used as a feedstock in pure form but mixed with propane and isobutane [24,28]. A mixture of propane, normal butane, and isobutane, commonly called liquefied petroleum gas (LPG), is preferred due to its availability.

However, pyrolytic decomposition of normal butane received significant attention in the past. The studies were focused at low conversion. The major products were methane, ethane, ethylene, and propylene. Minor products were hydrogen, trans-2-butene, 1-butene, and cis-2-butene. The number of reactions and products increase as an increase in molecular weight of reactants. Nevertheless, a reasonably simple mechanism for normal butane cracking has been proposed [27].

Table 2.4 product distribution of propane pyrolysis

Feed (wt%)	
C_2H_6	0.15
C_3H_6	4.34
C_3H_8	86.40
n-C_4H_{10}	5.72
i-C_4H_{10}	2.51
C_4H_8	0.85
Operating conditions	
Residence time (s)	0.80
Hydrocarbon partial pressure out (atm)	1.91
Coil outlet temperature (°C)	824
Yields (wt%)	
H_2	1.2
CH_4	20.9
C_2H_2	0.1
C_2H_4	27.5
C_2H_6	4.6
C_3H_4	0.1
C_3H_6	19.1
C_3H_8	17.0
C_4H_6	1.4
C_4H_8	2.0
C_4H_{10}	0.7
Other	5.4
total	100.00

Initiation

$$C_4H_{10} \longrightarrow C_2H_5^* + C_2H_5^*$$

$$C_4H_{10} \longrightarrow C_3H_7^* + CH_3^*$$

Propagation

$$C_2H_5^* + C_4H_{10} \longrightarrow C_2H_6 + C_4H_9^*$$

$$CH_3^* + C_4H_{10} \longrightarrow CH_4 + C_4H_9^*$$

$$p\text{-}C_4H_9^* \longrightarrow C_2H_4 + C_2H_5^*$$

$$s\text{-}C_4H_9^* \longrightarrow C_3H_6 + CH_3^*$$

$$C_4H_9^* \longrightarrow C_4H_8 + H^*$$

$$C_4H_9^* \longrightarrow C_4H_8 + H^*$$

$$H^* + C_4H_{10} \longrightarrow H_2 + C_4H_9^*$$

$$C_3H_7^* \longrightarrow C_2H_4 + CH_3^*$$

Termination

$$C_2H_5^* + C_2H_5^* \longrightarrow C_2H_4 + C_2H_6$$

$$C_2H_5^* + C_2H_5^* \longrightarrow C_4H_{10}$$

2.5 Pyrolysis of Naphtha and Gas Oil

Naphtha is a complex mixture composed of hydrocarbon with different structures and molecular configurations. Since liquefied petroleum gas is not available in sufficient amount at some places, naphtha becomes a significant feedstock for commercial pyrolysis. About ninety percent of the ethylene produced in Europe was manufactured from naphtha in 1975. Naphtha was the major feedstock even in the duration of energy crisis.

Naphtha are obtained by distillation of crude oil. Densities, boiling ranges, and compositions vary with crude oil source and refinery conditions. Nature and composition of naphtha from different sources are summarized in Table 2.5 [29].

Table 2.5 nature and composition of naphtha from different sources.

Characteristics	Sources of naphtha			
	1	2	3	4
Density	0.675	0.685	0.695	0.723
Boiling range (°C)	35-145	35-155	35-165	38-193
H content (wt%)	15.9	15.7	15.4	15.0
PONA analysis (wt%)				
Normal paraffins	42	39	37	34
Isoparaffins	41	40	38	35
Naphthenes	13	15	17	20
Aromatics	14	6	8	11
Characteristics	**Sources of naphtha**			
	5	6	7	8
Density	0.681	0.700	0.679	0.710
Boiling range (°C)	52-162	35-140	40-163	51-176
H content (wt%)	15.6	15.5	15.6	-
PONA analysis (wt%)				
Normal paraffins	26	38	39.5	29
Isoparaffins	67	34	42	40.5
Naphthenes	5	20	16	23.5
Aromatics	2	8	2.5	6.5

Due to the complexity of the feedstocks, many factors are introduced to describe the nature of components in the feedstocks, e.g. the UOP-K factor, the BMCI factor, the branching degree of dearomatized fractions, and the PONA analysis (the distribution of normal paraffins, isoparaffins, olefins, naphthenes, and aromatics).

There are several parameters, which affect product yields, such as the overall tube length of the furnace, the tube diameter, the maximum heat flux, and the maximum tube wall temperature. These parameters are usually determined by furnace designer, while temperature, residence time, hydrocarbon partial pressure, and the nature of the feedstocks can be varied and controlled by process engineer.

Naphtha, which is rich in normal paraffins,is usually converted to ethylene preferentially, while propylene is predominantly obtained from isoparaffins. Naphtha with high content of naphthene is a favourable feedsotck for the production of diolefins. In addition, aromatics commonly proceed only dealkylation reaction.

The yields of olefins can be maximized when the operting temperature is raised. While the reduction in hydrocarbon partial pressure and residence time improves olefin yields. Consequently, new furnaces are designed to operate at extremely high temperature and short residence time.

To control the hydrocarbon partial pressure, nitrogen or steam is used as a diluent in the cracking reactor but only steam is used in commercial practice. Moreover, the purpose of steam dilution is not only to improve olefin yields but to mitigate surface coking as well [30].

