SYNTHETIC FUELS FROM CRACKING OF POLYETHYLENE WASTE USING ZEOLITE BETA CATALYST IN CONTINUOUS PROCESS

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หัวข้อวิทยานิพนธ์	เชื้อเพลิงสังเคราะห์จากการแตกตัวของพอลิเอทิลีนที่ใช้แล้วโดยใช้ซีโอไลต์บีต้าเป็นตัวเร่งปฏิกิริยาในกระบวนการแบบต่อเนื่อง
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บทคัดย่อ

งานวิจัยนี้เป็นการปรับปรุงชุดปฏิกรณ์ที่ใช้สำหรับกระบวนการแบบต่อเนื่อง เพื่อศึกษาการแตกตัวของพอลิเอทิลีนเป็นเชื้อเพลิงสังเคราะห์โดยใช้ตัวเร่งปฏิกิริยาซีโอไลต์บีต้า ชุดปฏิกรณ์ประกอบด้วย 4 ส่วนคือ ส่วนป้อนสาร ถังปฏิกรณ์ ส่วนเก็บผลิตภัณฑ์ และส่วนเก็บกากที่เหลือจากการแตกตัว โดยตัวเร่งปฏิกิริยาที่ใช้แล้วสามารถแยกออกจากส่วนล่างของถังปฏิกรณ์ การศึกษาการแตกตัวของพอลิเอทิลีนเป็นเวลามากกว่า 8 ชั่วโมง ที่อุณหภูมิ 430 องศาเซลเซียส โดยใช้ก๊าซไนโตรเจนเป็นก๊าซตัวพาด้วยอัตราการไหล 10, 20, 50 และ 100 มิลลิลิตรต่อนาที อัตราการป้อนสารประมาณ 120, 200, 280, 400 และ 600 กรัมต่อชั่วโมง ปริมาณตัวเร่งปฏิกิริยา 0, 0.25, 0.5, 1, 2 และ 5 เปอร์เซ็นต์โดยน้ำหนักของพอลิเมอร์ จากการศึกษาพบว่าได้ผลิตภัณฑ์ก๊าซ 4-35 เปอร์เซ็นต์ ผลิตภัณฑ์ของเหลว 40-73 เปอร์เซ็นต์ และกากที่เหลือ 0-56 เปอร์เซ็นต์ ความสามารถในการเกิดปฏิกิริยาเพิ่มขึ้นด้วยการเพิ่มปริมาณตัวเร่งปฏิกิริยาและอัตราการไหลของก๊าซตัวพา อย่างไรก็ตามการเพิ่มอัตราการป้อนสารทำให้ความสามารถในการเกิดปฏิกิริยาลดลง ตัวเร่งปฏิกิริยาสามารถควบคุมการกระจายตัวของผลิตภัณฑ์ให้อยู่ในช่วงแคบซึ่งอยู่ในช่วงของแก๊สโซลีน มีการเลือกสรรของผลิตภัณฑ์ของเหลวประมาณ 70-80 เปอร์เซ็นต์โดยน้ำหนักซึ่งมีการเลือกสรรของก๊าซโซลีนมากกว่า 80 เปอร์เซ็นต์โดยน้ำหนักของผลิตภัณฑ์ของเหลว โดยการเลือกสรรของก๊าซโซลีนลดลงด้วยการลดอัตราการไหลของก๊าซตัวพา เมื่อเพิ่มปริมาณตัวเร่งปฏิกิริยาเป็น 2 เปอร์เซ็นต์โดยน้ำหนักของพอลิเมอร์ พบว่าเกิดปฏิกิริยาดิสโพรพอร์ชันเนชันขึ้น อัตราเร็วในการเกิดการถ่ายโอนไฮโดรเจนสามารถเพิ่มขึ้นได้ด้วยการการเพิ่มปริมาณตัวเร่งปฏิกิริยา และการลดอัตราการไหลของก๊าซตัวพา จากการศึกษาการแตกตัวของพอลิเอทิลีนที่ใช้แล้ว พบว่าสามารถแตกตัวได้ง่ายและได้ปริมาณผลิตภัณฑ์ที่เป็นก๊าซมากว่าเปรียบเทียบกับพอลิเอทิลีนที่ยังไม่ผ่านการใช้งาน การวิเคราะห์ผลิตภัณฑ์ด้วยเทคนิคนิวเคลียร์แมกเนติกเรโซแนนซ์ (NMR) พบว่าผลิตภัณฑ์ของเหลวมีค่าออกเทนประมาณ 90-102 และมีองค์ประกอบของไอโซพาราฟินและโอเลฟินมาก ส่วนอะโรเมติกมีน้อยมากเมื่อเปรียบเทียบกับแก๊สโซลีนทางการค้า

Thesis Title Synthetic Fuels from Cracking of Polyethylene Waste using Zeolite Beta Catalyst in Continuous Process

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ABSTRACT

In this thesis, development of a reactor for continuous catalytic cracking of polyethylene was studied for production of liquid fuel. The apparatus consisted of four sections: a feeder (single screw extruder), a reactor, a product collector, and a residue chamber. Used catalysts can be separated from the bottom of the reactor chamber. Catalytic cracking of polyethylene was carried out at 430°C for over 8 hours time on stream. Zeolite beta was used as a catalyst and nitrogen was fed as carrier gas with flow rate of a 10, 20, 50 and 100 ml/min. The polymer feed rate of 120, 200, 280, 400 and 600 g/h and catalyst content of 0, 0.25, 0.5, 1, 2 and 5 %wt. were investigated. It was found that 4-35 % gas products, 40-73 % liquid products and 0-56 % residue were produced. The catalytic activity was increased with an increase in catalyst loading and carrier gas flow rate. However, an increase in polymer feeding rate leads to a reduced activity. The results showed that the catalyst can significantly control the product distribution within a narrow range of gasoline fraction. The high liquid selectivity (70-80 %wt) was obtained with over 80 %wt gasoline selectivity. It was also found that the gasoline selectivity was decreased with a decrease in carrier gas flow rate. In addition, disproportionation can occur when the catalyst content increases to 2 %wt. Rate of hydrogen transfer can be increased by increasing catalyst loading or decreasing carrier gas flow rate. The waste polyethylene can be easily cracked, leading to higher gas yield, as compared with the virgin polyethylene. From Nuclear Magnetic Resonance results, cracked liquid products possessed an estimate octane number of 90-102 and contained large amounts of isoparaffins and olefins, with small amounts of aromatics, as compared to those of the commercial gasoline.

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Teerawat Chalermsuksri

CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF ABBREVIATIONS

DSC	Differential Scanning Calorimeter
FID	Flame Ionization Detector
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectrometer
HCL	Heavy Cracked Liquid Products
LCL	Light Cracked Liquid Products
MFI	Melt Flow Index
NMR	Nuclear Magnetic Resonance
PE	Polyethylene
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analyzer
XRD	X-ray Powder Diffractometer
XRF	X-ray Fluorescence Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Statement and significance of the problems

Plastics have become essential materials due to their numerous applications in daily life such as packaging, thermal and electric insulation, households, medical devices, etc. [1]. Increase in polymer products leads to generation of enormous polymer waste. Approximately, half of the waste is generated from factories and households such as low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET). Plastic wastes have been traditionally disposed of in landfills, which causes a high environmental impact because of the low degradation rate of plastics under ambient conditions [2,3]. The necessary for searching new technology to reduce the negative environmental impact of wastes accumulation together with the need of finding alternative fuels, has led to chemical recycling method. By chemical recycling, plastic wastes can be converted to mixtures of lower molecular weight hydrocarbons, which can be used as valuable chemicals and fuels. However, chemical recycling has a disadvantage of high-energy demand and, furthermore, thermal cracking of plastic results in a poor product distribution with low economical value [4]. Catalytic cracking provides a means to solve these problems. Zeolite catalyst, in particular, possess an ability to control product distribution, as well as that to reduce the reaction temperature [5,6].

Most of previous reports on the catalytic process have been studied in batch reactor systems. In order to scale up the waste plastics recycling to industrial level, it is necessary to operate continuously. However, only a few researches have been carried out using continuous reactors [2,7]. Thus, in this thesis, a flow reactor system is designed and developed for the catalytic cracking of polyethylene to liquid fuels. Synthetic fuels with high gasoline yield using zeolite Beta as catalyst in continuous reactor are focused.

1.2 Goal and Objectives

The objective of this thesis is to study the cracking of polyethylene using zeolite Beta as catalysts in a continuous process. The specific objectives are as follows :

1.2.1 To develop a reactor for continuous catalytic cracking of polyethylene waste.

1.2.2 To understand the effect of catalyst content, carrier gas flow rate and polymer feeding rate on the cracking of polyethylene in continuous process.

1.2.3 To obtain suitable operating condition for high selective, gasoline range hydrocarbons production.

1.3 Scopes of the study

The scopes of the study on catalytic cracking of polyethylene waste in continuous process are as follows :

1.3.1 Characterization of zeolite catalysts and polymer materials.

1.3.2 Development and construction of a reactor for cracking of polyethylene in continuous process.

1.3.3 Study on appropriate factors influencing the continuous cracking of virgin low-density polyethylene namely catalyst content, polymer feed rate, and carrier gas flow rate.

1.3.4 Study on the catalytic cracking of polyethylene waste in continuous process.

1.3.5 Analyses and evaluation of the products from the reaction based on their compositions and quality as liquid fuel.

1.4 Expected results

1.4.1 This research would provide a technology for high yield gasoline production from the cracking of polyethylene waste, from which an industrial scale process may be developed.

1.4.2 The reduction of the environmental problem due to polyethylene waste.

1.4.3 This process can be applied as a model for resource recycling and cleaner production technology.

1.4.4 This research would obtain an alternative approach for energy resource.

CHAPTER 2

LITERATURE REVIEWS AND THEORY

2.1 Zeolites

The word "zeolite" is Greek in origin, derived from the words "zein" and "lithos" meaning to boiling stone. It was first used by the Swedish chemist who found that upon heating the zeolite sample evolved steam. This property, of course, illustrates their easy water loss and is described as "intumescence" [8,9].

Zeolites are natural or synthetic microporous crystalline aluminosilicates with ion exchange, sorption, and molecular sieving properties. Zeolites are built from an infinite extending three dimensional network, composed of SiO_4 and AlO_4 tetrahedra with O atoms connecting neighboring tetrahedra [10]. For a completely siliceous structure, combination of SiO_4 units in this fashion leads to silica (SiO_2), which is an uncharged solid. Upon incorporation of Al into the silica framework, the +3 charge on the Al makes the frame work negatively charged, and requires the presence of extraframework cations (inorganic and organic cations can satisfy this requirement) within the structure to keep the overall framework neutral, normally from the group IA or IIA. The zeolite composition can be best described as having three components :

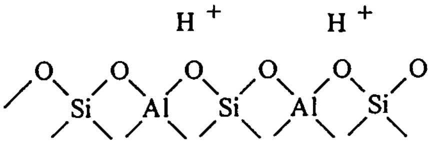
$$\underset{\text{exchangeable cations}}{M^{m+}_{n/m}} \quad \bullet \quad \underset{\text{framework}}{[Si_{1-n}Al_nO_2]} \quad \bullet \quad \underset{\text{sorbed phase}}{nH_2O}$$

The exchangeable cations give rise to the rich ion-exchange chemistry of these materials. The novelty of zeolites stems from their microporosity and is a result of the topology of the framework.

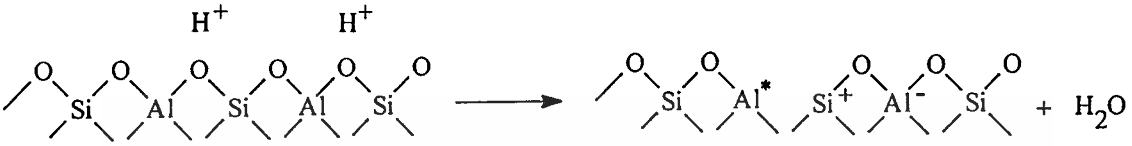
Generally the starting point for zeolite synthesis is crystalllization from an inhomogeneous gel, created from a silica source (e.g., sodium silicate, silica sols) and alumina source (e.g., sodium aluminate), in combined with water under high pH conditions generated by OH^- ion concentrations. Control of the SiO_2:Al_2O_3 ratio in this gel qualifies the final framework composition of the product and usually all the aluminium available is taken in to the zeolite final composition. Other compounds, such as organic templates (polyamines, polyalcohols), may also be present during synthesis. In the presence of organic amines, new structures can be formed and that in some cases the organic ions are traps inside the pores. These additives behave as structure-direction agents or templates around which the zeolite pores are formed. The organic templates are held tightly at these sites and can be removed only by calcination. The temperature, alkalinity (pH), the composition of the reaction mixture, nature of reactants and pretreatments can all affect crystallization kinetics and the type of zeolite formed. The synthesized zeolite is modified by ionic exchange and thermal or chemical treatment in order to obtain an active catalyst.

Zeolites are further grouped into families on the basis of composition, namely, the Si/Al ratio. The amount of Al within the framework can vary over a wide range, with Si/Al = 1 to ∞, the completely siliceous form being polymorphs of SiO_2. Lowenstein proposed that the lower limit of Si/Al = 1 of a zeolite framework arises because placement of adjacent AlO_4^- tetrahedra is not favored because of electrostatic repulsions between the negative charges. The framework composition depends on the synthesis conditions. Since the ion exchange capacity is equal to the concentration of Al^{3+} ions in the zeolite, the structures with low Si/Al ratios can have higher concentrations of catalytic sites than the others. There are other transitions in properties exemplified by the acid from zeolites, those incorporating H^+ as the exchangeable ion. Postsynthesis modifications that insert Si of Al in to the framework have also been developed, as in production of siliceous zeolite Y by removal of framework aluminum for catalytic cracking. As the Si/Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity increases and enhanced catalytic properties.

Most industrial applications of zeolites are based upon technology adapted from the acid silica/alumina catalysts originally developed for the cracking reaction. This means that the activity required is based upon the production of brønsted sites arising the creation "hydroxyls" within the zeolite pore structure.



When a hydrogen form zeolite is heated to high temperature, water is driven off and coordinatively unsaturated Al^{3+} ions are formed with the consequent formation of Lewis sites. These are strong Lewis acids; a base like pyridine is typically more strongly bonded to these sites than to strong proton-donor sites, as shown by infrared spectra and temperature-programmed desorption. Formation of the Lewis acid sites is depicted schematically as follows :



Brønsted acid site Lewis acid site

The Lewis sites in turn are unstable, especially in the continued presence of water vapour and an annealing process stabilizes the structure. This produces the so-called "true" Lewis sites by ejecting Al species from the framework, i.e. :

Lewis site "True" Lewis site

One interesting in zeolite synthesis is zeotype materials which are the zeolite containing elements other than Si or Al in tetrahedral framework sites. Other elements, such and B, Ge,Zn, P, and transition elements, can also be incorporated into the framework and are referred to as crystalline molecular sieves. Aluminophosphates (AlPOs) have strictly alternating AlO_2^- and PO_2^+ units, and the framework is neutral, organophilic, and nonacidic. The alternation of Al or P leads to structures lacking in odd-numbered rings. Substitution of P by Si leads to silicoaluminophosphates (SAPOs), with cation-exchange abilities. Metal cations can also be introduced into the framework, including transition metal ion such as Co, Fe Mn, and Sn. Discovery of these solids has led to the development of several new structures.

2.1.1 Applications of zeolites [9,10]

2.1.1.1 Ion-exchange applications

The major use of zeolites as ion-exchange agents is for water softening applications in the detergent industry and substitute use of phosphates. Hydrated cations within the zeolite pores are bond loosely to the zeolite framework, and can be readily exchanged with other cations in aqueous media. The selectivity of zeolite A for Ca^{2+} provides a unique advantage. Natural zeolites find considerable use for removal of Cs^{+} and Sr^{2+} radioisotopes by ion exchange from radioactive waste streams.

2.1.1.2 Adsorbent applications

The geometry is the source of the ability of zeolites to separate mixtures of molecules (in both the gas and liquid phases) on the basis of their effective sizes-hence their description as "molecular sieves". Molecules have certain dimensions and allow them to enter the pores, such as *n*-paraffins from branched paraffins. This property can be fine-tuned by variation the structure by changing the size and number of cation around the pores.

2.1.1.3 Catalyst applicaions

Zeolites are extremely useful as catalysts for several important reactions involving organic molecules. Zeolites can promote a diverse range of catalytic reactions including acid-base and metal induced reactions. The reactions can take place within the pores of the zeolite, which allows a greater degree of product control. In the industrial application, the major employment of zeolite is as acid cracking catalysts. Zeolites are catalyst that offer the advantages of high densities of catalytic sites combined with stability at high temperatures. Almost the reactions catalyzed by acids in solutions and in polymer matrices are catalyzed by zeolites incorporation acidic groups. This generalization is based on experimental evidence for hundreds of catalytic reactions. The exceptions involve reactants too large to enter the zeolite pores and products too large to form in, or leave, the pores. The commercial processes using zeolite catalysts are listed in Table 2.1

Table 2.1 Commercial processes using zeolite catalysts [9]

Process	**Catalysts**	**Advantage in using zeolite-based catalysts**
Catalytic cracking	REY (REX, REHY, REMgY, HY)	Selectivity and high conversion rates
Hydrocracking	X, Y, mordenite, erionite loaded with Co, Mo, W, Ni, also HY, US-Y, Ca MgY and H-ZSM-5	High conversion rates
Selectoforming	Ni erionite, clinoptilolite	Increase in octane number via LPG production
Hydroisomerization	Pt mordenite	Converts low octane, pentane and hexane feeds to higher octane yields
Dewaxing	Pt mordenite, ZSM-5	Improved pour points
Benzene Alkylation	ZSM-5	Ethylbenzene and styrene production with low by-product yield
Xylene isomerization	ZSM-5	Increase in p-xylene yield with low by-product yield
Methanol to gasoline conversion	ZSM-5	High gasoline yield with high octane rating
No_x reduction	H-mordenite	Effluent clean-up in nitric acid and nuclear reprocessing plants

2.1.2 Zeolite Beta [8,10-12]

A zeolite of substantial industrial importance is zeolite beta. It is a crystalline aluminosilicate molecular sieve zeolite which finds application in a number of industrial processes including as a catalyst in various hydrocarbon conversion reactions such as hydrocracking, hydroisomerization and dewaxing. The zeolite Beta has three-dimensional interconnecting channel system with 12-membered ring pore opening and with two different pore sizes of 5.5x5.5 and 6.4x7.6 diameter (Figure 2.1). It can be crystallized in a claimed range of silica to alumina ratio, $10 < SiO_2/Al_2O_3 < 200$, but the efficiency of crystallization is lower when it crystallizes at silica to alumina ratio lower than 19 (6 aluminium atoms per 1 unitcell). Zeolite Beta, like many other molecular sieve zeolites, is synthesized by the hydrothermal digestion of a reaction mixture comprising silica, alumina, an alkaline earth metal and an organic templating agent. The organic agent acts as a template in the nucleating and growth of the zeolite Beta crystal. Once the crystals are formed, it is conventional practice to carry out a calcination treatment in order to remove the organic material from the interstitial channels of the molecular sieve network. In addition, it can be used in alkylation process. Alkylation process employing zeolite Beta which is said to be especially useful in the production of ethylbenzene from benzene and ethylene and production of cumene from benzene and propylene. Moreover, it may often be desirable to incorporate a metal component into the zeolite Beta. Suitable metal components include those found in groups VIB and VIII of the periodic table. Specific metals include chromium, molybdenum, tungsten, vanadium, iron, cobalt, nickel, copper, platinum and palladium.

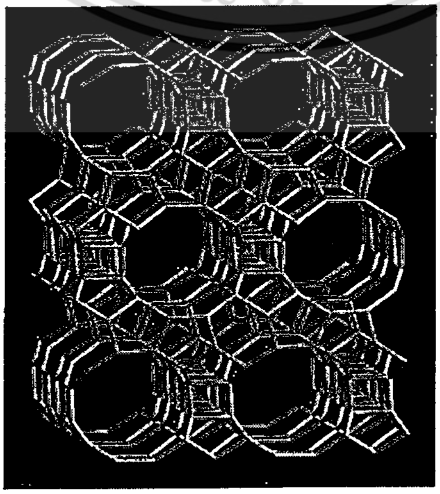


Figure 2.1 Structure formed by stacking of sequences of layers [13]

2.2 Cracking reaction

The term "cracking" usually applies to decomposition induced by elevated temperatures whereby the high molecular weight materials are converted into lower molecular weight products at elevated temperatures. Cracking reactions involve carbon-carbon bond cleavage and are thermodynamically favored at high temperatures. However, certain products may interact with one another to produce material of even higher molecular weight than that in the original feedstock. The cracking of petroleum products is of primary importance in the production of gasoline. Cracking also provides gasoline with sufficiently high octane number, although frequently further enhancement is needed [14,15]. Cracking is effected by one of three general methods, i.e., thermal cracking, catalytic cracking, or hydrocracking.

2.2.1 Thermal cracking [15-17]

One of the earliest processes used in petroleum, after distillation, is the noncatalytic conversion of higher boiling point petroleum stocks into lower boiling point products, known as thermal cracking. The mechanism of thermal cracking process generally proceed via free radical chain reaction and does not produce any degree of branching in the products other than that already present in the feedstock. However, certain products may interact with one another to produce higher molecular weight products than that in the original feedstock.

Two general types of reactions occur during cracking are:

1. Primary reactions in which decomposition molecules into small molecules :

$$R\text{-}CH_2CH_2CH_2CH_3 \longrightarrow CH_4 + R\text{-}CH_2CH{=}CH_2$$

$$R\text{-}CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_3 + R\text{-}CH{=}CH_2$$

2. Secondary reactions by which some of the active primary products interact to form higher molecular weight materials

$$CH_2{=}CH_2 + CH_2{=}CH_2 \longrightarrow CH_3CH_2CH{=}CH_2$$

$$RCH{=}CH_2 + R'CH{=}CH_2 \longrightarrow \text{tar, heavy oil, coke, others}$$

Free radicals are very reactive. A free radical reacts with a hydrocarbon by abstracting a hydrogen atom to produce a stable end product and a new free radical:

Initiation

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2^{\bullet} + CH_3^{\bullet}$$

Propagation

$$\begin{aligned} CH_3CH_2CH_2CH_3 + CH_3^{\bullet} &\longrightarrow CH_3\overset{\bullet}{C}HCH_2CH_3 + CH_4 \\ CH_3\overset{\bullet}{C}HCH_2CH_3 &\longrightarrow CH_2{=}CHCH_2CH_3 + H^{\bullet} \\ CH_3^{\bullet} + CH_3CH_2CH_3 &\longrightarrow CH_4 + CH_3CH_2CH_2^{\bullet} \end{aligned}$$

Termination

$$\begin{aligned} 2CH_3CH_2^{\bullet} &\longrightarrow CH_3CH_2CH_2CH_3 \\ CH_3CH_2^{\bullet} + H^{\bullet} &\longrightarrow CH_3CH_3 \end{aligned}$$

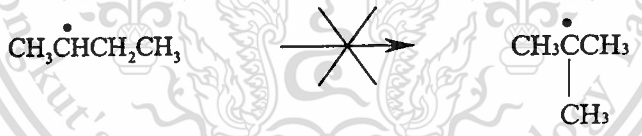
Disproportionation

$$\begin{aligned} CH_2{=}CH_2 + CH_3CH_2^{\bullet} &\longrightarrow CH_3CH_2CH_2CH_2^{\bullet} \\ 2CH_3CH_2CH_2^{\bullet} &\longrightarrow CH_3CH{=}CH_2 + CH_3CH_2CH_3 \end{aligned}$$

Other reactions, such as

$$CH_3CH_2CH_2CH_2^{\bullet} \longrightarrow CH_2{=}CH_2 + CH_3CH_2^{\bullet}$$

One of the significant features of hydrocarbon free radicals is their resistance to isomerization, for example, migration of an alkyl group:



$$CH_3\overset{\bullet}{C}HCH_2CH_3 \;\not\longrightarrow\; CH_3\underset{\displaystyle CH_3}{\overset{\bullet}{C}}CH_3$$

An increase in pressure favours the shift of equilibrium towards the polymerzation of olefins and the alkylation of paraffins. Because of this, a high pressure prevents a deep cracking of the raw material, which inhibits the formation of low molecular weight gaseous products and therefore promotes the formation of higher molecular weight materials [18].

2.2.2 Catalytic cracking

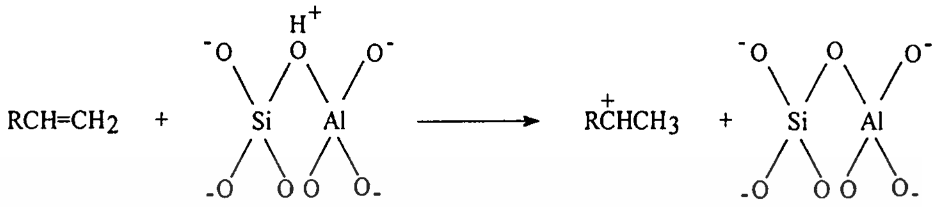
Catalytic cracking is the most important and widely used in refinery process for converting heavy oils into more valuable gasoline and lighter products. But this reaction is not a major route to petrochemicals, except to insure and ample supply of propylene for the United States [16]. Catalytic cracking is basically the same as the thermal decomposition of hydrocarbons but it differs in the use of a catalyst, which is not consumed in the process [19].

Serveral reactions take place in a catalytic cracking unit with varying degree of importance. These include carbon-carbon bond breaking, disproportionation, olefin formation and cyclization. Thermal cracking has essentially been replaced by catalytic cracking as the process for gasoline manufacture. The main advantage of catalytic cracking over thermal cracking is the increased gasoline production and the formation of hydrocarbon components having more gasoline of higher octane and anti-knock properties than thermal cracking because gasoline produced by catalytic cracking is richer in branched paraffins, cycloparaffins, and aromatics [15,20]. This is due to the effect of the catalyst, which promotes isomerization and dehydrocyclization reactions. Another advantage of catalytic cracking process is the production of C_3 and C_4 hydrocarbons for LPG uses. Catalytic cracking also produces less methane and C_2 hydrocarbons than thermal cracking. These differences are due mainly to the presence of an acid catalyst which promotes carbonium ion intermediates that are more selective than the free radicals formed in the thermal cracking reaction.

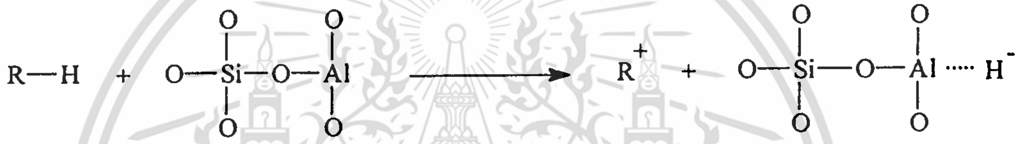
Catalytic cracking may be regarded as the modern method for converting high boiling point petroleum fractions, such as gas oil, into high quality gasoline and other low boiling point fractions. Thus, catalytic cracking in the usual commercial process involves contacting a gas oil fraction with an active catalyst under suitable conditions of temperature, pressure, and residence time, so that a substantial part (50-60%) of the gas oil is converted into gasoline and lower boiling products, usually in a single-pass operation. [20] However, during the cracking reaction, formation of high molecular weight aromatic products called coke can be obtained. Solid deposits of coke accumulate in the catalyst; the deposits clog the pores and cover the catalytically active sites. Coke is a catalyst poison, which markedly reduces its activity, and removal of the deposit is extremely necessary. This is usually accomplished by burning the deactivated catalyst in the presence of air until the catalyst activity is reestablished.

A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate, compared to the free radical intermediate in thermal cracking. Carbonium ions are longer lived and accordingly more selective than free radicals [21]. Moreover, the degradation products are distributed in a narrow range of carbon number compared with those obtained by thermal degradation. However, this type of catalyst is now being replaced by crystalline aluminosilicates (zeolites) or molecular sieves. [15] Low gas and coke yields, less sensitivity to poisoning, lower operation temperature, and low contact time are the main features of the new generation of cracking catalysts. [14] The formation of carbonium ions during catalytic cracking may be generated by:

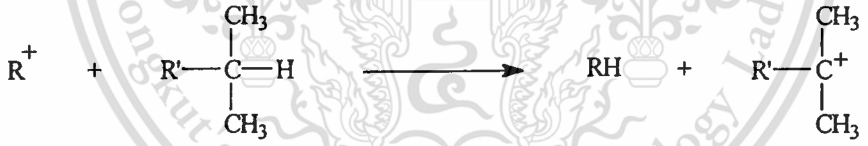
1. By a proton from the Brønsted acid site (H^+) in zeolite adding to an olefin hydrocarbon which was formed by a cracking process.



2. By a Lewis acid site abstracting a hydride ion (H^-) from a hydrocarbon.



3. By a carbonium ion formed from step 1 or 2 abstracting a hydride ion from another hydrocarbon to form another carbonuim ion.



However, carbonium ions are not formed by cleavage of a carbon-carbon bond:

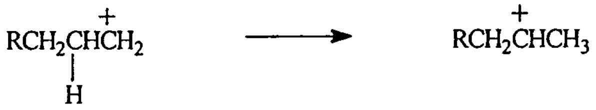
$$RCH_2CH_2R \not\longrightarrow RCH_2^+ + RCH_2^- \qquad 260\ \text{kcal/mol}$$

but

$$RCH_2CH_2R \longrightarrow 2RCH_2^\bullet \qquad 76\ \text{kcal/mol}$$

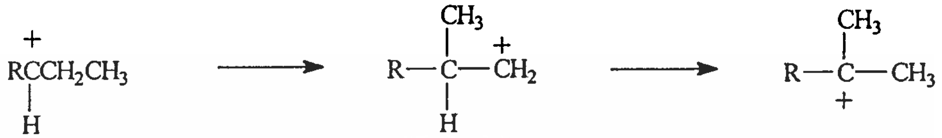
Once the carbonuim ions are formed, can isomerize through either a hydride shift, a methide shift or both.

1,2 Hydride shift :



$$RCH_2\underset{|\atop H}{C}H\overset{+}{C}H_2 \longrightarrow RCH_2\overset{+}{C}HCH_3$$

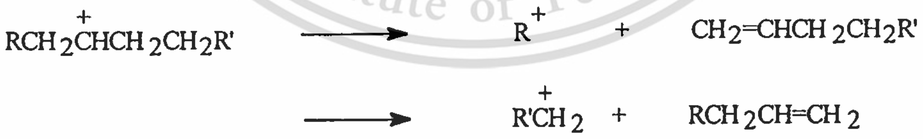
Methide shift-hydridr shift :



$$R\underset{|\atop H}{\overset{+}{C}}CH_2CH_3 \longrightarrow R-\underset{|\atop H}{\overset{CH_3\atop |}{C}}-\overset{+}{C}H_2 \longrightarrow R-\underset{+}{\overset{CH_3\atop |}{C}}-CH_3$$

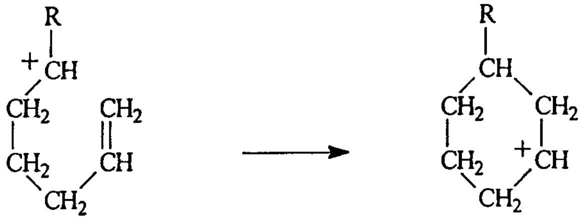
Abstraction of a hydride ion from a tertiary carbon is easier than from a secondary, which is easier than from a primary position. The formed carbonium ion can rearrange through a methide-hydride shift similar to catalytic reforming. This isomerization reaction is responsible for a high ratio of branched isomers in the products. The cracking rate is also influenced the structure of the molecule, with those containing tertiary carbon atoms cracking most readily while quaternary carbon atoms are most resistant.

Many reactions take place starting form a carbonium ion in addition to hydride and methide shifts. Among these are the important carbon-carbon beta bond scission and cyclization. The carbon-carbon beta bond scission is the most important cracking reaction of catalytic cracking. A bond at a position beta to the positively-charged carbon breaks heterolytically, yielding an olefin and another carbonium ion. This can be represented by the following example:

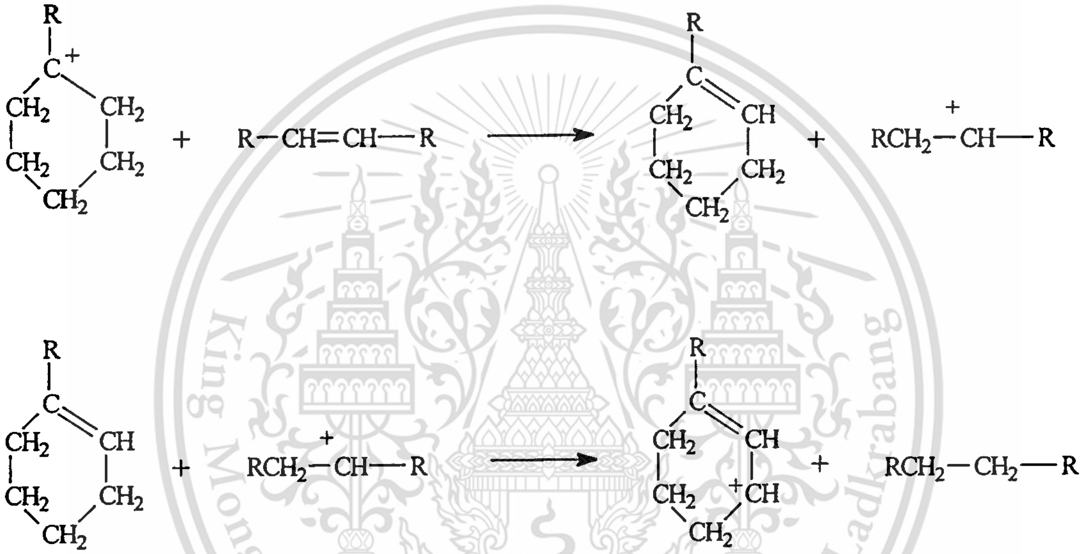


$$RCH_2\overset{+}{C}HCH_2CH_2R' \longrightarrow \overset{+}{R} + CH_2{=}CHCH_2CH_2R'$$
$$\longrightarrow R'\overset{+}{C}H_2 + RCH_2CH{=}CH_2$$

The new carbonium ion may experience another beta scission, rearrange to a more stable carbonium ion, or react with a hydrocarbon molecule in the mixture and produce a paraffin. Cyclization can take place by carbonium ion addition to a carbon-carbon double bond in the same molecule.



Cyclic olefins and aromatics can be produced by a two step hydrogen transfer sequence. The first is a proton transfer and the second is a hydride transfer. A continuation of these sequence converts the cyclic carbonium ion to an aromatic hydrocarbon and paraffins.



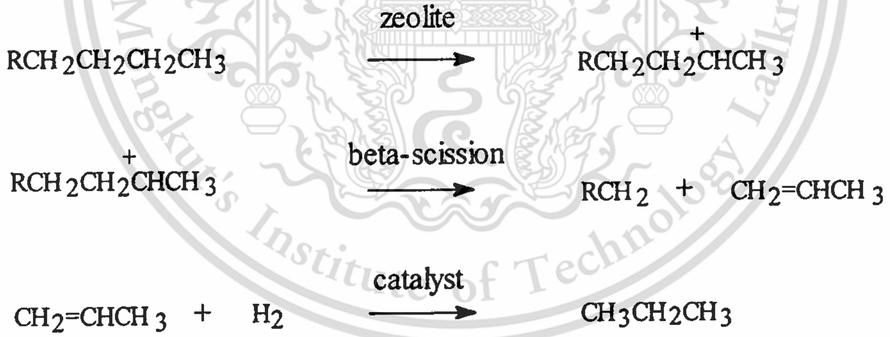
In essence, the use of a catalyst permits alternate routes for cracking reactions, usually by lowering the free energy of activation for the reaction. [20]

2.3.3 Hydrocracking

Hydrocracking is essentially catalytic cracking reaction whereby higher molecular weight hydrocrabons pyrolyze to lower molecular weight paraffins and olefins in the presence of hydrogen. Relatively high pressures of hydrogen (100-2000 psi) are employed, and the overall result is usually a change in the character or quality of the products. It produces less olefinic hydrocarbons whatsoever as the added hydrogen traps the intermediate species to yield saturated products. Since the hydrocarbon molecules in naphtha are relatively low molecular weight, hydrocraking forms molecules boiling in the gas range. Thus hydrocracking competes with the aromatization reaction by elimination hydrocarbons that can be aromatized. Such processes are generally expensive because of the considerable amount of hydrogen used and the high operating pressure. [15,20]

The wide range of product possible from hydrocracking is the result of combining catalytic cracking reactions with hydrogenation. The reactions are catalyzed by bifunctional catalysts used in hydrocracking provide high surface area cracking sites and hydrogenation-dehydrogenation sites. The cracking function is provided by an acid support such as silica-alumina or zeolite catalyst, whereas the hydrogenation-dehydrogenation function is provided by metals such as noble metals (palladium and platinum), or nonnoble metal sulfides from group VIA (molybdenum and tungsten) and group VIIIA (cobalt and nickel). [22] Catalysts with strong acidic activity promote isomerization, leading to a high iso/normal ratios. These metals catalyze the hydrogenation of the feedstock, making it more reactive for cracking and heteroatom removal, as well as reducing the coking rate. The metals also initiate the cracking by forming a reactive olefin intermediate via dehydrogenation.