There is a tendency to process high-boiling-point hydrocarbon fractions because of the increase in demand of light olefins whereas the amount of ethane, propane, LPG, and naphtha are limited. Although the technology of gas oil cracking is available, it is not economically feasible at this moment.

Pyrolysis of gas oil is more complicated than that of naphtha. Existence of bicyclic and polycyclic naphthenes and aromatics, as well as, difference in the hydrocarbon with relatively high molecular weight have a significant effect on the product distribution. In addition, the formation of coke becomes one of dominant reaction.

The product patterns from pyrolysis of naphtha and gas oil are summarized in Table 2.6. The C_3 fraction is mainly composed of propylene while the C_4 fraction is mainly comprised of butenes and butadiene. The number of carbon atom in the molecules of hydrocarbon compounds in pyrolysis gasoline and pyrolysis gas oil is equal or higher than five atoms. It can be seen in Table 2.6 that naphtha gives higher yields of olefins than those of gas oil. On the contrary, C_{5+} fraction from gas oil becomes a dominant product [29].

Table 2.6 Typical yields of naphtha and gas oil

	Light naphtha	Heavy naphtha	Light gas oil	Heavy gas oil
Boiling range (^{o}C)	36-110	40-164	176-343	335-515
Aromatic content (wt%)	2.6	12.1	24.1	48.0
Product yields (wt%)				
Methane	17.4	13.8	11.6	8.9
Ethylene	31.0	25.5	24.1	18.9
C_3 fraction	18.8	15.3	14.3	13.9
C_4 fraction	10.0	8.3	8.4	9.7
Pyrolysis gasoline	14.4	26.9	18.1	19.0
Pyrolysis gas oil	2.0	5.1	18.9	24.4

2.6 Pyrolysis of Coal

Coal, which has been understood partially, has an extremely complex structure containing nitrogen, oxygen, and sulfur, besides hydrogen and carbon. It has been believed that coal is made up of large molecules containing mainly fused aromaic and hydro-aromatic rings. A typical approximate constitution is $(C_{135}H_{97}O_9NS)_n$.

Due to the complex structure of coal, it is difficult to produce important chemicals from coal. Furthermore, coal exists in the form of solid, which hardly handles easily in large scale. On the other hand, coal occurs on earth in much larger quantities than pettroleum and natural gas. Although coal has been a major carbon sources, it has caused environmental problems [31].

Chapter III

Mathematical Modelling for Cracking Process

3.1 Introduction

Chemical process industry transforming raw materials into valuable products is a significant industry. A large amount of products used in every day life is made from chemical process. Consequently, chemical reactor design and operation, the heart of chemical process, can not be overlooked.

To solve reactor problems, the rate and equilibrium conversion are both considered. Chemical equilibrium provides information of reactor performance limit of a given operating temperature [32]. For example, if a fifty percent yield is required by economic analysis while only twenty percent yield is achieved at equilibrium, the experiment should not be set up. Additionally, equilibrium approach is useful in choosing operating conditions. The equilibrium conversion of some exothermic reactions decrease as an increase in operating temperture. While the rate conversion or kinetics of reaction is essential for reactor design since many reactions are not proceed to equilibrium. Chemical reaction rate is usually used to calculate residence time and reactor volume. It also involve in control system.

In this study, the equilibrium approach is chosen to determine the product distribution of cracking hydrocarbon compounds from palm oil because of the high operating temperature of the process. Furthermore, cracking process involves large number of chemical species. In addition, the data of actual reactions and kinetic constant for each reaction are inadequate.

Hydrocarbon compounds from palm oil are straight chain hydrocarbons and the experiment for cracking this mixture has not been conducted. While a large munber of experiments has been carried out on naphtha. Therefore equilibrium models for multiple reaction have to be developed on naphtha for verification purpose. Finally, the model will be modified for cracking hydrocarbon from palm oil.

Although, the model is generated by equilibrium approach in this work, some concepts used in the development of kinetics model for naphtha cracking are helpful. Thus the details of both kinetics and equilibrium approaches are presented in this chapter.

3.2 Kinetics Approach

Usually, an overall model for pyrolysis reactor involve heat balance, momentum balance, mass balance, physicochemical properties, firing-box patterns, and fluid dynamic characterization. However, the most important is the reaction modelling (i.e. kinetic scheme, reaction rates expressions, and related kinetic constants) [25]. The model can be classified into two types, molecular (stoichiometric) model and mechanistic model.

3.2.1 Molecular Model

The kinetic scheme is generated on the basis of global molecular reactions and kinetic constants are determined from expermental data. This is possible in the case of light components but it is too complicated for naphtha, which is a complex mixture. Naphtha might be represented by a mixture of a few pseudo components. The product distribution is correlated with the extent of hydrocarbon decomposition. Some models for naphtha in this category have been proposed by de Blieck and Goossens (1971), Fernades-Baujin and Solomon (1976), Illes et al (1976), and Shu et al (1978) [25]. The major disadvantages of the model are the large number of experimental data required and should not be extrapolated. However, it is proper for process computer control and optimization [24].

3.2.2 Mechanistic Model

When accurate and detailed thermochemical kinetic data and pyrolysis data over a wide range of conditions are available, the development of mechanistic model is enabled. Using structural analogies among similar reactions, the kinetic parameters are estimated and found to be coherent with the theoretical predictions of thermochemical kinetics [25].

Even though the mechanistic model is simplified, about two thousand reactions are involved in the cracking of complex mixtures like naphtha and gas oil. The simulation results of both models for cracking light and heavy napththas are demonstrated in Table 3.1 [25]. The results have agreed with the corresponding experiments. However, the mechanistic model is more advantageous in that it can be extrapolated. The disadvantage is the requirement of large memory computers. The furnace design is the major application of this model [24].

Table 3.1 simulation results of cracking light and heavy naphthas

Feed description	Light naphtha			Heavy naphtha		
API 60°F	79.4			67.4		
ASTM D 86 (°F)						
IBP	100			102		
50%	149			210		
95%	220			310		
Paraffin content(wt%)	86			67		
H_2 content (wt%)	16.0			15.2		
Yields (wt%)	Exp.	Molecular	Mechanistic	Exp.	Molecular	Mechanistic
H_2	0.73	0.93	0.77	0.95	0.85	0.81
CH_4	16.11	16.27	16.58	14.80	14.90	15.71
C_2H_2	0.37	0.37	0.36	0.50	0.40	0.49
C_2H_4	28.71	28.04	28.46	26.60	26.09	26.80
C_2H_6	4.87	4.83	5.32	4.09	4.07	4.00
C_3H_4	0.48	0.87	0.72	1.07	0.81	0.76
C_3H_6	16.7	16.25	16.40	13.84	14.43	14.29
C_3H_8	0.47	0.54	0.61	0.16	0.46	0.45
C_4H_6	4.20	4.27	4.27	4.65	4.46	4.49
C_4H_8	5.19	4.54	5.15	3.78	4.03	3.99
C_4H_{10}	0.48	0.34	0.41	0.40	0.43	0.26
C_{5+}	22.02	22.85	20.96	29.16	29.08	27.96
total	100.00	100.00	100.00	100.00	100.00	100.00

3.3 Equilibrium approach

In general, the product distribution at chemical equilibrium is determined by using chemical equilibrium constant. This technique is suitable when no more than three reactions are considered [33]. If three or more reactions involve in the system, it is convenient to compute product distribution by minimizing total Gibbs free energy.

3.3.1 Minimization of Gibbs free energy [34]

It is known that the total Gibbs free energy of a system of reactions reaches a minimum at chemical equilibrium. At given temperature and pressure, the total Gibbs free energy is a function of chemical composition.

$$G_{T,P} = f\,(n_1, n_2, \ldots, n_n) \qquad (1)$$

Therefore the product distribution of multiple reaction system at chemical equilibrium can be obtained by minimizing the total Gibbs free energy with conservation of atomic species. There are several methods for the optimization of a function with constraints. However, ordinary way of solving this problem is lagrangian-multiplier technique. The equations are developed through the following steps.

For gas phase reactions

(1) Generate atom balance equations.

$$\sum_i n_i a_{ik} = A_k \qquad (2)$$

$$\text{or} \quad \sum_i n_i a_{ik} - A_k = 0 \quad ,(k=1,2,\ldots,m) \qquad (3)$$

(2) Multiply atom balance with λ_k

$$\lambda_k \left(\sum_i n_i a_{ik} - A_k\right) = 0 \qquad (4)$$

Sum over k elements.

$$\sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k\right) = 0 \qquad (5)$$

Combine to Gibbs function.

$$F = G + \sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k\right) \tag{6}$$

$F \equiv G$, since the right term is zero. Moreover, the minimization of function F equals the minimization of function G with atom balance constraints.

(3) Take the partial derivatives to F and set them to zero.

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} + \sum_k \lambda_k a_{ik} = 0 \tag{7}$$

$$= \mu_i + \sum_k \lambda_k a_{ik} = 0 \tag{8}$$

Substitute $\mu_i = \Delta G^\circ_{fi} + RT \ln \hat{f}_i$ (9)

$$\Delta G^\circ_{fi} + RT \ln \hat{f}_i + \sum_k \lambda_k a_{ik} = 0 \tag{10}$$

Substitute $\hat{f}_i = y_i \hat{\phi}_i P$ (11)

$$\Delta G^\circ_{fi} + RT \ln (y_i \hat{\phi}_i P) + \sum_k \lambda_k a_{ik} = 0 \tag{12}$$

For ideal gas system

$$\Delta G^\circ_{fi} + RT \ln (y_i P) + \sum_k \lambda_k a_{ik} = 0 \tag{13}$$

where $y_i = \dfrac{n_i}{\Sigma n_i}$ (14)

number of unknowns = *n* (n_i of each chemical species i)

+ *m* (λ_k of each element k)

number of equations = *n* (equilibrium equations) + *m* (atom balance equations)

Solving these *n+m* equations gives the number of moles of chemical species i at the equilibria.

3.3.2 Application in Cracking of Naphtha

It is significant to generate equilibrium model for naphtha cracking. The model for naphtha is developed. Moreover, the effect of temperature and steam ratio on product distribution are investigated. The following assumptions are applied for the model.

(1) The reactions occur in the way of reduction in molecular weight.

(2) The naphthene and aromatic compounds forming from paraffins are negligible. Thus paraffins are converted to other paraffins and α-olefins only.

(3) Coking are excluded from the model.

Naphtha is a multicomponent mixture. Consequently, it is normally characterized by other properties such as boiling range, density, hydrogen content, and PONA analysis. Hence, the idea of "pseudo components" from molecular model is applied with the PONA analysis. The content of paraffins, naphthenes, and aromatics in the feed can be represented by appropriate real components. For instance, benzene and cyclohexane are chosen to represent aromatics and naphthenes, respectively. While the hydrogen content of the naphtha has to be balanced with an appropriate normal paraffin.