Essentially all the initial reactions of catalytic cracking occur, but some of the secondary reactions are inhibited or stopped by the presence of hydrogen. The following is a representative hydrocracking reaction.

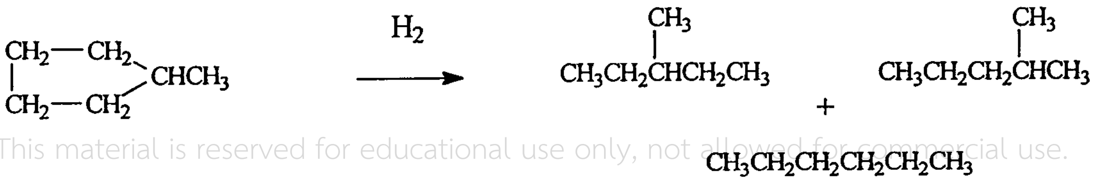


$$RCH_2CH_2CH_2CH_3 \xrightarrow{\text{zeolite}} RCH_2CH_2\overset{+}{C}HCH_3$$

$$RCH_2CH_2\overset{+}{C}HCH_3 \xrightarrow{\text{beta-scission}} RCH_2 + CH_2{=}CHCH_3$$

$$CH_2{=}CHCH_3 + H_2 \xrightarrow{\text{catalyst}} CH_3CH_2CH_3$$

The effect of hydrogen on naphthenic hydrocarbons is mainly that of ring scission followed by immediate saturation of each end of the fragment produced. The ring is preferentially broken at favored positions, although generally all the carbon-carbon bond positions are attacked to some extent.



Aromatic hydrocarbons are resistant to hydrogenation under mid conditions, but under more severe conditions the main reactions are conversion of the aromatic to naphthenic rings and scissions within the alkyl side chains. The naphthenes may also be converted to paraffins.

As anticipated, most products from hydrocracking are saturated. For this reason, gasolines from hydrocracking units have lower octane ratings than those produced by catalytic cracking units since they have a lower aromatic content due to the high hydrogenation activity. Products from hydrocracking units are suitable for jet fuel use. Hydrocracking also produces light hydrocarbon gases suitable as petrochemical feedstocks.

2.3 Polyethylene (PE)

2.3.1 Introduction of polyethylene [1-2,23-24]

Polyethylene is the major member of a group of chemical compounds known as poly olefins. It is one of the most widely used polymers of any of the thermoplastic materials and has the simplest basic structure of any polymer [22]. The study of polyethylene begins most conveniently with low density polyethylene (LDPE), the most general and fundamental model for organic polymer structures. The simple chemical composition, derived directly from very low-cost petrochemical sources, provides a polymer whose low price may be its most important property in the tremendous markets where other properties are relatively unimportant.

Commercially, polyethylene is produced by polymerizing high-purity ethylene gas under high pressure (1400 to 2400 bar) and high temperature (200 to 250°C) using free radical catalysts. The basic patent relating to the polymerization of ethylene was applied in 1936 by ICI. Under those conditions, ethylene molecules link up in long chains of 50 to 50,000 units, transforming ethylene gas to a white, partially crystalline solid. The product of this reaction is extruded as a hot ribbon, cooled, and chopped into pellets. There are both short and long chain branches on the molecules because of side reactions in the process. If the polymerization pressure is increased, the molecular mass increases and the number of branch decreases. However, about 1954 two other routes were developed, one using metal oxide catalysts (e.g. the Phillips process) and the other using aluminium alkyl or similar materials (the Ziegler process). By these processes polymers could be prepared at lower temperature and pressure and with a modified structure. Because of these modifications these polymers had a higher density, were harder and had high softening points. These materials are known as high density polyethylene (HDPE), while the earlier materials are known as low density polyethylene (LDPE). At the end of the 1970s considerable interest developed in what became known as linear low density polyethylene (LLDPE) which are intermidiate in properties and structure to the high pressure and low pressure material.

Mention may also be made of catalyst systems based on iron and cobalt announced in 1998 by BP Chemicals working in collaboration with Imperial college London and, separately, by DuPont working in collaboration with the University of North Carolina. The Dupont/UNC catalysts are said to be based on tridentate pyridine bis-imine ligands coordinated to iron and cobalt. These are capable of polymerising ethylene at low pressure (200-600 psi) yielding polymers with very low branching (0.4 branches per 1000 carbon atoms) and melting points as high as 139 ^{O}C. The BP/ICL term claim that their system provides many of the advantages of metallocenes but at lower cost.

2.3.2 Structure and properties of polyethylene

Polyethylene is a long chain aliphatic hydrocarbon of the type and would thus be thermoplastic. The following chemical structure illustrates basic structure of polyethylene.

$$—[CH_2CH_2]_n—$$

Some side-chain branching of the main polymer chain occurs during polymerization. If the branches are relatively few and short, the long parent chains will fold and pack neatly together in crystalline-like structures as the polyethylene cools from a melt. With small amounts of short-chain branching, the material produced is high density polyethylene (HDPE). HDPE is defined as a PE with a density greater than 0.941 g/cm^3.

Extensive side-chain branching is encouraged by polymerizing the ethylene at higher temperatures and pressures. Long-chain branching interferes with orderly packing, resulting in low density polyethylene (LDPE), a material that is less crystalline and less dense. LDPE is defined as a PE with a density between 0.910 and 0.925 g/cm^3.

Linear low density polyethylene (LLDPE) is a polyethylene in which side chain branching has been deliberately introduced by including monomers such as butene, hexene, or octene with the ethylene. The resulting polyethylene contains sufficient copolymer short-chain branching to decrease density to the LDPE range, but unlike in LDPE, the branches tend to be short, giving LLDPE properties somewhat different from LDPE's

The flexibility of the C-C bonds would be expected to lead to low values for the glass transition temperature (T_g). The T_g is associated with the motion of comparatively long segments in amorphous matter and since in a crystalline polymer there is only a small number of such segments the T_g has little physical significance. Far more important is the crystalline melting temperature T_m, which is usually in the range 108-132°C for commercial polymers, the exact value depending on the detailed molecular structure. Such low values are to be expected of a structure with a flexible backbone and no strong intermolecular forces. There are no strong intermolecular forces and most of the strength of the polymer is due to the fact that crystalization allows close molecular packing. Crystalline growth into spherulites can produce translucency and opacity, unless they are kept small by quenching or stretching during processing. Crystallinity produces high solvent resistance; but rigidity accentuates the danger of stress-cracking, unless a little comonomer is used to soften and flexibilize the structure somewhat. The polyethylene has a low cohesive energy density (the solubility parameter is about 16.1 $MPa^{1/2}$) and would be expected to be resistant to solvents of solubility parameter greater than 18.5 $MPa^{1/2}$. The polyethylene, in the absence of impurities, would also be expected to be an excellent high-frequency insulator because of its non-polar nature. Polyethylene appears in its natural form as a milky white, waxy feeling material. In general, as the density increases, the stiffness, hardness, strength, heat distortion point, and ability to transmit gasses increases. As density decreases, impact strength and stress crack resistance increases. Stress cracking is a surface change that polyethylene, and some plastics, undergo when exposed to oils, gasoline and other hydrocarbons. It appears on the material as a flaky, cracked surface.

At the present time there are many hundreds of grades of polyethylene available, most of which differ in their properties in one way or another.

2.3.3 Product applications

Polyethylene not only finds many products but also because of the many forms in which it is produced as a resin. It may be obtained in granules, powders, film, rod, tube and sheet form and molded through such processes as injection molding, fluidized bed coating, blow molding, extrusion, vacuum forming, casting and calendering. Polyethylene is used for many purposes, including: containers, electrical insulation, house-wares, chemical tubing, toys, freezer bags, flexible ice cube trays, snap-on lids and battery parts. Two major applications of polyethylene are films for packaging soft goods and other nonperishable and blow molded bottles. Squeeze bottles from low densitypolyethylene and detergent bottles from high density are typical products.

2.4 Fuel

The fuel products that are derived from petroleum supply more than half of the world's total supply of energy [25]. Gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships. Fuel oil and natural gas are used to heat homes and commercial buildings, as well as to generate electricity. The constant demand for products, such as liquid fuels, is the main driving force behind the petroleum industry. Other products, such as lubricating oils, waxes, and asphalt, have also added to the popularity of petroleum s a national resource. However, for the main part, the petroleum industry was inspired by the development of the automobile and the continued demand for gasoline, and other fuels. Such a demand has been accompanied by the demand for other products: diesel fuel for engines, lubricants for engine and machinery parts, fuel oil to provide power for the industrial complex, and asphalt for roadways.

2.4.1 Gaseous fuels

The principal types of gaseous fuels are oil gas, reformed natural gas, and reformed propane or liquefied petroleum gas (LPG). Mixed gas is a gas prepared by adding natural gas or liquefied petroleum gas to a manufactured gas, giving a product of better utility and higher.

Liquefied petroleum gas (LPG) is the term applied to certain specific hydrocarbons and their mixtures, which exist in the gaseous state under atmospheric ambient conditions but can be converted to the liquid state under conditions of moderate pressure at ambient temperature.

Thus, liquefied petroleum gas is a hydrocarbon mixture containing propane, butane, iso-butane and to a lesser extent propylene, or butylene. The most common commercial products are propane, butane, or some mixture of the two and are generally extracted from natural gas or crude petroleum. Propylene and butylenes result from cracking other hydrocarbons in a petroleum refinery and are two important chemical feed stocks

2.4.2 Gasoline

Gasoline is a mixture of volatile, flammable liquid hydrocarbons derived from petroleum that boil off over a range from about 25°C (77 $^{\circ}$F) to below 185°C (365°F). The hydrocarbon constituents in this boiling range are those that have four to twelve carbon atoms in their molecular structure. The hydrocarbons of which gasoline is composed fall in to three general types: paraffins (including the cycloparaffins and branched material), olefins, and aromatics. It is used as fuel for internal-combustion engines and also used as a solvent for oils and fats. Originally a byproduct of the petroleum industry (kerosene being the principal product), gasoline became the preferred automobile fuel because of its high energy of combustion and capacity to mix readily with air in carburetor. Gasoline was at first produced by distillation, simply separating, more valuable fractions of crude petroleum. Later processes, designed to raise the yield of gasoline from crude oil, split higher molecular weight products by processes known as cracking. And like typical gasoline, several processes (Table 2.2) produce the blending stocks for reformulated gasoline.

Table 2.2 Refining technologies for producing reformulated gasoline constituents

Technology	Objective
Catalytic reformer prefractionation	Reduce benzene
Reformate fractionation	Reduce benzene
Isomerization	Increase octane
Aromatics saturation	Reduce total aromatics
Isobutane dehydrogenation	Feedstock for oxygenate synthesis
Catalytic cracker naphtha fractionation	Increase alkylate and oxygenates Reduce olefins and sulfur

For use in motor vehicles, the gasoline must have certain chemical and physical properties, otherwise it will not pass satisfactorily up from the tank to the carburetor or injectors, form a suitable mixture with the air and burn efficiently in the cylinders to produce adequate power. These properties are:

1. *Calorific value.* The greater the quantity of thermal energy a fuel contains per unit of volume and weight, the smaller is the quantity required to be carried in the tank in the vehicle to provide enough energy to transport a given load at a given speed over a given distance. High density fuels contain the most energy and they have the lowest volatility.

2. *Latent heat of vaporisation.* A high latent heat of vaporisation causes the charge to be cooled, and therefore become more dense, as the fuel mixes with the air, so the charge passing into the cylinders of the engine will contain more energy than if that cooling had not taken place.

However, it can also cause freezing of atmospheric moisture in carburetors, which can severely interfere with the running of engines.

3. *Boiling point.* The fuel must comprise a mixture of volatile liquids. Called fractions, each having a different boiling point over the previously mentioned range of ambient to 185°C. Their individual boiling points affect not only its suitability for cold starting and use in both hot and cold ambient temperatures but also, if too high a proportion of the fractions have low boiling points, a risk arises of vapor lock occurring in the supply system.

4. *Octane number.* A high octane number is perhaps the most important of all the properties required for gasoline fuel. With a low octane number, it will burn explosively instead of progressively in the engine cylinders, and this can cause overheating and severe damage to the parts that are in any case very hot and their strength therefore reduces. Actually there are two different octane numbers. One is called the Research octane number (RON) because it is obtained in a single cylinder laboratory engine called the Co-operative Fuel Research Engine (CFR). However, in practice, the knock resistance of a fuel in multi-cylinder engine under normal running conditions is rarely as high as is indicated by the RON, so another method, called the Motor method. It was developed in which a more widely representative type of engine is used to determine the Motor octane number (MON). In the test methods used to determine the antiknock properties of gasoline, comparisons, are made with blends of two pure hydrocarbons, n-heptane and iso-octane (2,2,4-trimethylpentane). Iso-octane has an octane number of 100 and is high in its resistance to knocking. n-Heptane is quite low (with and octane number of 0) in its resistance to knocking.

2.4.3 Kerosene

Kerosene, also called paraffin or paraffin oil, is a flammable pale-yellow or colorless oily liquid with a characteristic odor. It is obtained from petroleum and used for burning in lamps and domestic heaters or furnaces, as a fuel or fuel component for jet engines, and as a solvent for greases and insecticides. Kerosene is also defined as a refined petroleum distillate that has a flash point of about 25°C (77°F) and is suitable for use as an illuminant when burned in a wide lamp. The term kerosene is also too often incorrectly applied to various fuel oils, but a fuel oil is actually any liquid or liquid petroleum product that produces heat when burned in a suitable container or that produces power when burned in an engine. Kerosene originated as a straight-run petroleum fraction that boiled between approximately 205 and 260°C

(400-500^{O}F). Chemically, kerosene is usually consists of about 10 different hydrocarbons, each containing from 10 to 16 carbon atoms per molecule; the constituents include *n*-dodecane (n-$C_{12}H_{26}$), alkyl benzenes, and naphthalene and its derivatives. Kerosene, because of its use as burning oil, must be free of aromatic and unsaturated hydrocarbons, as well as free of the more obnoxious sulfur compounds. It is a stable product, and additives are not required to improve the quality. Apart from the removal of excessive quantities of aromatics by the Edeleanu process, kerosene fractions may need only a lye wash or a doctor treatment if hydrogen sulfide is present to remove mercaptans. The essential properties of kerosene are flash point, fire point, distillation range, burning sulfur content, color, and cloud point. In the case of the flash point, the minimum flash temperature is generally placed above the prevailing ambient temperature; fire point determines the fire hazard associated with its handling and use. The boiling range is of less importance for kerosene than for gasoline, but it can be taken as an indication of the viscosity of the product. The ability of kerosene to burn steadily and cleanly over an extended period is an important property and gives some indication of the purity or composition of the product. The significance of the total sulfur content of a fuel oil varies greatly with the type of oil and the use to which it is put. Sulfur content is of great importance when the oil to be burned produces sulfur oxides that contaminate the surroundings. The color of kerosene is of little significance, but a product darker than usual may have resulted from contamination or aging, and in fact a color dark than specified may be considered by some users as unsatisfactory. Finally, the cloud point of kerosene gives and indication of the temperature at which the wick may become coated with wax particles, thus lowering the burning qualities of the oil.

2.4.4 Diesel

Diesel fuel oil is also a distillate fuel oil. In general, it is a blend of straight-run gas oil and cracked gas oil to produce a product boiling in the 175-345^{O}C (350-650^{O}F) range. Diesel fuel oil is essentially the same as furnace fuel oil, but the proportion of cracked gas oil is usually less since the high aromatic content of the cracked gas oil reduces the cetane value of the diesel fuel. Cetane number is a measure of the tendency of a diesel fuel to knock in a diesel engine. The scale is based upon the ignition characteristics of two hydrocarbons n- hexadecane (cetane) and 2,3,4,5,6,7,8-heptamethylnonane. Cetane has a short delay period during ignition and is assigned a cetane number of 100; heptamethylnonane has a long delay period and has been assigned a cetane number of 15. Just as the octane number is meaningful for automobile fuels, the cetane number is a means of determining the ignition quality of diesel fuels and is equivalent to the percentage by volume of cetane in the blend with heptamethylnonane, which matches the ignition quality of the test fuel.

The boiling range, carbon atom and phase of petroleum products are shown in Table 2.3.

Table 2.3 Boiling range of petroleum products

Product	Boiling range, °C	Phase	Carbon atoms
Gas petroleum	< 10	Gas	1-4
Gasoline	30-185	Liquid	4-13
Kerosene	170-250	Liquid	10-14
Diesel	175-350	Liquid	14-19
Lubricant	350-500	Liquid	19-35
Wax	350-500	Solid	19-35
Fuel oil	> 500	Liquid	> 35
Bitumen	> 500	Solid	> 35

2.5 Literature reviews

In the past, one of the technologies which is receiving a great deal of interest in the recycling of polymeric waste streams is pyrolysis. However, the reaction requires extreamly high temperature over 500°C. In 1996, Sean *et al* [26] performed the pyrolysis of low density polyethylene in batch reactor under atmospheric pressure. 75 wt% of light olefin was obtained with only gas yield 32 % at 800°C. Increasing the reaction temperature to 900°C can produce gas yields up to 95 wt%. Excessive coke formation, in addition, is a serious shortcoming of thermal cracking processes. Moreover, thermal conversion of polyolefin leads to a wide product distribution with poor economical value and low yield [4-6,27]. Consequently, many workers attemped to reduce the reaction temperature by utilizing catalyst. Numerous papers have been reported on the use of both non-acid and acid catalysts. The non-acidic catalysts including silicalite, mesoporous silica gel, and mesoporous folded silica have been used for polyolefin degradation. It was found that the non acidic mesoporous silica catalyst showed a very low catalytic activity, as compared with the conventional solid-acid catalyst [27-28]. Therefore, an interesting alternative is based on the use of solid-acid catalyst to promote the polyolefin degradation, which results in hydrocarbon mixtures with higher commercial value.