Ordinarily, if the experiment has not been carried out, reactions involving the process are generated and screened by comparing the Gibbs free energy change (ΔG°) for the corresponding chemical reactions [35]. On the other hand, products from pyrolysis of naphtha is known. Thus it is suitable to generate reactions corresponding to the experimental data. On the above assumptions, the reactions have been proposed as follows [36].

a)Cracking Reactions

(1) Cracking of paraffins into paraffins and olefins with shorter chain length

$$C_mH_{2m+2} \rightleftharpoons C_nH_{2n} + C_pH_{2p+2} \quad , \quad n+p = m$$

(2) Cracking of olefins into olefins with shorter chain length

$$C_nH_{2n} \rightleftharpoons C_{n'}H_{2n'} + C_{n''}H_{2n''} \quad , \quad n'+n'' = n$$

(3) Cracking of naphthenes into olefins

$$C_nH_{2n} \rightleftharpoons C_{n'}H_{2n'} + C_{n''}H_{2n''} \quad , \quad n'+n'' = n$$

(4) Decyclization of naphthenes into paraffins

$$C_nH_{2n} + H_2 \rightleftharpoons C_nH_{2n+2}$$

b)Dehydrogenation Reactions

(1) Olefins from paraffins

$$C_nH_{2n+2} \rightleftharpoons C_nH_{2n} + H_2$$

(2) Benzene from cyclohexane

$$C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$$

These reactions can be divided into two groups related to feed components; one is a group of reactions related to paraffins, the other is the group related to naphthenes and aromatics.

For a given maphtha, it can be simplified as a mixture of normal pentane, cyclohexane and benzene. Therefore, reactions, corresponding to the feed, can be written as follows.

Reaction Set 1 normal pentane

Cracking

$$C_5H_{12} \rightleftharpoons C_4H_8 + CH_4$$

$$C_5H_{12} \rightleftharpoons C_3H_6 + C_2H_6$$

$$C_5H_{12} \rightleftharpoons C_2H_4 + C_3H_8$$

Dehydrogenation

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2$$

$$C_4H_{10} \rightleftharpoons C_4H_8 + H_2$$

Reaction Set 2 cyclohexane

Cracking

$$C_6H_{12} + H_2 \rightleftharpoons C_6H_{14}$$

$$C_6H_{14} \rightleftharpoons C_5H_{10} + CH_4$$

$$C_6H_{14} \rightleftharpoons C_4H_8 + C_2H_6$$

$C_6H_{14} \rightleftharpoons C_3H_6 + C_3H_8$

$C_6H_{14} \rightleftharpoons C_2H_4 + C_4H_{10}$

$C_6H_{12} \rightleftharpoons C_2H_4 + C_4H_8$

$C_6H_{12} \rightleftharpoons 2C_3H_6$

Dehydrogenation

$C_2H_6 \rightleftharpoons C_2H_4 + H_2$

$C_3H_8 \rightleftharpoons C_3H_6 + H_2$

$C_4H_{10} \rightleftharpoons C_4H_8 + H_2$

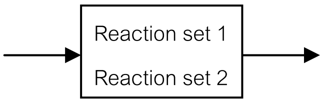
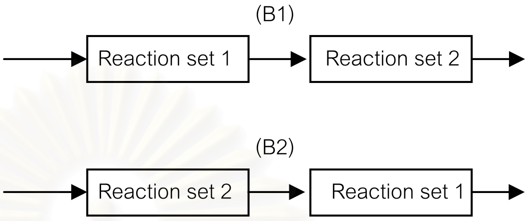
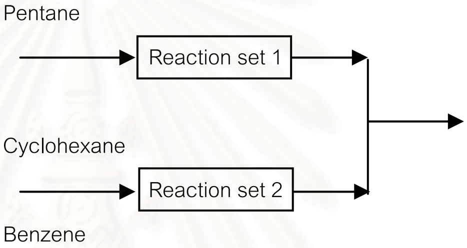
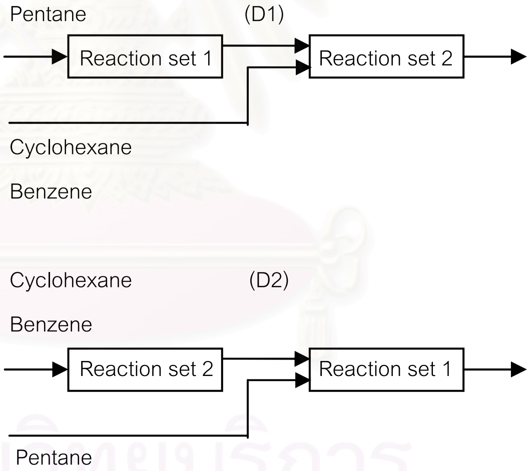
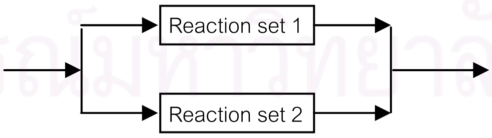
$C_5H_{12} \rightleftharpoons C_5H_{10} + H_2$

$C_6H_{12} \rightleftharpoons C_6H_6 + H_2$

The reaction system is simulated with Pro II Provision version 4.13. By following a guideline in the manual of Pro II Provision, Soave-Redlich-Kwong equation is chosen for all reactions in gas phase. Other equations of state should be selected for the simulation involving vapor-liquid-liquid equilibrium such as in separation section.

Although all reactions above occur in a cracking reactor, it may not necessary to simulate all reactions in a single reactor. Therefore 5 possible systems of reactors, as illustrated in Table 3.2, are proposed for this investigation. The reactor system B and D are splitted into B1, B2, D1, and D2 respectively to represent the reaction set, which is specified to the first reactor. For example, in the reactor system B1, the reaction set 1 is specified to the first reactor while in reactor system B2, the reaction set 2 is specified to the first reactor. In addition, the reactor system E requires some experimental results, such as conversions or yields of key products for each reaction set. Thus it is not considered in this investigation.

Table 3.2 flow diagram of the reactor system

Reactor system	Flow diagram
A Single reactor for all reactions	
B Two series reactors for each reaction set	
C Two parallel reactors for each reactant group	
D Two series reactors For each Ractant group	
E Two parallel reactors for each reaction set	

Chapter IV

Simulation Results and Discussion

4.1 Verification of the Reaction Model for Naphtha

Although, product yields of naphtha cracking have been published at various places, some operating conditions such as temperature, pressure, and steam ratio, which are important to simulation, are inadequate. Fortunately, sufficient data are found in Ullmann's Encyclopedia of Industrial Chemistry [24] and are used to verify the model.

The naphtha feedstock contain 70.4% paraffins, 17.66% naphthenes, and 11.94% aromatics. Some real components, representing the feedstock, have to be selected. For example, benzene is a respresentative of aromatics, while cyclohexane is selected for naphthenes. To balance the amount of carbon and hydrogen atom in the feedstock, normal pentane is opted for paraffin fraction. Hence a pseudo naphtha contains normal pentane, cyclohexane and benzene with the same composition above. The simulation results are summarized in Table 4.1.

For the reactor system A that all reactions are occurred in a single reactor gives methane and C_{5+} fraction as chief products. The C_{5+} fraction is benzene only. Both methane and benzene have the first two lowest Gibbs free energy of formation among the given products. With the limitation of hydrogen to carbon atomic ratio, a small fraction of other products can be formed instead of only methane and benzene.

Because the total Gibbs free energy is a function of the composition of chemical species at chemical equilibrium but it is not a function of feed composition, the simulation result is not different if the products specified to the reactor are similar and the feeds are equal in carbon and hydrogen atom.

Table 4.1 product distribution (wt%) of different reactor systems

Operating conditions

Temperature ($^{\circ}C$) 800

Pressure (kPa) 205

Steam ratio (kg steam/kg feed) 0.50

Products	ΔG_f° /g atom C	Exp.	A	B1	B2	C	D1	D2
H_2	0.00	0.63	1.47	1.47	1.47	0.30	1.47	0.08
CH_4	27.74	13.67	35.29	35.29	35.29	20.43	35.29	22.08
C_2H_6	63.01	4.02	0.07	0.07	0.07	0.37	0.07	0.46
C_3H_8	71.96	0.54	0.00	0.00	0.00	0.02	0.00	0.02
C_4H_{10}	75.61	1.96	0.00	0.00	0.00	0.00	0.00	0.00
C_5H_{12}	78.57	2.44	0.00	0.00	0.00	0.00	0.00	0.00
C_2H_4	62.30	21.67	0.35	0.35	0.35	37.19	0.35	37.74
C_3H_6	65.30	15.91	0.01	0.01	0.01	17.07	0.01	15.15
C_4H_8	71.55	6.79	0.00	0.00	0.00	0.73	0.00	0.57
C_2H_2	83.04	0.15	-	-	-	-	-	-
C_3H_4	78.52	0.47	-	-	-	-	-	-
C_4H_6	68.43	3.92	-	-	-	-	-	-
C_{5+}	46.00	27.83	62.81	62.81	62.81	23.89	62.81	23.89
Total		100.00	100.00	100.00	100.00	99.99	100.00	99.99

C_3H_4 means propyne and propadiene (average ΔG_f° /g atom C = 78.52 kJ/mol).

C_{5+} fraction does not include pentanes.

C_{5+} fraction in the model is composed of 1-pentene, hexane, cyclohexane, and benzene (ΔG_f° /g atom C = 46.00 kJ/mol).

This results in similar product pattern of the reactor system A, B1, B2, and D1. Moreover, that the products specified in the model are not different is caused by the overlap of products from two reaction sets. Cyclohexane is hydrocracked into normal hexane. Then normal hexane is cracked further causing one part of products from cyclohexane similar to those of normal pentane, which is a representative of paraffin fraction. The product distribution from the first reactor of the reactor system B1 and B2 are different. Normal pentane is converted mainly to methane, ethylene, and propylene in the first reactor of the reactor system B1 because benzene is not a product from reaction set 1. Consequently, ethylene and propylene, with lower hydrogen to carbon atomic ratio than paraffins, are produced instead of benzene. In the reactor system B2, methane and benzene are major products from both reactors since benzene is produced in the first reactor already.

In the reactor system C, methane, ethylene, and propylene are chief products in the first reactor while the other is composed mainly of methane and benzene. The product pattern of the reactor system C is caused by the same reason described above. The product distribution of the reactor system D1 is like that of the reactor model B1. While normal pentane is bypassed to the second reactor in the reactor system D2. As a result, the product pattern of the reactor D2 is similar to that of the reactor system C. However the reaction model D2 is discarded to avoid the problem that which reaction set should be specified to the first reactor, if the model is adapted to other processes.