Recently, polymer degradation has been extensively investigated over amorphous silica-alumina and different types of zeolite [29-30]. Since the early 1960s, the first acidic catalyst used for polymer degradation was synthetic faujasite (Linde X) modified with rare-earth metal ions. These active catalysts gave upto 10-50% higher yield of gasoline, as compared to that produced by the completely amorphous catalysts. Furthermore, higher selectivity and lower coking were obtained [14]. In addition, the zeolite has the ability to control both product yield and product distribution from polymer cracking as well as to significantly reduce the reaction temperature. The most common zeolites used as cracking catalysts are Y, ZSM-5, Theta-1, EMT, Mordenite, Beta and MCM-41 [2,12,28-34]. The product composition can be controlled depending upon structure, acidity, acid strength, crystal size and pore size of the zeolite catalysts [30-31]. Zeolites with channel structure provide low deactivation rate, as compared to that with cage structure [31,34].

Regarding to the reactors used for plastic cracking, most of the previous work have been carried out in batch system, and focused particularly on the effect of the operating conditions. Secondary cracking of the cracked product easily causes a coke formation in the batch process, leading to catalyst deactivation. This is because the fact that the product are unable to be separated from the catalysts. Continuous process can be employed to solve this problem. More complicate designs have been applied including fixed beds, fluidized bed, screw kilns, circulating bed reactors and stepwise pyrolysis reactor [2-5,7,34,35]. In spite of the fact that these systems are conventionally applied for the processing of most thermoplastic materials, a few continuous reactor is designed for separation the used of catalyst [2-4].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagents

1. Air zero (99.9%, TIG)
2. Acetone (99.5%, Carlo Erba Reagenti)
3. Benzene (99.8 %, Carlo Erba Reagenti)
4. Cyclohexane (99.5 %, Carlo Erba Reagenti)
5. Cyclohexene (>99.0 %,Carlo Erba Reagenti)
6. Cumene (>98.0 %, Fluka)
7. Ethylene gas (>99.95%, TIG)
8. Gasoline fuel, octane 91 and 95 (PTT)
9. Helium gas (99.9%, TIG)
10. Isooctane (99.5 %, Carlo Erba Reagenti)
11. Liquid nitrogen (TIG)
12. Liquefied petroleum gas (Siam Gas)
13. *m*-Xylene (>99.0 %, Fluka)
14. Nitrogen gas (99.9%, TIG)
15. *n*-Heptane (99.5 %, Carlo Erba Reagenti)
16. *n*-Hexane (99.9 %, Mallinckrodt)
17. Methylcyclopentane (>98 %, Merck)
18. *n*-Nonane (>99.0 %, Merck)
19. *p*-Xylene (99.0 %, Fluka)
20. Paraffin liquid (Fisher chemicals)
21. Polyethylene (Melt flow index, MFI = 45 g/10 min, powder form, TPI)
22. Polyethylene bag (Srisakul factory)
23. Petroleum ether (Lab scan)
24. Toluene (99.5%, Lab scan)
25. Zeolite Beta (Tosoh Corporation)

3.2 Apparatus

1. Automatic distillation analysis (AD86 5G B.P.40 14790 version, ISL)
2. Bunsen burner
3. Condenser
4. Differential scanning calorimeter (Pyris Diamond DSC, Perkin Elmer)
5. Furnace (Vecstar Furnaces)
6. Gas adsorption analyzer (Autosorb-1, Quantachrome)
7. Gas chromatograph (3800 Gas Chromatograph, Varian)
8. Gas chromatograph/Mass spectrometer (6892N/5973N, Agilent Technologies, Instruments Service Centre, KMITL)
9. Gasoline analyzer (IROX 2000, Grabner Instruments)
10. Heating tape
11. Hotplate
12. Laboratory glassware
13. Motor
14. Melt flow indexer (CEAST 6841.000 ASTM D1238,CEAST)
15. Nuclear magnetic resonance spectrometer (AVANCE DPX300, Bruker)
16. Oven
17. Reactor (see figure 3.1)
18. Scanning electron microscope (LEO 1455VP, LEO Electron Microscopy, Scientific Instruments Service Centre, KMITL)
19. Single screw extruder (D-76227 KARLSRUHE, Thermo Haake Polydrive)
20. Thermogravimetric analyzer (Pyris 1 TGA, Perkin Elmer, Scientific Instruments Service Centre, KMITL)
21. Vacuum oven
22. Water circulator
23. X-ray fluoresence spectroscopy (SRS 3400, Bruker AG, Scientific Instruments Service Centre, KMITL)
24. X-ray powder diffractometer (D8 Advance, Bruker AG, Scientific Instruments Service Centre, KMITL)

3.3 Experimental details

3.3.1 Characterization of zeolite and polymer

3.3.1.1 Determination of zeolite structure using X-ray Powder Diffractometer (XRD)

The zeolite structure was determined by X-ray powder diffractometer. The sample was prepared by packing the zeolite in the sample holder. CuK_{α} X-ray beam was used for analysis at 40 kV, 40 mA. The sample was scanned from 2θ angle 5° to 50° with 1 second/step time and 0.02 2θ/step increment. X-ray diffraction pattern of the sample was compared with the X-ray diffraction pattern of standard zeolite for structure determination.

3.3.1.2 Determination of zeolite crystal morphology using Scanning Electron Microscope (SEM)

The crystal morphology and crystal size of zeolite were determined by scanning electron microscope. The sample was prepared by thoroughly placing zeolite powder onto the sample holder. It was then coated with gold by ion sputtering. The sample was placed in the sample chamber of SEM and evacuated from ambient pressure to 10^{-4} torr. The scanning electron micrographs was taken at the magnification of 6,000 and 10,000 times and scan speed of 9.

3.3.1.3 Determination of zeolites surface area using Gas Adsorption Analyzer (Autosorb-1C)

Surface area of the zeolites was determined by gas adsorption analyzer. The sample was prepared by weighing approximately 20 mg of zeolite sample into the clean and dry sample cell. The sample cell was attached to the out gassing station. Heating mantle was installed and the temperature was raised to 350 °C under vacuum. The sample was out-gassed for 24 hours. The sample cell was then removed from the out gassing station after the nitrogen was filled and was attached to the analysis station. The equilibration time was set to 3 minutes and the nitrogen adsorption was measured at the partial pressure (P/P_0) ranged from 10^{-6} to 1.0 at 77.4 K.

3.3.1.4 Determination of silicon/aluminium ratio of the zeolites using X-ray Fluorescence spectroscopy (XRF)

The silicon/aluminium ratio of the catalysts was determined by X-ray fluorescence spectrometer. The sample was prepared by mixing 4.5 g of boric acid and 0.5 g of zeolite. The mixture was packed onto sample holder and compressed at 150 KN. The sample was then be placed in the sample chamber of X-ray fluoresence spectroscopy. Rhodium was used as source for analysis at 50 KV, 60 mA, and WDX of 0.3 to 188.5.

3.3.1.5 Determination of melt flow index of polymer material using melt flow indexer (ASTM D 1238, ISO 1133)[36]

The melt flow index of virgin polyethylene (powder form) and waste polyethylene (bag) was determined by melt flow indexer. The melt flow index apparatus was preheated at 190°C. The polymer material will then be loaded into the cylinder from the top and a dead weight was placed on a piston with total weight of 2.16 Kg. The polymer material was allowed to flow through the die. Depending on the material or its flow rate, cuts for the test were taken at different time intervals. The extrudate was weighed and the melt index values was calculated in g/10 min.

3.3.1.6 Determination of polymer material heat of fusion and melt temperature using Differential Scanning Calorimetry (DSC)

The heats of fusion of virgin polyethylene (powder form) and waste polyethylene were determined by differential scanning calorimeter. A small quantity of sample, usually 5-10 mg, was weighed into an inert capsule made of aluminum. The encapsulated sample was placed in the DSC sample holder furnace and reference was placed in the DSC reference holder furnace. Those were heated from 50°C to 200°C at a heating rate of 10°C/ min.

3.3.2 Development and construction of reactor

The reactor for cracking of polyethylene in continuous process has been developed from the model designed by previous work [35]. Since the feeding rate for this study is relatively high, the amount of volatile products from the reaction has been markedly increased. The capacity of condenser used in the previous work is somewhat inadequate for trapping the cracked liquid product from the reaction. In this work, another condenser will then be constructed and added to the condensing unit which shall enhance the overall performance of the condensers. The additional condenser is controlled at -5°C using ethylene glycol-water coolant.

In addition, residue driven by screw from bottom end of the reactor, also carry some of the volatile cracked products. This produces pollutant gas and also causes the loss of cracked products. The problem was promptly solved by attaching a residue chamber to the end of the reactor. The residue chamber was made of glass, having an inlet line for carrier gas, which carries the volatile cracked product into condensers via an outlet line. The outlet line is connected to the product line from the reactor exit. The cracked products from top of the reactor and those from the residue chamber shall then be carried to the condenser within the same line. An on-off ball valve is installed between condenser and residue chamber to prevent loss of products when residue is periodically removed during the reaction.

Furthermore, the polymer having low melt flow index is difficult to move through the reactor. This reduces cracking efficiency and leads to accumulate of the polymer melt on the top of the reactor. Thus, the direction of rotating paddles is changed to help driving molten polymer into the reactor.

3.3.3 Catalytic testing

3.3.3.1 Study on cracking of polyethylene using Thermogravimetric Analyzer (TGA)

Thermogravimetric behavior of polyethylene was investigated using TGA. Approximately 30 mg of polyethylene, virgin and waste, or polyethylene mixed with catalyst (catalyst content ranging from 0 to 5%) was placed in a platinum pan hanging from a thermobalance, and nitrogen is introduced as a carrier gas. The sample will then be heated under a nitrogen flow (50 ml/min) from 50°C to 800°C at a heating rate of 10°C/ min. The %weight loss due to the degradation was measured with the sample temperature.

3.3.3.2 Study on cracking of polyethylene in continuous process

The schematic diagram and reactor unit employed for continuous process, which has been developed from the previous work [35] is shown in Figure 3.1. Simply the continuous flow reactor system could be consisted of four sections: a feeder (5) (single screw extruder), the reactor chamber (7), the product collector (8) and residue chamber (10).

Polyethylene was primarily baked at 80°C about 24 hours and the catalyst was dried at 180°C in vacuum oven for 24 hours. Polyethylene, in powder form (MFI = 45 g/10min), without or with catalyst (0.25-5%w) was loaded into the extruder. The barrel temperature was controlled at 100, 150, 200 and 220°C for feeding, mixing, melting and the die, respectively. The material is molten and continuously fed into the top of the reactor. The feeding rate was controlled by adjusting screw speed. The reactor consists of 8-stacked paddles and a screw at the terminal end of the reactor. Stirring and mixing of the material inside the reactor was achieved by means of an electric motor and the rotating paddles. The temperature of the reactor is controlled at 430°C by a three-zone vertical tube furnace. Prior to start of the reaction, the reactor was preheated at 300°C and purged with nitrogen for at least 20 minutes to flash out oxygen from the reactor. Nitrogen was used as carrier gas with a flow rate of 0-100 ml/min. The output for volatile products is connected to the series of three cooling condensers. The liquid products were trapped at approximately 40°C in the first cooling condenser and at -5°C in the second and third condensers. The gaseous products were periodically sampled and the rest was burned out using a burner. The waxy material mixed with coking catalyst was driven out of the reactor by a screw at the bottom end. A glass chamber is attached and used to collect the residue in a close system.

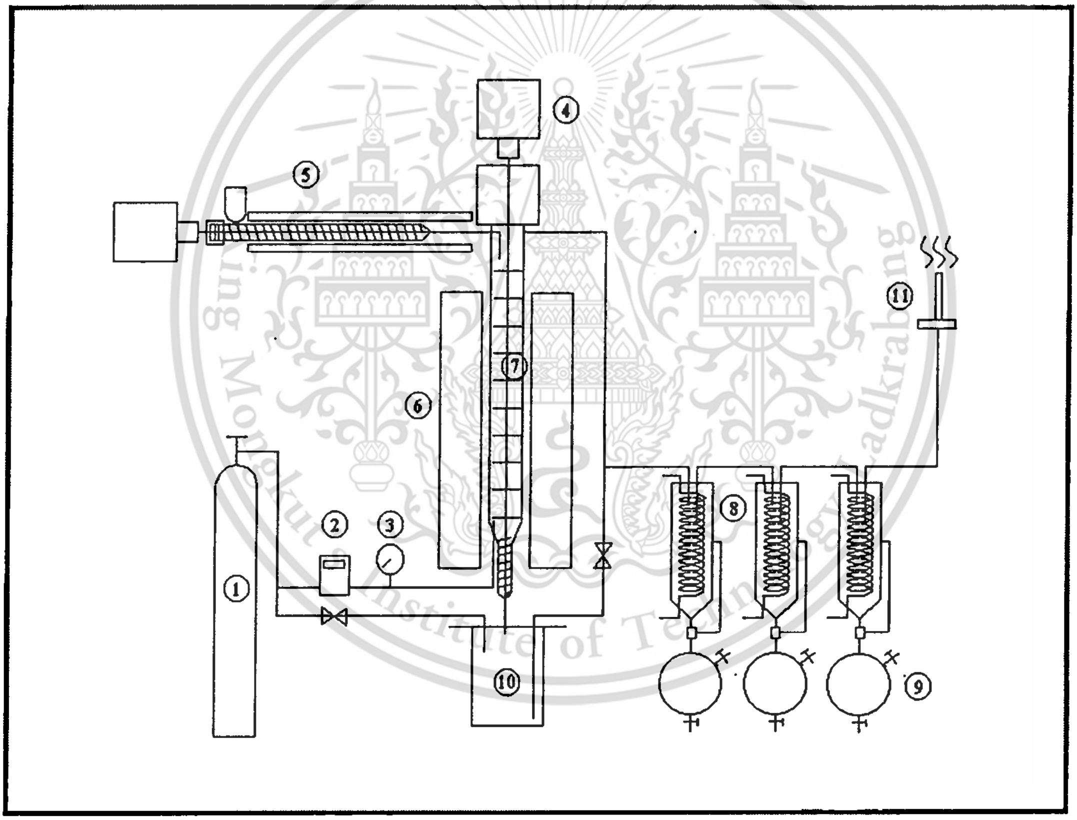


Figure 3.1 Schematic representation of continuous process : 1. Gas N_2 ; 2. Flow meter; 3. Pressure gauge; 4. Motor; 5. Extruder; 6. Furnace; 7. Reactor chamber; 8. Liquid trap condenser; 9. Product collector; 10. Residue chamber; 11. Flair

1) Effect of catalyst content

The effect of catalyst content was determined by the reactions using catalyst contents of 0.25, 0.5%, 1%, 2%, and 5% at reaction temperature of 430°C. The reactions were investigated with an approximate polymer feeding rate of 120 and 400 g/hr. Thermal reaction will also be compared with the catalytic cracking under the same conditions.

2) Effect of carrier gas flow rate

The effect of carrier gas flow rate was determined by the reactions using carrier gas flow rates of 10, 20, 50, and 100 ml/min at the reaction temperature of 430°C. The reactions were investigated with a constant polymer feeding rate, approximately 400 g/hr and with catalyst content of 1%.

3) Effect of polymer feeding rate

The effect of polymer feeding rate was determined by the reaction using an approximate polymer feeding rate of 120, 200, 280, 400 and 600 g/hr at reaction temperature of 430°C. The reactions were investigated with catalyst content of 1%.

3.3.3.3 Study on cracking of waste polyethylene in continuous process

Catalytic cracking of the waste polyethylene from used polyethylene bag was studied in a continuous process. The used polyethylene bag was melted and extruded by a single screw extruder. It was cut into pellets of approximately 2 mm in diameter. The polyethylene and catalyst were mixed to give a catalyst content of 1%. The reaction can be carried out with a constant polymer feeding rate, approximately 400 g/hr at 430°C.

3.3.4 Analysis of products

3.3.4.1 Determination of product composition using Gas Chromatograph (GC)

The gas and liquid products at -5°C and 40°C was analyzed by gas chromatograph using 3800 Gas Chromatograph, Varian, with a capillary column (Equity-1, 30 m, 0.53 mm I.D.) and a flame ionization detector (FID). Helium was used as carrier gas with a linear velocity of 20 cm/sec. Approximately 0.5 ml of gas products was injected to the injection port (injection port temperature at 220°C) using a split ratio of 200. The oven temperature was started at 30°C and held for 10 minutes. Then, the temperature was raised to 160°C with a heating rate of 5°C/min and held at that temperature for 5 minutes. For liquid products, the 0.1 μl of sample (trapped at -

5°C) was injected to the injection port (injection port temperature at 220°C) that using the split ratio of 100. The oven temperature was started at 30°C and held for 5 minutes. Then, the temperature was raised to 160°C with a heating rate of 5°C/min and held at that temperature for 1 minutes. After that, the temperature was raised to 220 °C with a heating rate of 20 °C/min and held at that temperature for 11 minutes. Whilst, the liquid products trapped at 40°C were analyzed with the same condition, except in the last step, the final temperature was raised to 250 °C with a heating rate of 20 °C/min and held at that temperature for 18 minutes.

3.3.4.2 Determination of product composition using Gas Chromatograph/Mass Spectroscopy (GC/MS)

The structure of liquid products trapped at 40°C were confirmed by gas chromatograph/mass with a capillary column (HP-1, 30 m, 0.25 mm I.D.). Helium was used as a carrier gas with an initial flow 0.6 ml/min and an average velocity of 28 cm/sec. Approximately 0.1 μl of the sample was injected to the injection port (injection port temperature at 220°C) using a split ratio of 200. The oven temperature was used the same with the FID gas chromatograph.