Since the system does not reach chemical equilibrium, the amount of methane, ethylene, and propylene calculated by the reaction model C is higher than that of experimental data, while the amount of ethane, propane, butane, pentane, and C_{5+} fraction has the opposite result as demonstrated in Table 4.1. In addition, the reaction model is simplified by pseudo naphtha so the difference between simulation result and experimental data occurs. However, the objective of the development of this model is not to fit the experimental data but to predict product distribution. Additionally, the reaction model C can describe product pattern reasonably. Therefore, the reaction model C is chosen to generate the reaction model for cracking hydrocarbon compounds from palm oil.

Another pseudo naphtha, containing hexane, cyclohexane, and toluene, is used in the simulation. The results are summarized in Table 4.2. At the equilibria, the result of the lattter pseudo naphtha is similar to the former one. For the reactor system C, in spite of the identical mass fractions for paraffins, naphthenes and aromatics, the hydrogen to carbon atomic ratio for hexane is lower than that for pentane, whereas the ratio for toluene is higher than that for benzene. Therefore ethylene and propylene fraction is increased slightly, while methane and benzene fraction is reduced slightly.

Table 4.2 effect of pseudo naphtha on the reaction model

Feed description	Feed 1	Feed 2
Pseudo naphtha		
Paraffins	Pentane	Hexane
Naphthenes	Cyclohexane	Cyclohexane
Aromatics	Benzene	Toluene
Operating conditions		
Temperature (°C)	800	800
Pressure (kPa)	205	205
Steam ratio (kg steam/kg feed)	0.50	0.50
Product distribution (wt%)		
Products	Result	Result
H_2	0.30	0.31
CH_4	20.43	18.50
C_2H_6	0.37	0.32
C_3H_8	0.02	0.02
C_4H_{10}	0.00	0.00
C_5H_{12}	0.00	0.00
C_2H_4	37.19	38.51
C_3H_6	17.07	18.15
C_4H_8	0.73	0.80
C_2H_2	-	-
C_3H_4	-	-
C_4H_6	-	-
C_{5+}	23.89	23.39
Total	99.99	100.00

C_3H_4 means propyne and propadiene.

C_{5+} fraction does not include pentanes.

C_{5+} fraction in the model is composed of 1-pentene, hexane, cyclohexane, benzene, and toluene.

According to the results, the product distribution will vary with the components in pseudo naphthas. Therefore, it is necessary to have more information of naphtha characteristics, such as average density, molecular weight, and boiling range etc., in order to define an appropriate components for pseudo naphtha.

There are four components, which exist in the experimental data and are not computed in the reaction model, acetylene, propyne, propadiene, and 1,3-butadiene. These componets occur in small amount, thus they are discarded from the reaction model. However, 1,3-butadiene, the component with highest yield in this group, is added in the reaction model and the results are summarized in Table 4.3. A large fraction of 1,3-butadiene is obtained at the equilibria because of the low hydrogen to carbon atomic ratio in comparison with ethylene and propylene. Furthermore, the Gibbs free energy of formation of 1,3-butadiene is low. Therefore, both fraction of ethylene and propylene is reduced while the fraction of methane is increased. The reaction model with formation of diolefin, i.e. 1,3-butadiene, becomes inappropriate for the cracking naphtha.

Table 4.3 effect of 1,3-butadiene on the reaction model

Operating conditions			
Temperature (^{o}C)		800	
Pressure (kPa)		205	
Steam ratio (kg steam/kg feed)		0.50	
Product distribution (wt%)			
	Experimental	Without butadiene	With butadiene
H_2	0.63	0.30	0.36
CH_4	13.67	20.43	27.38
C_2H_6	4.02	0.37	0.37
C_3H_8	0.54	0.02	0.01
C_4H_{10}	1.96	0.00	0.00
C_5H_{12}	2.44	0.00	0.00
C_2H_4	21.67	37.19	17.36
C_3H_6	15.91	17.07	5.46
C_4H_8	6.79	0.73	0.16
C_2H_2	0.15	-	-
C_3H_4	0.47	-	-
C_4H_6	3.92	-	25.00
C_{5+}	27.83	23.89	23.89
Total	100.00	99.99	99.99

C_3H_4 means propyne and propadiene.

C_{5+} fraction does not include pentanes.

C_{5+} fraction in the model is composed of 1-pentene, hexane, cyclohexane, and benzene.

The reactor system C is verified with another experimental data [29,36]. By following the same procedure, the pseudo naphtha consists of benzene, cyclohexane, and normal hexane. The simulation result, which is demonstrated in Table

4.4, agrees quite well with the experimental one. In other words, the chemical equiliria can almost be achieved at that temperature.

Table 4.4 simulation result of cracking naphtha from another source of data

Feed		
PONA analysis (vol. %)		
Paraffins		73.5
Naphthenes		21.2
Aromatics		5.3
H/C atomic ratio		2.16
Operating conditions		
Temperature (°C)		927
Pressure (psig)		22
Steam ratio (kg steam/kg feed)		0.50
Product distribution (wt%)		
Products	Experimental	Simulation
H_2	1.2	0.69
CH_4	15.2	17.82
C_2H_4	33.0	44.66
C_3H_6	11.6	12.53
C_4H_6	4.7	-
C_{5+}	26.5	23.65

4.2 Results on Cracking Hydrocarbon Compounds from Palm Oil

4.2.1 The Adaptation of Reaction Model

Although, naphtha are mainly composed of paraffins, the reaction model developed for naphtha should be modified for applying to cracking hydrocarbon compounds from palm oil.