3.3.4.3 Determination of the composition and predicted octane number of the gasoline products using Nuclear Magnetic Resonance (NMR)

The content of paraffins, olefins and aromatics of liquid products were determined using the NMR method developed by Myers *et al* [36-37]. The liquid products were diluted in deuterated chloroform with tetramethylsilane (TMS) internal reference. The measurement was performed on a Bruker AVANCE DPX300 NMR spectrometer with 300-MHz proton resonance frequency. The integral spectra are obtained in separated scans from 0 to 10 parts per million (ppm). The RON and MON was also calculated using the equations as shown [2-3] :

Isoparaffin index = CH_3/CH_2

RON = 80.2 + 8.90 (isoparaffin index) + 0.107 aromatics (vol.%)

MON = 70.8 + 10.0 (isoparaffin index) + 0.101 aromatics (vol.%)

Details of the method is described in appendix F

3.3.4.4 Determination of catalyst content in residue from reaction using thermogravimetric Analyzer (TGA)

The catalyst content in the residue was investigated using TGA. The residues from the reactor were cut into particles with 6 mm diameter. Approximately 30 mg of the sample was placed into a platinum pan hanging from a microbalance, then nitrogen was introduced as a carrier gas. The sample was heated under a nitrogen flow (50 ml/min) from $50^{\circ}C$ to $800^{\circ}C$ at a heating rate of $10^{\circ}C$/ min.

3.3.4.5 Determination of composition and density of liquid product using gasoline analyzer (ASTM D5845 and ASTM D 6277)

The content of paraffins, olefins, aromatics, and density of the liquid product were estimated by gasoline analyzer (IROX 2000, Grabner Instruments). The liquid product from reaction was introduced into the analyzer for 10 ml. Density of the liquid product is then measured. Infrared spectrum of the sample was compared with those in database and the composition with approximate RON and MON was determined.

3.3.4.6 Determination of gasoline yield and distillation characteristics of the liquid product using Automatic distillation analyzer [38]

The distillation (volatility) characteristics of liquid product was determined by automatic distillation analyzer (AD86 5G B.P.40 14790 version, ISL) using ASTM D 86. A 100 ml of liquid product was distilled under prescribed conditions for the group in which the sample falls. The distillation was performed in a batch distillation unit at ambient pressure under conditions that was designed to provide approximately one theoretical plate fractionation. Systematic observations of thermometer readings and volumes of the condensate was made. The volume of the residue and the losses will also be recorded. The results of the test were calculated and reported. Measurement of the liquid product trapped at $-5^{\circ}C$ was carried out in program A. While that of the liquid product trapped above $40^{\circ}C$ was carried out in program B as shown in Tables 3.1 and 3.2, respectively. From the distillation data, yield of gasoline fraction could be calculated.

Table 3.1 Preparation of apparatus

	Program A	Program B
Temp. of Stored Sample: °C	0 to 4.5	0 to 10
Flask, ml	100	125
Ip Distillation Thermometer	5C	5C
Flask Support	A	B
Diameter of hole, mm	32	38
Flask and thermometer, °C	0 to 4.5	13 to 18
Flask support and shield	Not above ambient	Not above ambient
Graduate and 10 ml charge, °C	0 to 4.5	13 to 18

Table 3.2 Distillation condition of programs A and B

	Program A	Program B
Method	ASTM D86	ASTM D86
Group	0	2
Distillation rate, %/min	4.5	4.5
Condenser setpoint, °C	1	2
Bath temperature delta, °C	0	0
Graduate setpoint , °C	2	15
First level heating , W	125	18
First level heating time, min	1.5	3.0
Second level heating, W	29	39
Final heating adjustment, W	0	40
Barometric correction	1 (1= yes, 0 = no)	1(1= yes, 0 = no)
Coefficient	0	0
Rounded temperature, °C	0	0
Expected volume – Hold up, %	97	98
FBP detection, °C	-1.0	-5.0

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of zeolite and polymer

4.1.1 Determination of the zeolite structure using XRD

Catalyst used in this work was zeolite Beta type. X-ray diffraction pattern of the zeolite was obtained from X-ray powder diffractometer using Cu-Kα-radiation as shown in Figure 4.1.

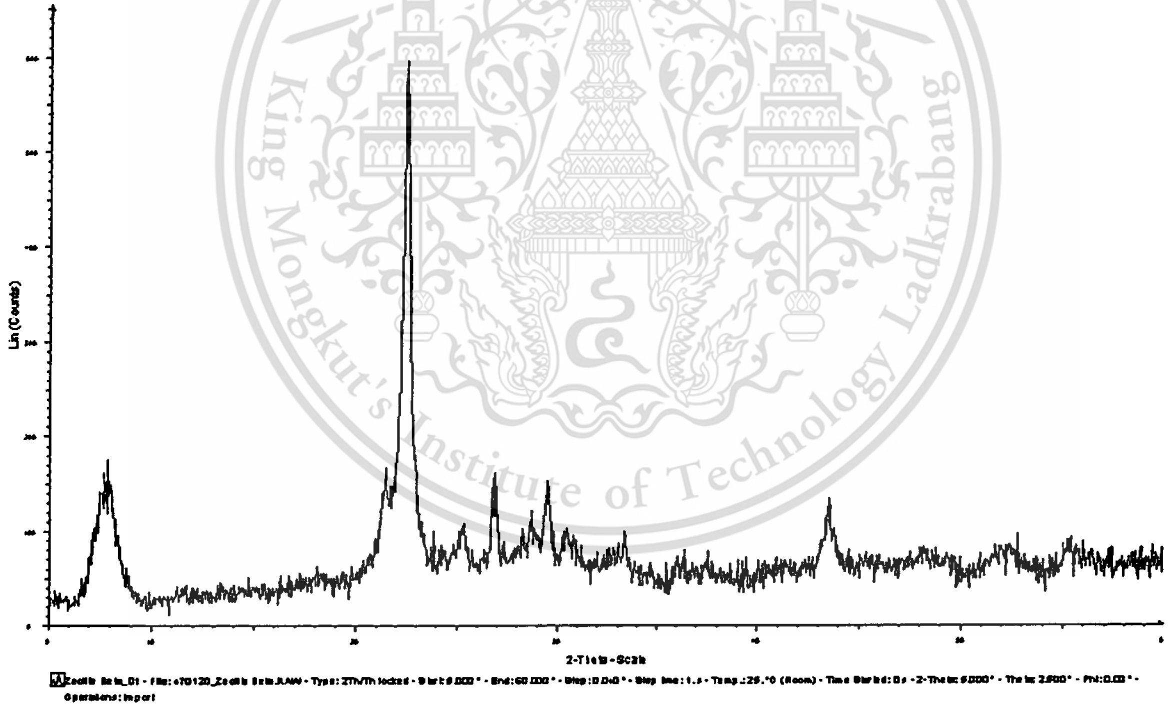


Figure 4.1 X-ray diffraction pattern of zeolite Beta

The X-ray diffraction pattern of zeolite Beta was compared to X-ray diffraction pattern of the standard zeolite Beta (Figure B.1). It revealed characteristic peaks at 2θ 7.68, 21.42, 22.50, 25.27, 26.93 and 29.51. The X-ray diffraction pattern was similar to the X-ray diffraction pattern of the standard Beta. These results confirmed that the used catalyst was zeolite Beta.

4.1.2 Determination of the crystal morphology of zeolite using SEM

The crystal of zeolite Beta used in this work was shown in Figure 4.2. The electron micrograph of zeolite Beta showed a spherical shape with small crystallite size approximately 0.2 μm in diameter. Therefore, it was expected that these zeolite would have high external surface area.

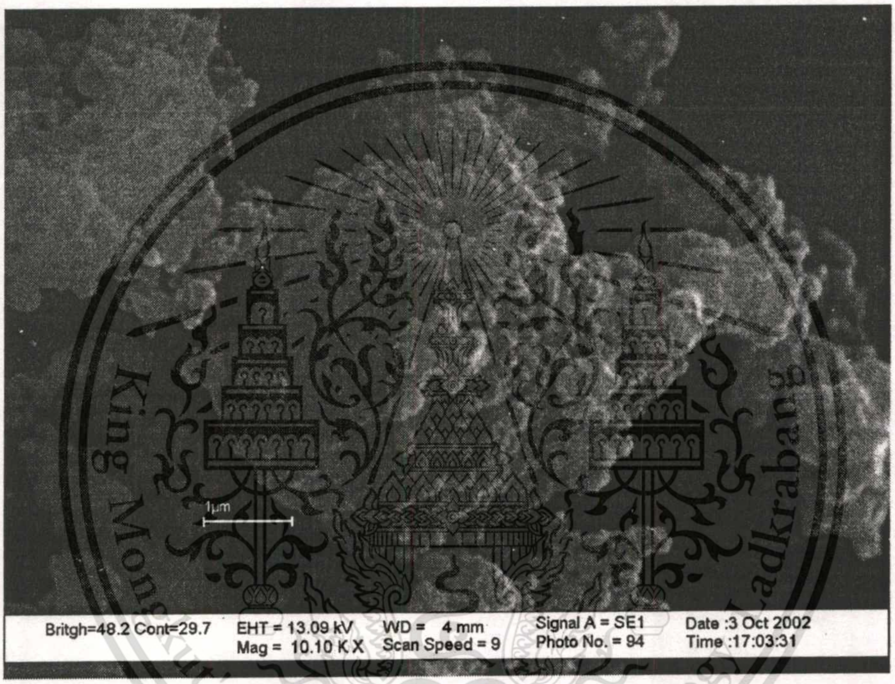


Figure 4.2 Scanning electron micrograph of the zeolite Beta

4.1.3 Determination of the surface area of zeolite using Gas Adsorption Analysis

The adsorption isotherm of nitrogen on zeolite sample was obtained using Autosorb-1C gas adsorption analyzer. The surface areas of zeolite Beta shown in Table 4.1 were determined by applying of the Brunauer-Emmet-Teller (BET) equation to the adsorption isotherm, which were measured at liquid nitrogen temperature.

Table 4.1 Crystal size, surface area, and Si/Al ratio of the zeolite

Catalyst	**Crystal size (μm)**	**BET area (m^2/g)**	**Si/Al ratio**
Zeolite Beta	0.2	644	12.84

4.1.4 Determination of the silicon/aluminium (Si/Al) ratio of zeolite using XRF

The silicon/aluminium (Si/Al) ratio of zeolite Beta was determined by SRS 3400 X-ray Fluorescence Spectroscopy as shown in Table 4.1. Zeolite Beta was classified as high silica sample (Si/Al =12.84). It was expected that these zeolites would possess a high thermal stability and acid strength.

4.1.5 Determination of melt flow index of polymer material using melt flow indexer

Melt flow index of polyethylene was obtained from CEAST 6841.000. Virgin polyethylene showed a high MFI (190^{O}C/2.16 kg) = 43.12 g/ 10 min as compared with that of waste polyethylene MFI (190^{O}C/2.16 kg) = 3.68 g/ 10 min. It was suggested that the waste polyethylene have somewhat higher molecular weight and degree of branching, as compared to the virgin.

4.1.6 Determination of polymer material heat of fusion and melting temperature using DSC

The heat of fusion of the virgin polyethylene (powder form) and waste polyethylene were obtained from Differential Scanning Calorimeter. The virgin polyethylene showed a high heat of fusion (62.89 J/g) as compared with that of waste polyethylene (38.27 J/g). The melting temperature of the virgin and the waste polyethylene is 102.8 ^{O}C and 101.3 ^{O}C, respectively. It is clear that both are low-density polyethylene.

4.2 Development and construction of reactor

From the problem found in previous work [35], the reactor unit was modified and employed for cracking of polyethylene in continuous process as shown in Figure 4.3. The modification has been made as follows:

1. A condenser (controlled at –5 °C) was added into the reactor unit which enhances the overall performance of the condensing system. The light cracked liquid products can be virtually collected.
2. A residue chamber was attached to the end of the reactor to prevent loss of cracked products.
3. The direction of rotating paddles was reversed to help driving molten polymer into the reactor.

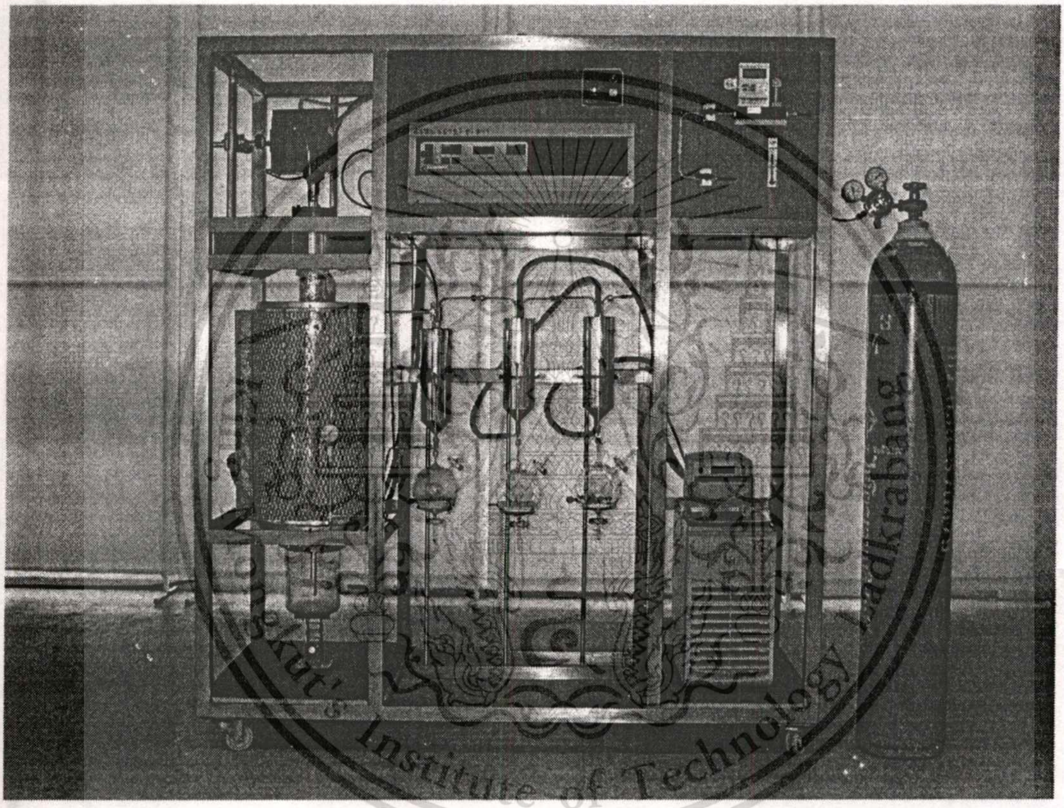


Figure 4.3 The developed reactor unit used in this work

4.3 Study on cracking of polyethylene using TGA

Thermogravimetric analysis was applied to investigate the decomposition of polyethylene. Virgin polyethylene was decomposed over zeolite Beta catalyst with different catalyst contents ranging from 0 to 10%. Thermograms of decomposition of polyethylene are shown in Figure 4.4. The initial degradation and degradation temperature of polyethylene are summarized in Table 4.2.

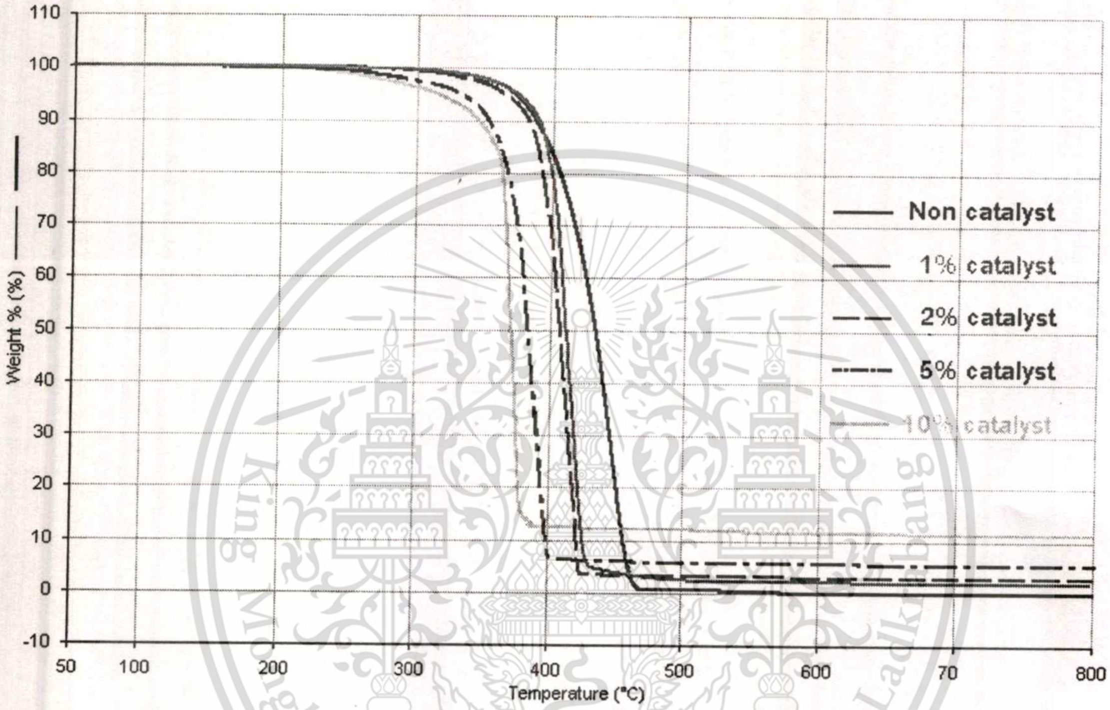


Figure 4.4 Thermogram curves of virgin polyethylene with different %catalyst contents as a function of temperature; heating rate, 10 ^{O}C/min; nitrogen, 50 ml/min

The results observed from TGA show that reaction using catalyst leads to lower decomposition temperatures (between 376-413 ^{O}C) as compared with a non-catalyst reaction (about 448 ^{O}C). The catalyst shifts degradation temperature towards lower temperature because the reaction proceed via carbocation intermediate, of which activation energy is reduced [4,30]. These results were in agreement with the fact that the catalytic cracking by strong acid catalysts could catalyze polyethylene into lighter hydrocarbons than the thermal cracking. Over the strong acid catalysts, the initial step of the degradation reaction is considered to occur by protonation of polyethylene chains. Successive β-scission of the main chain occurs to produce fragments containing lighter hydrocarbons. The braking of C-C bonds is also possible when polyethylene molecules are entering into the pores. Due to the fact that polyethylene are much larger than the pore size of zeolites, the catalytic degradation of polyethylene must be initiated on the external surface of zeolite particles. The acid sites located on the external surface of the zeolite crystal may also promote the initial steps of the polyethylene cracking to produce relatively small hydrocarbons [9,35,40]. These species can then diffuse into the pore of zeolite Beta and undergo further cracking to low molecular hydrocarbons in the pores. While, the thermal cracking required higher energies for cleavage of carbon-carbon and carbon-hydrogen bonds [26]. Since the crystal size of zeolite Beta is small, a high external surface area contributed to the catalytic activity can be expected. A large amount of acid sites, especially on the external surface, is essential to the fast degradation of polyethylene. In addition the small crystal size facilitates the fast diffusion of those hydrocarbon fragments to the acid sites within the zeolite pores. Fast diffusion of cracked product lead to the low extent of cracking hence, a high yield of liquid products is obtained. On the contrary, long residence of cracked products in the pores brings about a high yield of gas due to excessive further cracking. Therefore, rate of cracking can be improved for the small crystal [41].

Table 4.2 Degradation data of polyethylene with different types and %catalyst contents

Sample	% Catalyst content	Initial degradation temperature (°C)	Degradation temperature (°C)
PE	-	405	448
PE	1 %	392	413
PE	2 %	384	409
PE	5 %	367	388
PE	10 %	354	376
PE (waste)	-	394	434

The reaction using 10 % catalyst revealed a lower initial degradation temperature than that using only 5 % and without catalyst, respectively. It was seen clearly that the increase in the loading amount of the catalyst would increase the number of acid sites, which readily facilitate protonation and lead to rapid cracking of polyethylene.

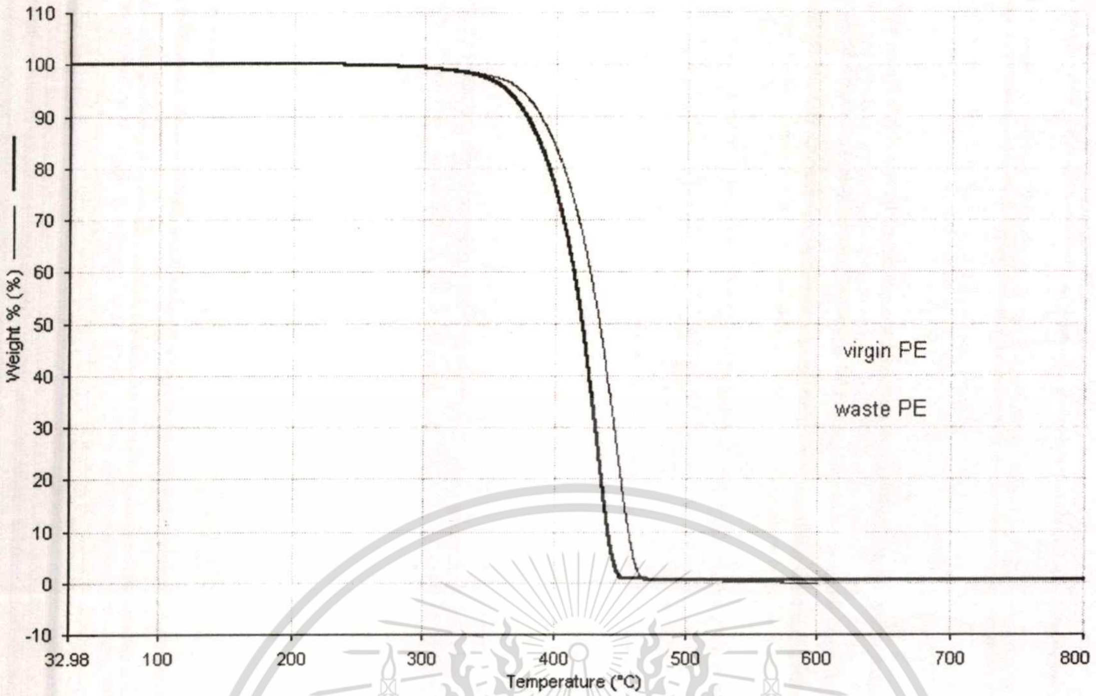


Figure 4.5 Thermogram curves of virgin and waste polyethylene without catalyst as a function of temperature; heating rate,10 °C/min; nitrogen, 50 ml/min

The thermograms from thermal cracking of polyethylene virgin and waste are shown in Figure 4.5 and the results are summarized in Table 4.2. Comparing the two types of polyethylene, the degradation temperature of the waste polyethylene (about 434°C) was lower than that of the virgin polyethylene (about 448°C). It was obvious that the degradation of the waste polyethylene was easier to than that of the virgin polyethylene. This is because waste polyethylene was primarily processed at high temperature. Therefore, it is less resistant to the thermal decomposition, as compared to the virgin polyethylene.

4.4 Study on cracking of polyethylene in continuous process

Cracking of polyethylene was investigated in a continuous system. The reaction is conducted using nitrogen as carrier gas with a flow rate of 50 ml/min at 430°C. Zeoite Beta was used as a catalyst for all experiments.

The cracked products are classified into 4 groups: gaseous product, light cracked liquid product (LCL), heavy cracked liquid product (HCL), and residue. The residue refers to the waxy material that are determined from the weight of the output material obtained from the bottom of reactor chamber, excluding the spent catalyst weight. The amount of liquid fraction was determined by the product obtained from the condensers. The conversion can be calculated as the fraction of the initial mass of polymer that converted to form gas and liquid products. The yield of liquid products was calculated as the mass of liquid collected divided by the initial mass of polymer. While yield of gas products was determined by subtracting the weight of all of liquids and residue from initial mass of polymer. In addition the selectivity of liquid product is the ratio of the mass of liquid product over the mass of all products obtained.

4.4.1 Reaction profile with time on stream

The catalytic cracking of virgin polyethylene was carried out at 430°C under nitrogen flow rate of 50 ml/min. The reaction was investigated with a constant polymer feeding rate, approximately 400 g/hr using 1%wt zeolite Beta as catalyst. The activity of thermal and catalytic cracking of polyethylene was plotted versus time on stream as shown in Figure 4.6. There was a clear difference between the products of thermal and catalytic cracking. The catalytic cracking give a markedly higher conversion to light hydrocarbons. This is because, in the catalytic cracking, the reaction can be explained by carbenium ion mechanism. In contrast, thermal cracking occurred via free radical intermediates. Therefore, the thermal cracking required a higher temperature for the reaction and, according to a random bond-breaking, light hydrocarbons with broad molecular weight distribution is particularly obtained in the free radical process.

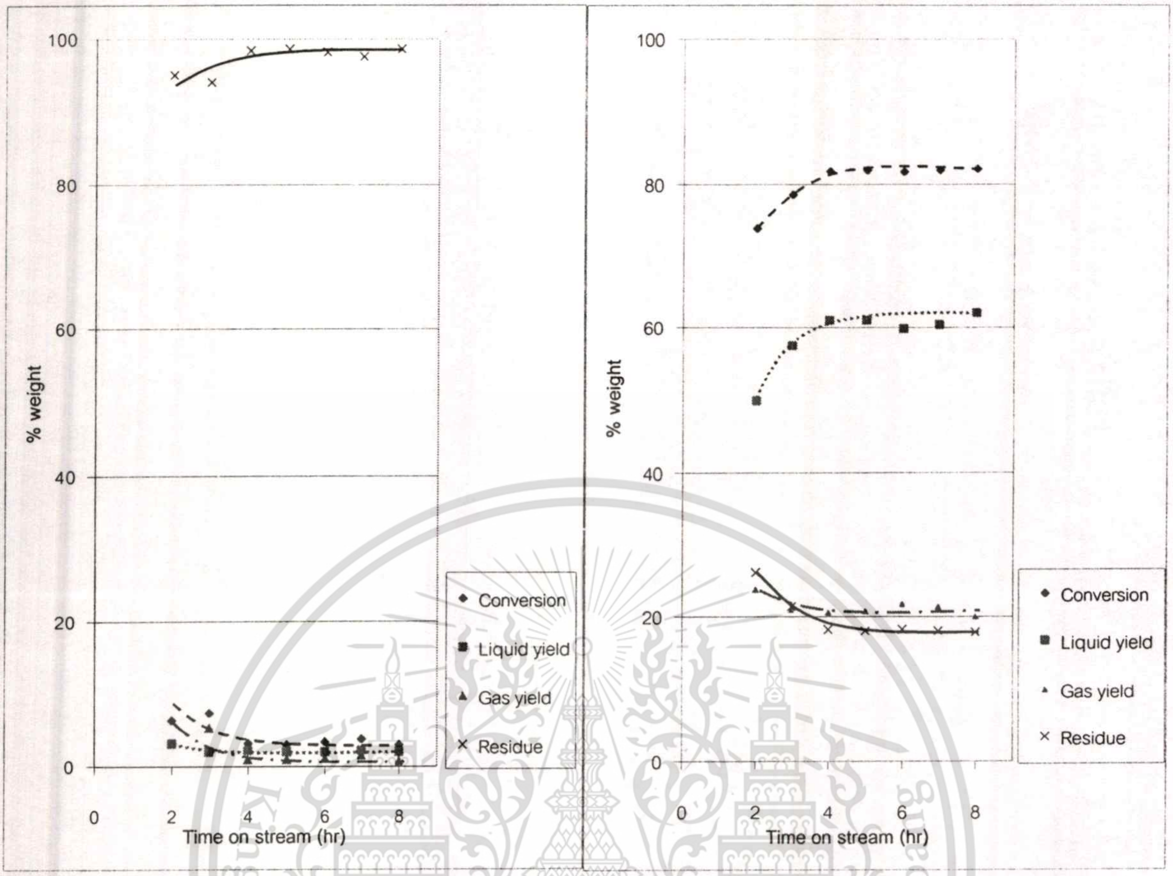


Figure 4.6 Conversion and yield from thermal and catalytic cracking of polyethylene as a function of time on stream; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; nitrogen 50 ml/min

In the catalytic cracking, it can be also noticed that yield of the residue and gas products at the start up were relatively high and gradually decreased to constant value with time on stream. On the other hand, yield of liquid products was low at the start up and slowly increased to a constant value after 4 hours on stream. This phenomenon indicated that the reaction approached a steady state after 4 hours. It can be explained that at the start up the polymer materials with absence of the catalyst still accumulated in the reactor. This is because prior to starting of each reaction, only polyethylene was fed for material balance testing at 350°C. Therefore, at the beginning of the reaction the catalyst content in the reactor was small but gradually increased to a certain content as the polymer/catalyst was continuously fed. Furthermore, after steady state, deactivation was not observed because the coking catalyst could be continuously removed and replaced by newly fed catalyst.

The carbon distribution of heavy cracked liquid products from catalytic cracking of polyethylene is shown in Figure 4.7. It can be seen that the product distribution was not significantly different after 4 hours. Therefore, the average value from 5 to 8 hours on stream will be used for the discussion.

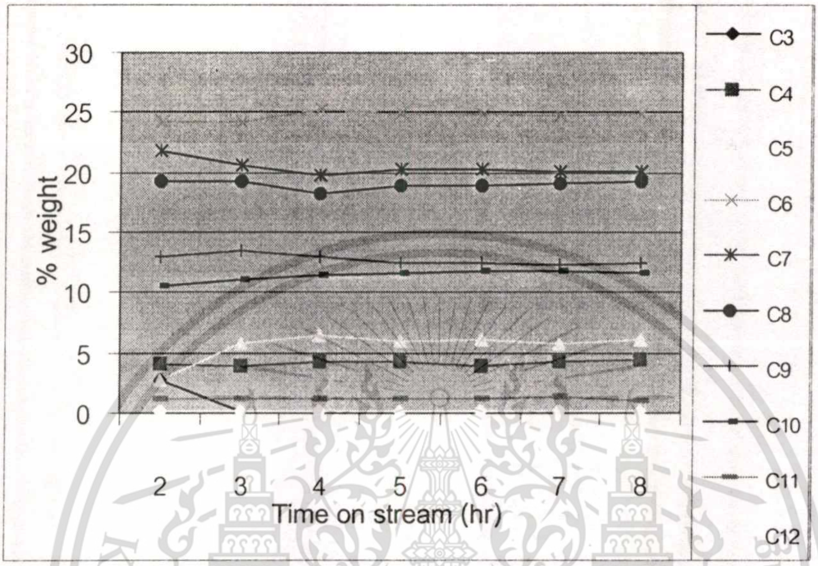


Figure 4.7 Composition of heavy cracked liquid products from catalytic cracking of polyethylene since 2^{nd} to 8^{th} hours; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen 50 ml/min

From Figure 4.8, the total carbon product from catalytic cracking of polyethylene was in a range of C_3-C_{12}. This result is interesting that major product obtained in catalytic cracking of polyethylene is similar to the carbon distribution of gasoline (C_5-C_{13}). This can be suggested that molecular weight of the product can be controlled by pore size of the catalyst. The zeolite Beta is a large pore zeolite which consists of two different pore sizes (0.55x0.55 and 0.64x0.76 nm). Since the reaction proceeded via carbocation intermediate within the restricted pore of zeolite, the products with certain molecular geometry and size can be obtained. Therefore, most of the products were liquid hydrocarbon (~70%) and some gaseous yield (~30%) was obtained. The gaseous product contained of C_2-C_6 hydrocarbon, which mostly consisted of C_3 and C_4. Whilst, the light and heavy cracked liquid products from cracking was obtained in range of C_4-C_{12} hydrocarbons.

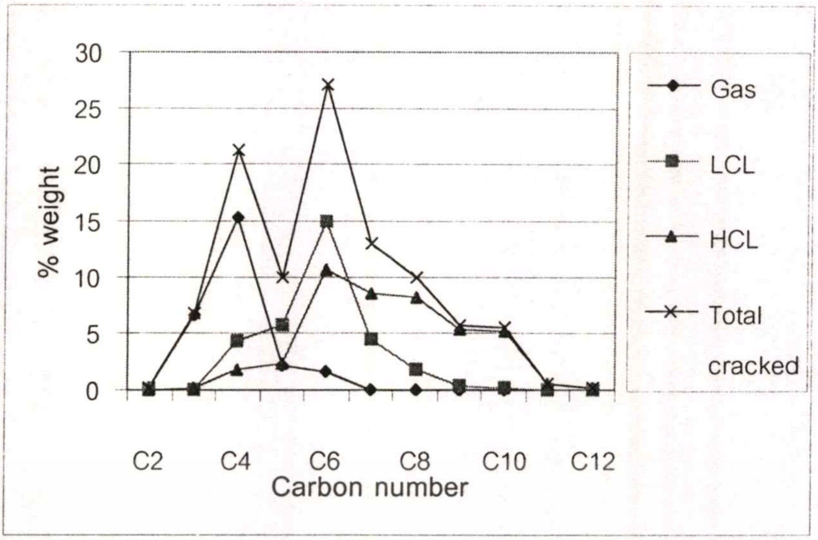


Figure 4.8 The product distribution from catalytic cracking at 8th hour; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen 50 ml/min

Catalytic degradation over acid catalyst proceeds via two possible pathways: (i) cracking at the end of the polymeric chains and (ii) random cleavage of the polymer molecules at any bonds in the chain. The first is responsible for the formation of C_2-C_5 products. Whereas, random cracking contributes the overall cracking process which lead mainly to middle distillates and waxy fractions. The primary products of the polyethylene cracking can be further cracked by secondary reactions forming gas and light liquid hydrocarbons. From the result, it can be seen that the high yield of C_6-C_7 hydrocarbons (~40%wt.) was obtained. This is probably due to the fact that pore of zeolite beta is fitted with the molecules of C_6-C_7 hydrocarbons. Detailed composition of heavy cracked liquid products was shown that in appendix D.

Gasoline selectivity of cracked products can be investigated from distillation characteristics using automatic distillation analyzer. The distillation data of light and heavy cracked liquid product and liquid product were compared to that of commercial gasoline (octane 91 and 95) as shown in Figure 4.9. Generally gasoline is boiled in the range of 25-185°C and it can be seen that most of the liquid products from catalytic cracking of polyethylene obtained are in gasoline fraction (~88 %vol). However, some of kerosene and diesel fraction (~22 %vol) are present in heavy cracked liquid products. Accordingly, yield and selectivity of gasoline can be calculated from distillation data.

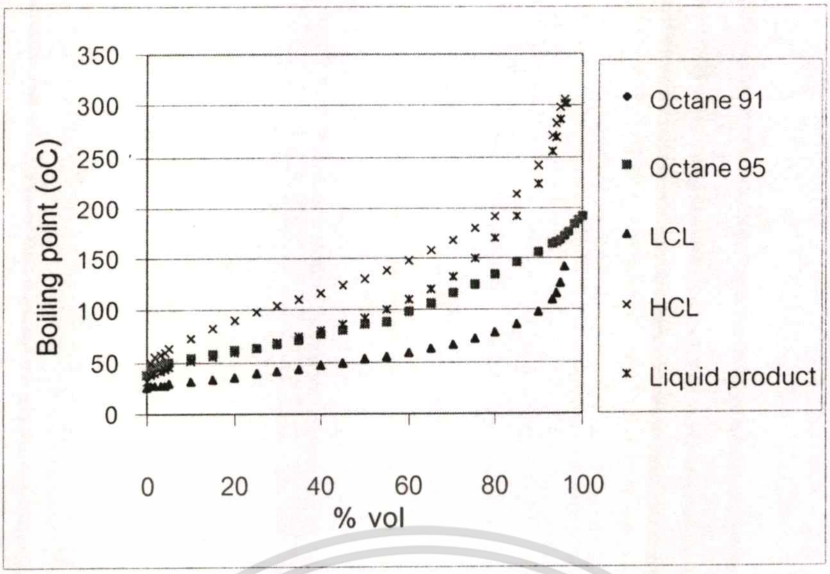


Figure 4.9 Distillation data of commercial gasoline and liquid products; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen 50 ml/min

Furthermore, products from the catalytic cracking of polyethylene over zeolite Beta showed high values of research octane number (RON) and motor octane number (MON) as shown in Figure 4.10. The RON and MON were used as an index of the quality of the liquid product. The higher of the octane number, the higher the efficiency for anti-knocking in benzine engine and the tendency for the liquid to burn evenly and completely [30]. One main indication of gasoline quality is the degree of branching in the paraffins, since the isoparaffins have much greater octane numbers than their normal counterparts. The high isoparaffin index causes high octane number products which was determined by a nuclear magnetic resonance (NMR) technique and calculated according to the method as shown in appendix F. It is because after initial formation of carbenium ions, tertiary carbenium ions can be readily formed by hydride abstraction at backbone sites where methyl groups are attached. In addition to that rearrangements from primary and secondary carbocations to be tertiary ones would be favored owing to the greater stability. Such phenomena lead to a large number of branch products. Heavy cracked products have high octane number as well as commercial gasoline. Moreover, it is interesting to remark that the light cracked liquid products possess an estimated very high octane number, which can be readily used for blending in a refinery gasoline pool to obtain a required octane level.