4.2.1.1 Selection of Pseudo Components

Because the composition of fatty acids in palm oil is already known, after hydrolysis of palm oil following by decarboxylation, the distribution of hydrocarbon compounds from palm oil is demonstrated in Table 4.5.

Table 4.5 distribution of hydrocarbon compounds from palm oil

Fatty acids from palm oil	Composition (wt%)	Hydrocarbon compounds	Composition (wt%)	Pseudo mixture	Composition (wt%)
Myristic acid	1.0	$C_{13}H_{28}$	0.97	$C_{13}H_{28}$	0.97
Palmitic acid	42.5	$C_{15}H_{32}$	42.05	$C_{15}H_{32}$	32.95
Stearic acid	4.0	$C_{17}H_{36}$	4.04	$C_{17}H_{36}$	4.07
Palmitoleic acid		$C_{15}H_{30}$		$C_{15}H_{30}$	8.58
Oleic acid	43.0	$C_{17}H_{34}$	43.37	$C_{17}H_{34}$	53.43
Linoleic acid	9.5	$C_{17}H_{32}$	9.57	$C_{17}H_{32}$	
Total	100	Total	100	Total	100

After decarboxylation, unsaturated hydrocarbon compounds have double bonds at the positions corresponding to the fatty acids. Because of the lack in thermodynamic data of these compounds, the isomers of them such as α-olefins are chosen. However the thermodynamic data of $C_{17}H_{32}$ and its isomers are limited. Therefore 1-heptadecene is selected to represent hydrocarbon which is derived from linoleic acid. In order to balance hydrogen atom, one part of n-pentadecane is changed to 1-pentadecene.

4.2.1.2 Reaction Scheme

All hydrocarbon compounds from palm oil are straight chain hydrocarbons. Consequently, the reaction set for naphthenes and aromatics is discarded and the reactor systems are reduced to a single reactor. Although, there is a work concerning pyrolysis of α-olefin at low conversion and found that diolefins and cyclic compounds are also obtained, the diolefins and cyclic compounds are assumed to be negligible. From the study about thermal cracking of canola oil at 300-500 °C, it has found that the amount of aromatics and liquid product decreases as an increase in reaction temperature. In this paper, a decrease of these compounds has been explained with condensation of aromatics to form polyaromatics, which is equivalent to the fraction of residual oil [37]. Again, the residual oil decreases as an increase in the reaction temperature. In other words, the rate of cracking reaction becomes much more faster than that of cyclization or aromatization reactions leading to an increase in light olefins and a decrease in aromatics and liquid products. The canola oil is composed mainly triglycerides of unsaturated fatty acids, while only a half of fatty acids from palm oil is unsaturated. Therefore, it may assumed that the formation of naphthenes and aromatics is negligible. Hence, the reaction model consists of reaction for cracking paraffins to small paraffins and α-olefins and dehydrogenation reactions of paraffins to α-olefins, as mentioned in section 3.3.2.

4.2.2 Results

The product distribution of cracking hydrocarbon compounds from palm oil is summarized in Table 4.6. The product yields are calculated based on hydrocarbon compounds from palm oil, fatty acids from palm oil, as well as palm oil.

Table 4.6 product distribution of cracking hydrocarbon compounds from palm oil

Operating conditions			
Temperature ($^{\circ}$C)	800		
Pressure (kPa)	205		
Steam ratio (kg steam/kg feed)	0.50		
	Product fractions (wt%) based on hydrocarbon	Product yields (wt%) based on fatty acids	Product yields (wt%) based on palm oil
H_2	0.01	0.01	0.01
CH_4	2.74	2.29	2.19
C_2H_4	62.52	52.33	49.98
C_3H_6	32.93	27.56	26.33
C_4H_8	1.62	1.36	1.30
C_5H_{10}	0.10	0.08	0.08

The hydrogen to carbon atomic ratio of paraffins from given naphtha is 2.34 and equals 2.05 in case of hydrocarbons from palm oil. Although methane has the lowest Gibbs free energy of formation at given temperature, the hydrogen to carbon atomic ratio of hydrocarbons from palm oil is not sufficient to form a large fraction of methane as the case of naphtha. A large fraction of ethylene and propylene are therefore produced instead.

4.3 Effect of Reaction Temperature on Product Distribution

Temperature is ranged from 600-1000 °C to study the effect on product distribution. The result is shown in Figure 4.1.