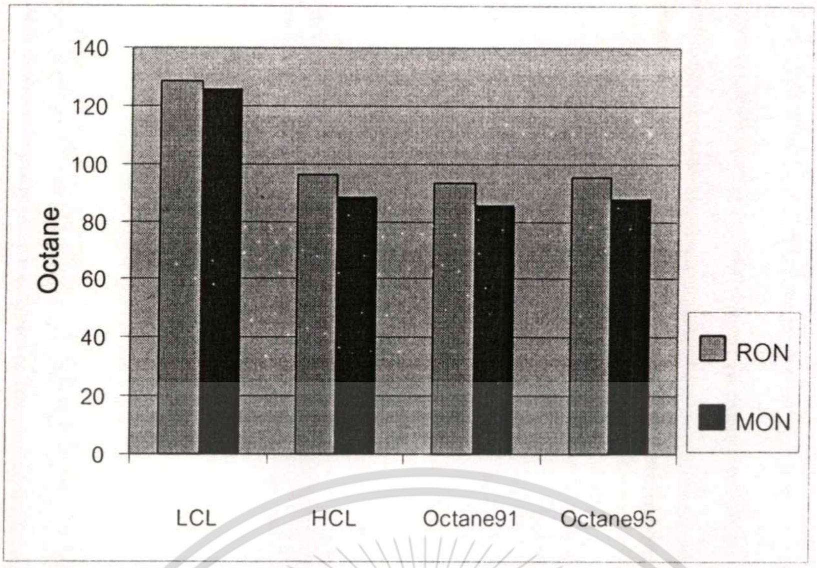


Figure 4.10 The Octane number of commercial gasoline and liquid products from cracking of polyethylene; reaction conditions: temperature, 430 °C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen 50 ml/min. (The result calculated average values from 5th to 8th hours)

The contents of paraffin, olefin and aromatics in liquid product obtained from catalytic cracking comparing with commercial gasolines were shown in Figure 4.11. It has been known that olefin productions are initially increased in most catalytic cracking because β-scission itself ends up with olefin or once followed by an elimination reaction leads to olefin formation. Paraffins are considered to be produced mainly by secondary reaction, with hydrogen transfer. Olefins, considered to be primary cracking products, are adsorbed on the zeolite framework undergoing hydrogen transfer reaction to paraffins and aromatics. For the heavy cracked liquid products (HCL, cooled at 40°C), the amount of aromatics was higher than that in the light cracked liquid products (LCL, cooled at -5°C). However, aromatic content of heavy and light cracked liquid products was much lower than that in the commercial gasolines. This is becoming more important due to the recently mandated reduction of aromatics content in the gasoline.

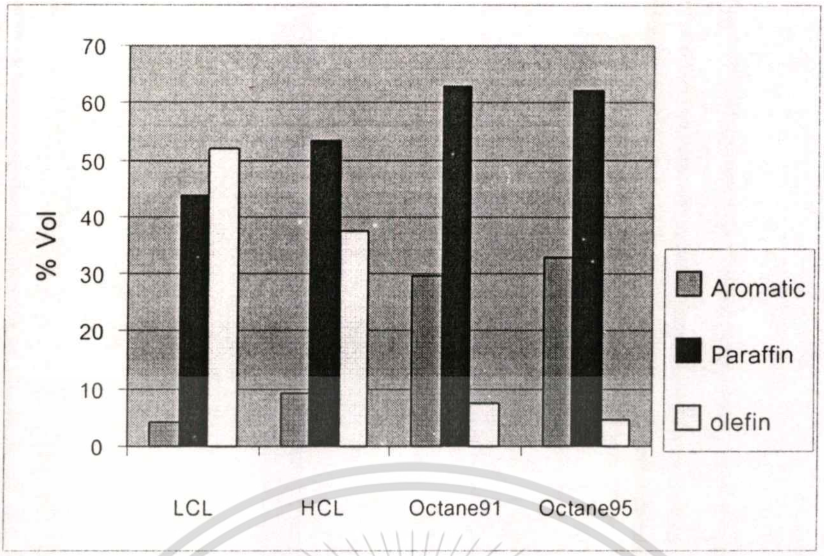


Figure 4.11 Hydrocarbon types of commercial gasoline and liquid products; reaction conditions: temperature,430 ^{O}C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen, 50 ml/min

(Octae 91 and 95 products obtained from Petroleum Authority of Thailand)

4.4.2 Effect of catalyst content

The effect of catalyst content on yield of products was investigated by the reactions using 0-5 % catalyst with a constant polymer feeding rate, approximately 120 g/hr at 430 ^{O}C. The steady state conversion and yield of products are shown in Figure 4.12. At this screw speed, it was found that the 100% conversion was obtained. The reaction using 1, 2 and 5 % catalyst contents produced similar amount of liquid (above 70 %wt.) and gaseous products (above 30 %wt.). Accordingly, the difference of the catalyst content could not be seen. Therefore, the effect of catalyst content was then studied at higher screw speed.

The effects of catalyst content over zeolite Beta were studied with 0.5, 1 and 2 %wt. catalysts using a constant polymer feeding rate, approximately 400 g/hr as shown in Figure 4.13. The results show that the increase in the loading amount of the catalyst increases the conversion and liquid yield of the reaction. This is because the loading amount of the catalyst is proportional to the number of acid sites and contact time. The catalyst would promote further cracking of wax materials, resulting in an increase in the yield of light products, particularity liquid fuel as shown in appendices C.7-C.9.

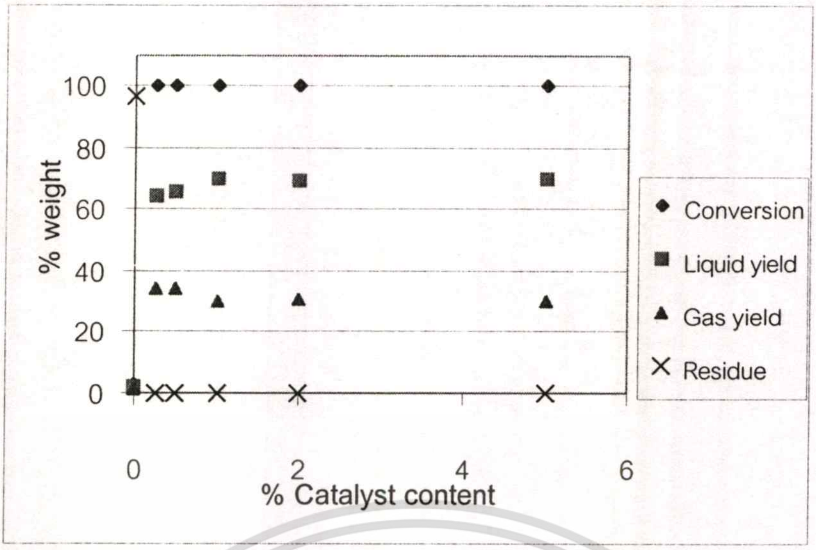


Figure 4.12 The average conversion and yield of products from cracking of polyethylene; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 0-5%; nitrogen, 50 ml/min

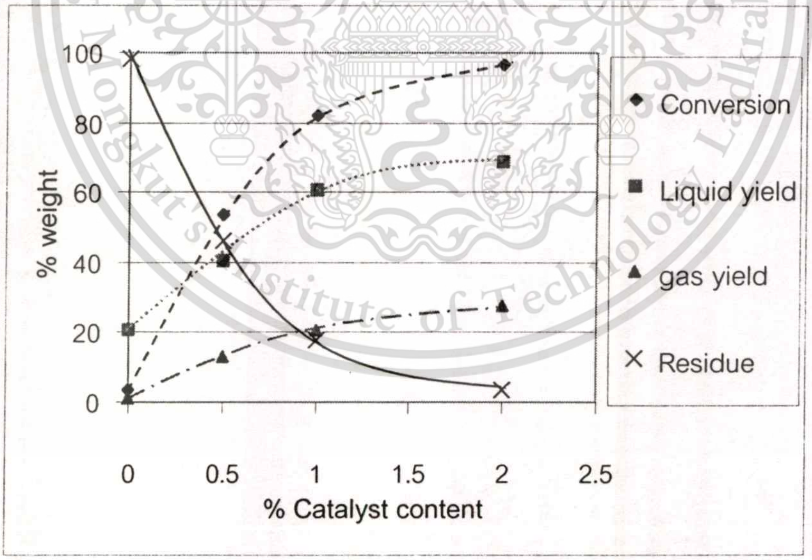


Figure 4.13 The average conversion and yield of products from cracking of polyethylene; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 0-2%; nitrogen, 50 ml/min

The product composition is a direct indication of the catalyst activity and selectivity. The carbon distribution of light and heavy liquid products are shown in Figure 4.14.

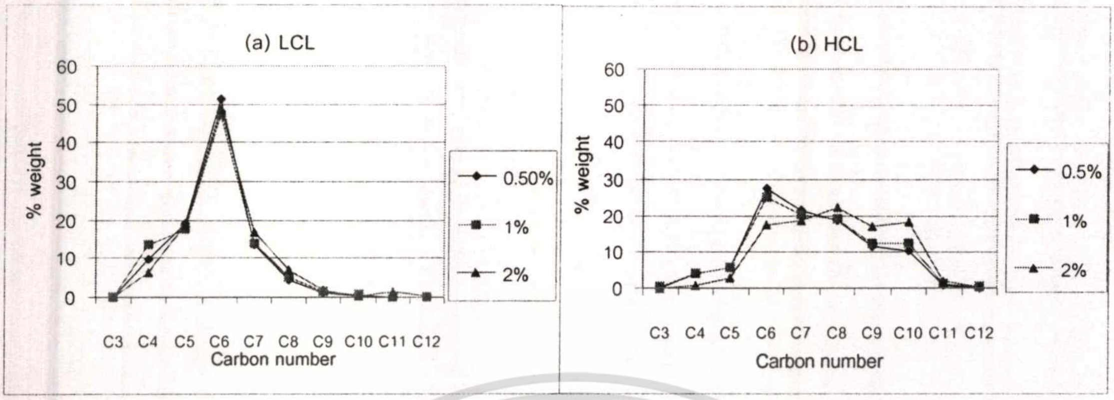


Figure 4.14 Product distribution of liquid product at different catalyst contents (a) light cracked liquid product (b) heavy cracked liquid product; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 0.5-2%; nitrogen, 50 ml/min

It can be observed that the composition of the light liquid products was not different. However, the carbon distribution of heavy liquid product is similar for 0.5 and 1%wt but markly shifts towards higher carbon number as the catalyst content increases to 2%wt. The increase in the composition of higher hydrocarbon with an increase in catalyst content is unusual. This is because the consecutive cracking in the zeolite pore should lead to a large amount of smaller hydrocarbon products. However, with 2 %wt loading of the catalyst, an increase in carbon number can be attributed from an increase in the active sites, so that enough to accelerate the disproportination of the hydrocarbon fragments. In such bimolecular reaction, C_5-C_7 components are converted over the zeolite Beta into C_8-C_{10} and C_3-C_4 which subsequently increased the gas products (Figure 4.13). The disproportination of cracked products can be illustrated as below:

$$C_5 + C_6 \xrightarrow{\text{Catalyst}} C_8 + C_3$$

$$C_6 + C_6 \xrightarrow{\text{Catalyst}} C_9 + C_3$$

$$C_7 + C_6 \xrightarrow{\text{Catalyst}} C_{10} + C_3$$

$$C_7 + C_7 \xrightarrow{\text{Catalyst}} C_{10} + C_4$$

In contrast, at 0.5 and 1 %wt catalyst, the total number of acid sites is relatively small. Rate of isomerisation which is a monomolecular reaction was readily facilitated, as compared to the disproportination. Therefore, the large pore zeolite Beta can control the product distribution in the range of liquids and disproportination does not occur.

The gasoline selectivity with different catalyst contents is shown in Figure 4.15. The loading of catalyst slightly affect to the liquid and gasoline selectivity. It is interesting to remark that the major product obtained in the catalytic cracking of polyethylene are the gasoline fraction with maximum selectivity close 90% at %1wt catalyst content. However, gasoline yield was increased with loading catalyst because of the enhanced conversion as discussed earlier. It was seen that liquid and gasoline selectivity decrease at 2% catalyst. This is because a longer contact time would promote a higher cracking rate of liquid products to gas products and also the disproportination to produce light and heavy hydrocarbons.

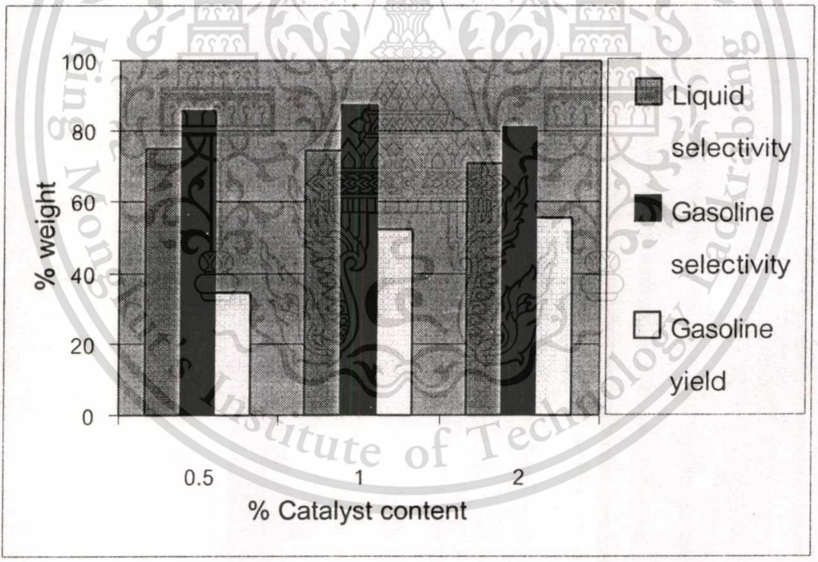


Figure 4.15 The selectivity of liquid product and gasoline fraction at different catalyst contents; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 0.5-2%; nitrogen, 50 ml/min

The contents of olefin, paraffin, and aromatics in the light and heavy cracked liquid products obtained from catalytic cracking over zeolite Beta for different catalyst contents is shown in Figure 4.16. It can be seen that the yield of olefin was decreased with an increase in catalyst loading. This is because a longer contact time would promote the secondary reaction for the cracked product, especially the hydrogen transfer, resulting in conversion of olefins to paraffins. Therefore, amount of paraffin was enhanced by high loading of catalyst [30,35].

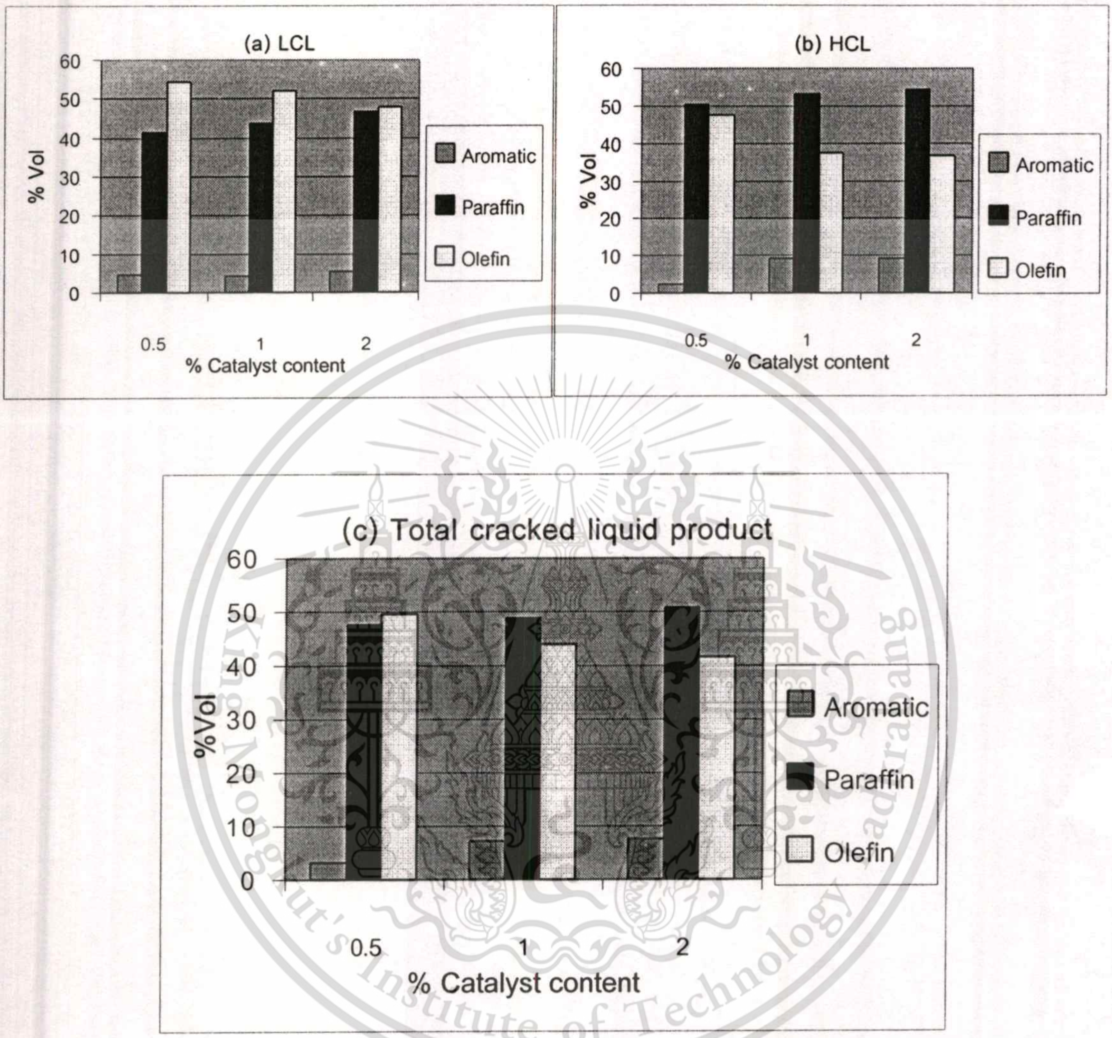


Figure 4.16 Hydrocarbon types of liquid products at different catalyst contents; (a) light cracked liquid product, (b) heavy cracked liquid product and (c) total cracked liquid product; reaction conditions; temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 0.5-2%; nitrogen, 50 ml/min

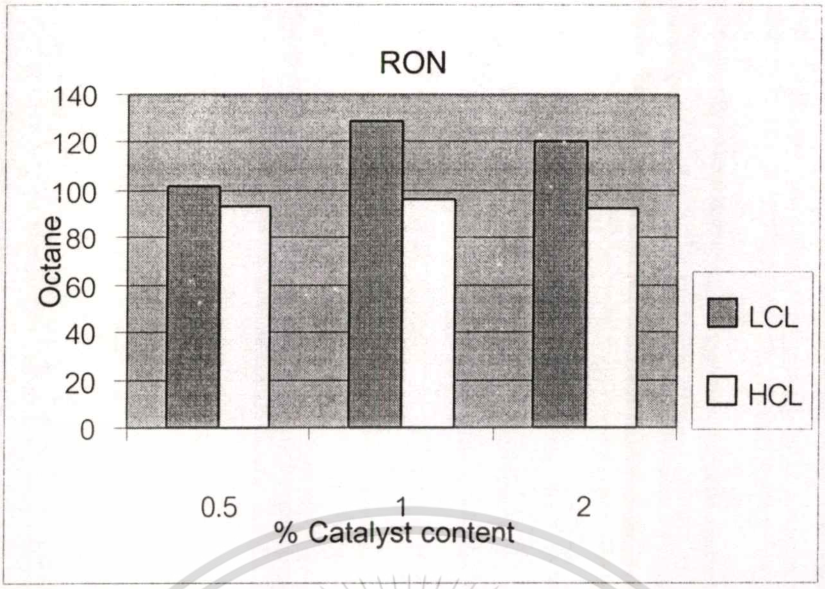


Figure 4.17 The Octane number of liquid product from catalytic cracking at different catalyst contents; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 0.5-2%; nitrogen, 50 ml/min

Figure 4.17 shows effect of catalytic cracking on the octane number of light and heavy cracked liquid products, which are determined by NMR analysis, compared with commercial gasoline. In order to olefin content, one main indication of gasoline quality is the degree of branching in the paraffins, since the iso-paraffins have much greater octane numbers than their normal counterparts. The octane number of light and heavy liquid products were increased with the catalyst loading. This is because isomerisation is largely promoted over acid catalyst. However, when the catalyst content was increased to 2 %wt., the octane number was then decreased. This was suggested that long contact time promote hydrogen transfer, resulting in low olefin content and hence octane number.