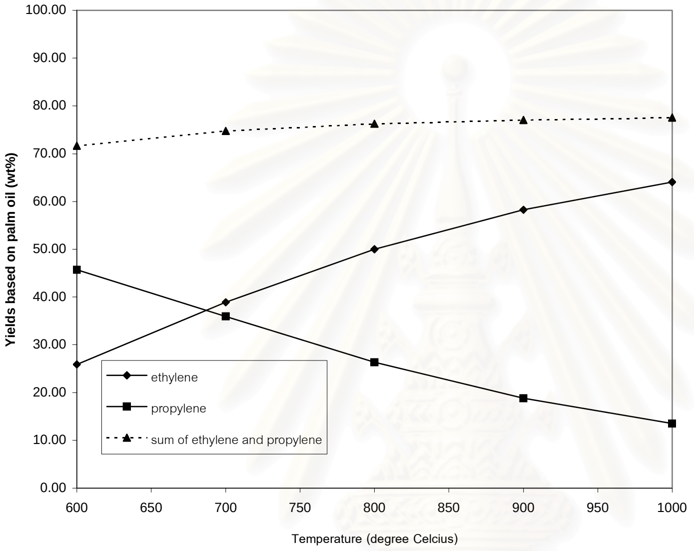


Figure 4.1 effect of reaction temperature on product distribution

Above 800 °C, the fraction of ethylene is improved 14.06 %, while the fraction of propylene is reduced 12.82 %, due to the variation of Gibbs free energy of formation with temperature, as shows in Figure 4.2. In addition, all reactions tend to reach the equilibrium as increasing reaction temperature. On the contrary, below 800 °C, the fraction of ethylene is reduced, while that of propylene is increased, corresponding to the Gibbs free energy of formation. The results suggest the limitation of the cracking reactions instead because the rates of reactions are reduced drastically as decreasing reaction temperature as described by Arrhenius equation.

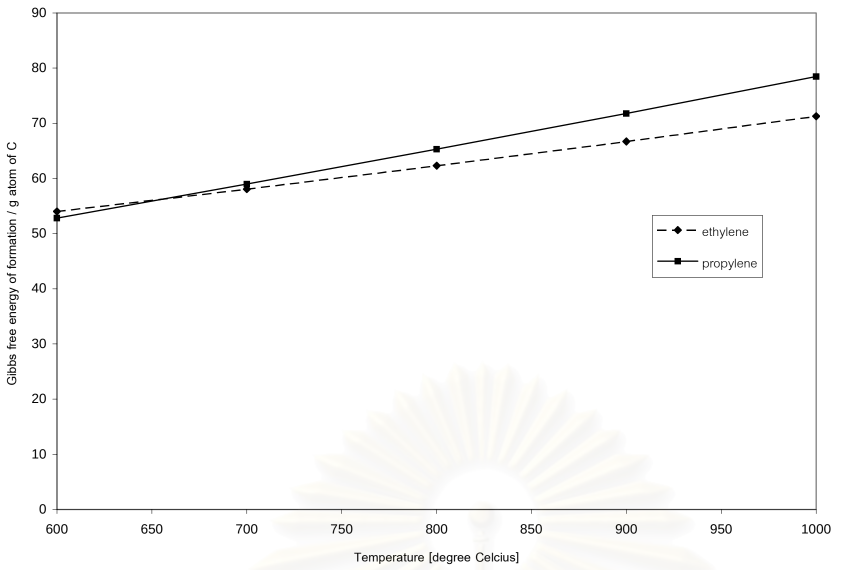


Figure 4.2 stability of ethylene and propylene

4.4 Effect of Steam Ratio on Product Distribution

In this reaction system, steam is limited as a diluent. For each mole of hydrocarbons from palm oil can produce more ethylene than propylene. Hence the equilibria are shifted to produce a large fraction of ethylene than that of propylene, see Figure 4.3. The effect of steam ratio on the chemical equilibria is similar to the system of single reaction.

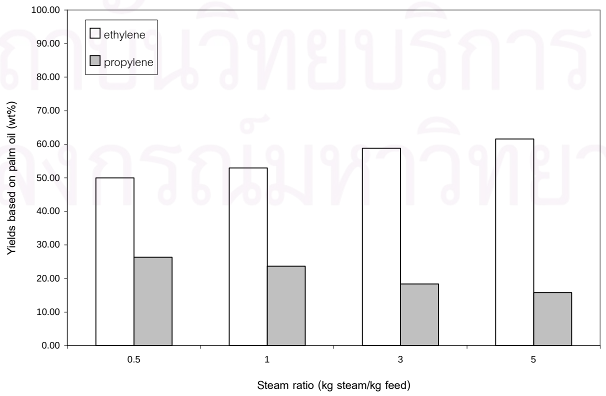


Figure 4.3 ethylene and propylene yields at various steam ratios

Chapter V

Conclusion and Recommendation

5.1 Conclusion

By PONA analysis and hydrogen content of naphtha feedstock, the pseudo naphtha is generated. The reactor system developed for naphtha cracking is composed of two parallel reactors. The first one is used to calculate the amount of products from pyrolysis of paraffins. The other one is used to compute the amount of products from naphthenes and aromatics. The results agree quite well with experimental data especially at temperature above 800°C.

The naphtha model is modified for applying to cracking hydrocarbon compounds from palm oil. The reactor system is reduced to one reactor. The product distribution of cracking hydrocarbon from palm oil is studied through the same procedure used in case of naphtha. The major products are ethylene and propylene. The effect of temperature and steam ratio is also studied. The amount of ethylene increases as an increase in reaction temperature while the amount of propylene decreases. Additionally, steam ratio has a similar result but less effect.

The cracking hydrocarbon compounds from palm oil can be used to produce light olefins. Ethylene production is recommended at reaction temperature above 800 °C, while propylene is proper to be produced at lower temperature. Although, the effect of steam is as same as that of reaction temperature, an increase in steam ratio causes an increase in the size of unit operations too.

5.2 Recommendation

In the modelling for cracking of naphtha, the pseudo naphtha is generated. However there are several possible sets of compounds, representing naphtha. Thus the selection of appropriate pseudo naphtha may be studied further.

Moreover, the pseudo mixture, representing hydrocarbon compounds from palm oil, is defined due to the lack in thermodynamic data. Hence the study of the thermodynamic properties is recommended. Finally, the experiment of cracking hydrocarbon compounds from palm oil is recommended in order to find the residence time, which is important in reactor design.

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Biography

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