4.4.3 Effect of carrier gas flow rate

The effect of carrier gas flow rate on yield of products was investigated by the reactions using 10-100 ml/min of carrier gas flow rate at a constant polymer feeding rate, approximately 400 g/hr. The results are shown in Figure 4.18

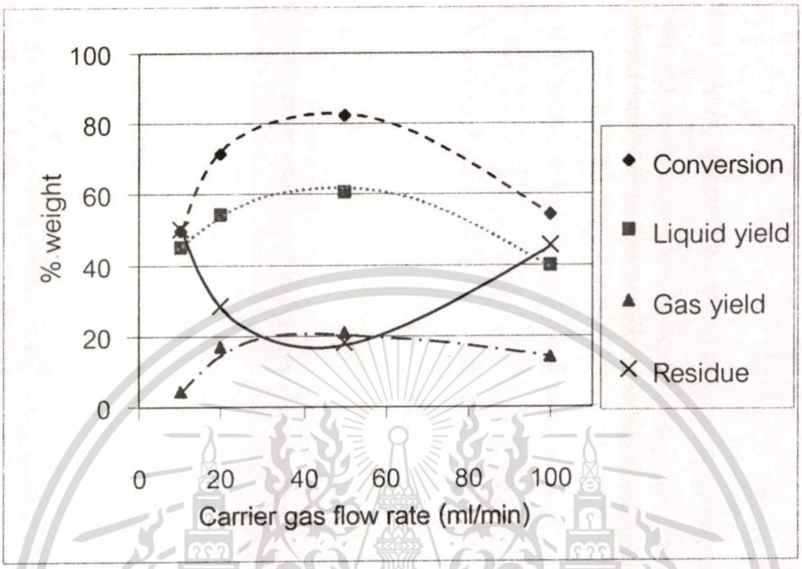


Figure 4.18 The average conversion and yield of products from cracking of polyethylene at different carrier gas flow rates; reaction conditions: temperature,430^{o}C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen, 10-100 ml/min

It was shown that using carrier gas flow rate of 10 ml/min gave low activity. This is because at lower carrier gas flow rate, a higher residence time can be expected. Therefore, oligomerisation of cracked hydrocarbons is readily promoted, forming high molecular weight products, which is referred to as residues. When carrier gas flow rate was increased (20 and 50 ml/min), conversion and liquid yield was increased because the cracked hydrocarbon can be driven out of reactor, leaving active acid site for further cracking. However, the catalytic cracking is known as endothermic reaction, increasing carrier gas flow rate to 100 ml/min can remove heat from the reactor. Hence, lower heat supply can result in a reduced conversion at such a high carrier gas flow rate. In addition, the cracked products are rapidly removed from the reactor. Thus the secondary cracking was suppressed, and, high yield of residue was obtained. It can be suggested that in this study the carrier gas flow rate of 50 ml/min give optimum conversion and liquid yield.

The carbon distribution of light and heavy liquid products with different carrier gas flow rate are shown in Figure 4.19.

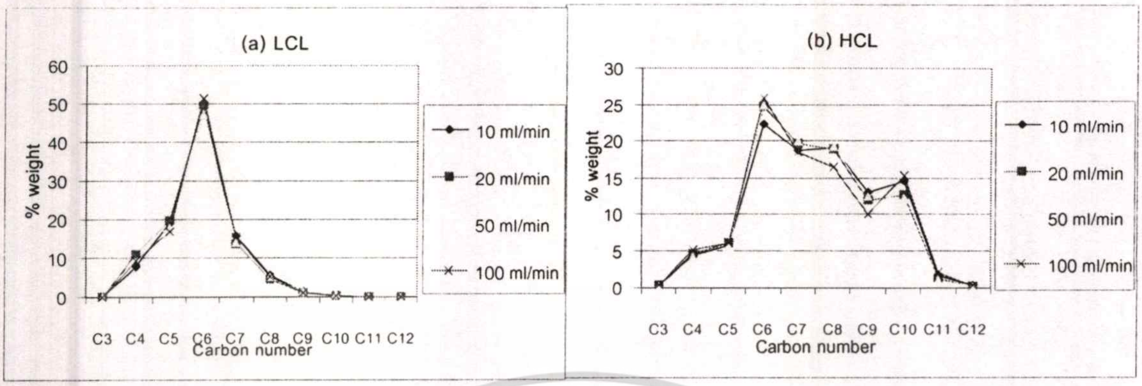


Figure 4.19 Product distribution of liquid product at different carrier gas flow rates (a) light cracked liquid product (b) heavy cracked liquid product ; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen, 10-100 ml/min

The liquid products remained in a narrow range of carbon number. Since the product distribution depends only on types of catalysts as discussed earlier in section 4.4.1. It seems that the product distribution slightly shifts towards higher carbon number with decreasing the carrier gas flow rate. This is because oligomerisation produces high molecular weight products as suggested.

Figure 4.20 shows the change in the gasoline selectivity with different of carrier gas flow rate. It can be seen that the liquid selectivity decreased with an increase in carrier gas flow rate. This is because using low carrier gas flow rate accelerated further oligomerisation of light molecular weight products that enhances yield of liquid product. The gasoline selectivity was increased with an increase in carrier gas flow rate because the oligomerisation was decreased, corresponding to higher amounts of small molecular weigh products in gasoline range. However, the gasoline yield also depends on the conversion as seen from Figures 4.18 and 4.20.

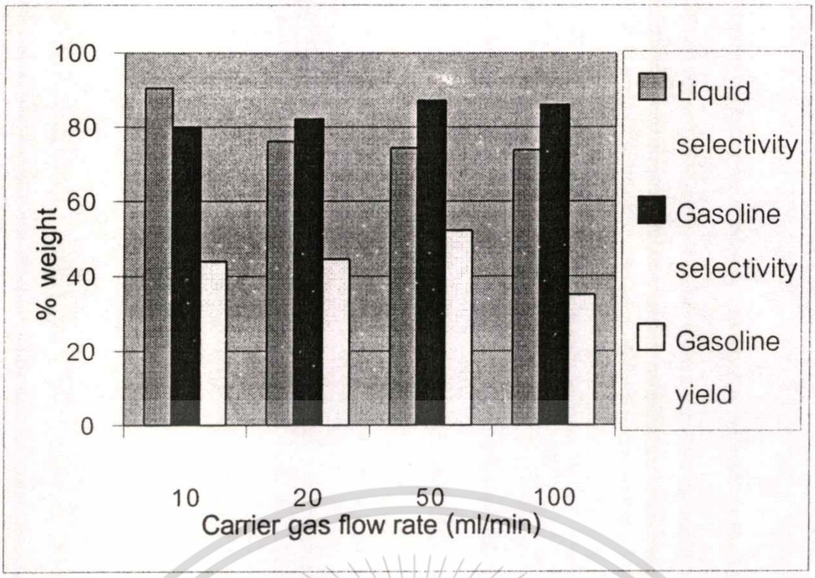


Figure 4.20 The selectivity of liquid product and gasoline fraction at different carrier gas flow rates; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen, 10-100 ml/min

The contents of olefin, paraffin, and aromatics in the liquid products obtained from catalytic cracking as shown in Figure 4.21. These results indicate that the rate of hydrogen transfer was decreased with an increase in carrier gas flow rate, resulting in higher amounts of olefins. This is because high residence time facilitate hydrogen transfer to produce paraffin from olefin product. Nevertheless, small amount of aromatics is obtained in low carrier gas flow rate. This may be because most of aromatic is present in residue.

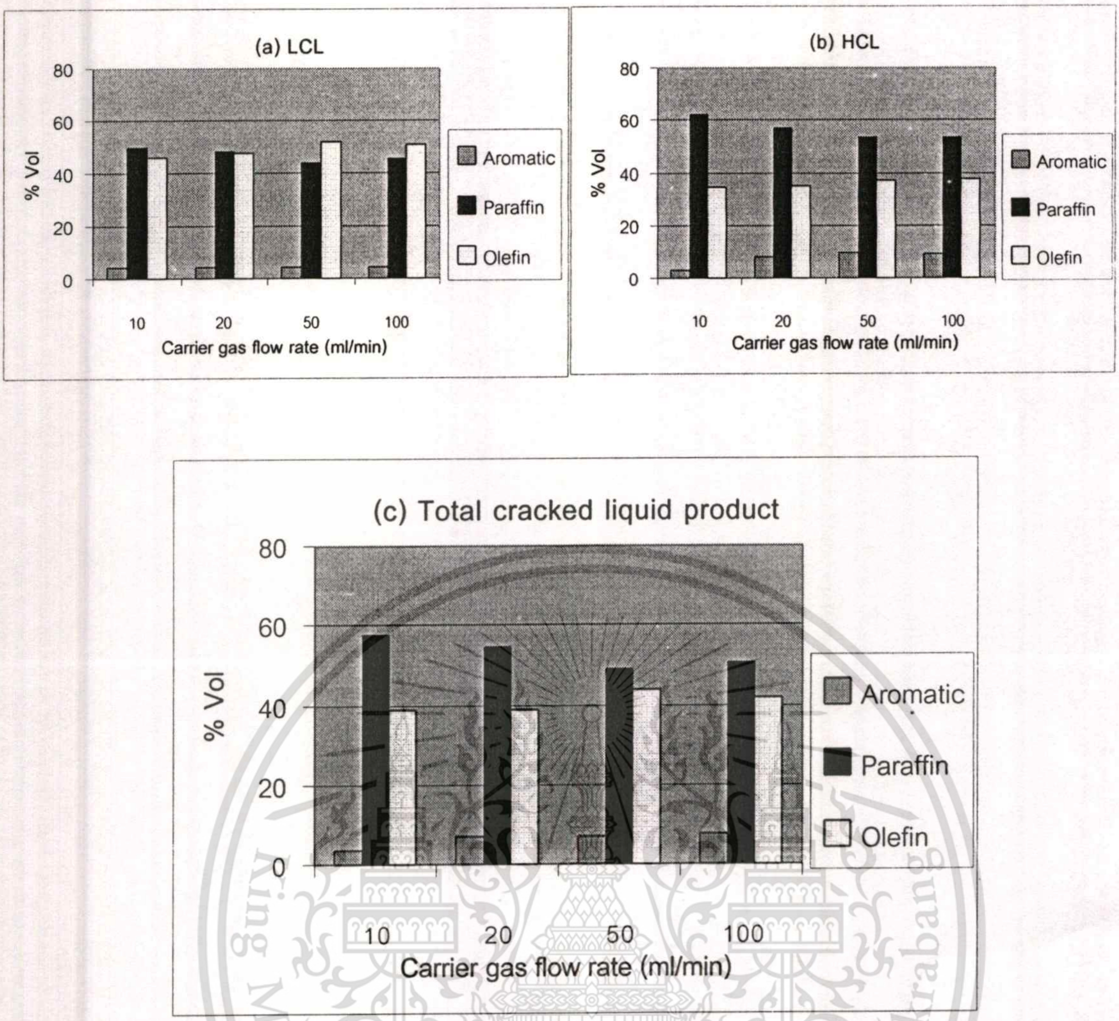


Figure 4.21 Hydrocarbon types of liquid products at different carrier gas flow rates (a) light cracked liquid product, (b) heavy cracked liquid product and (c) total cracked liquid product; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen, 10-100 ml/min

Figure 4.22 shows the effect of carrier gas flow rate on the octane number of liquid products. The octane value of light and heavy liquid products were increased with carrier gas flow rate. This is because hydrogen transfer has affect on amount of olefin in the liquid product as mentioned earlier.

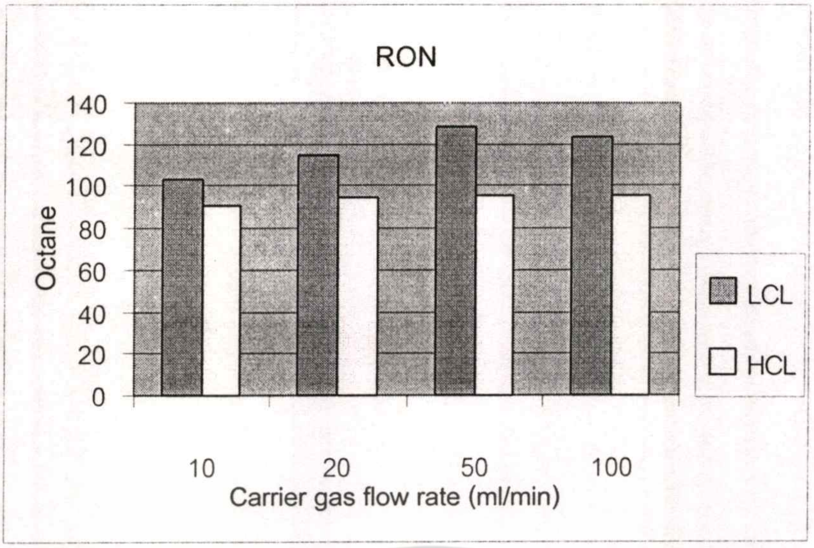


Figure 4.22 The Octane number of liquid product from catalytic cracking at different carrier gas flow rates; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen, 10-100 ml/min

4.4.4 Effect of polymer feeding rate

The effect of the polymer feeding rate on the yield of products were investigated by the reaction using 1% catalyst with approximate polymer feeding rate of 120-600 g/hr at 430 °C.

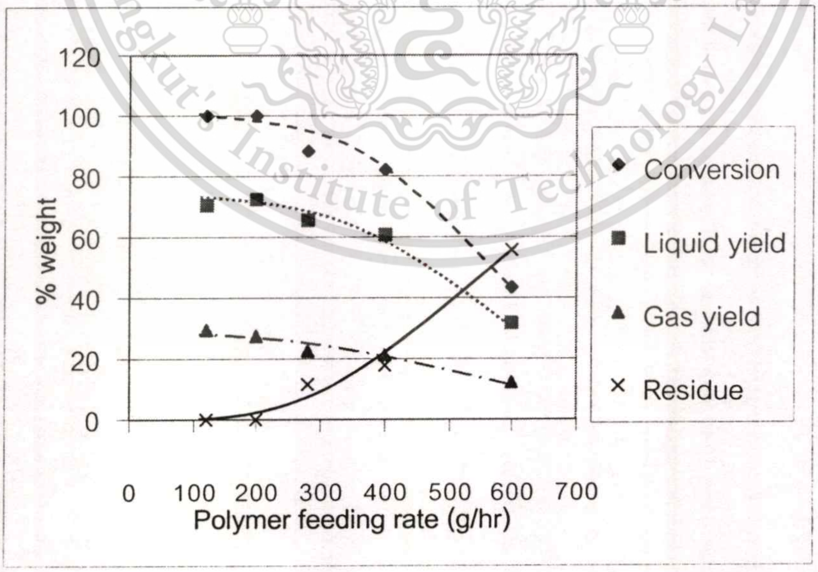


Figure 4.23 The average conversion and yield of products; reaction conditions: temperature, 430°C; polymer feeding rate, ~120-600 g/hr; catalyst content, 1%; nitrogen 50 ml/min

Increasing of screw speed decrease the residence time with a variation of the average product input from 120 to 600 g/hr. The conversion and yield of product are shown in Figure 4.23. The results show that longer residence times i.e. low screw speed, facilitates an extensive cracking providing an increase in the conversion and yield of liquid and gas products. However, 100% conversion cannot be applicable for this system, because the used catalyst must be removed by the residue from the bottom end of reactor. In the case of 100% conversion, used catalyst cannot be driven out of the reactor since no residues were obtained. For the case of continuous process, the operated conversion should be lower than 90%.

The carbon distribution of light and heavy liquid products with different polymer feeding rates are shown in Figure 4.24. It can be seen that change in the polymer feeding rate does not modify the product distribution. This is because the reactions proceed via similar pathways and the pore size of the catalyst plays essential role on product distribution as discussed earlier. This result indicates that only small amount of the catalyst (1%) can readily promote cracking reaction with narrow product distribution.

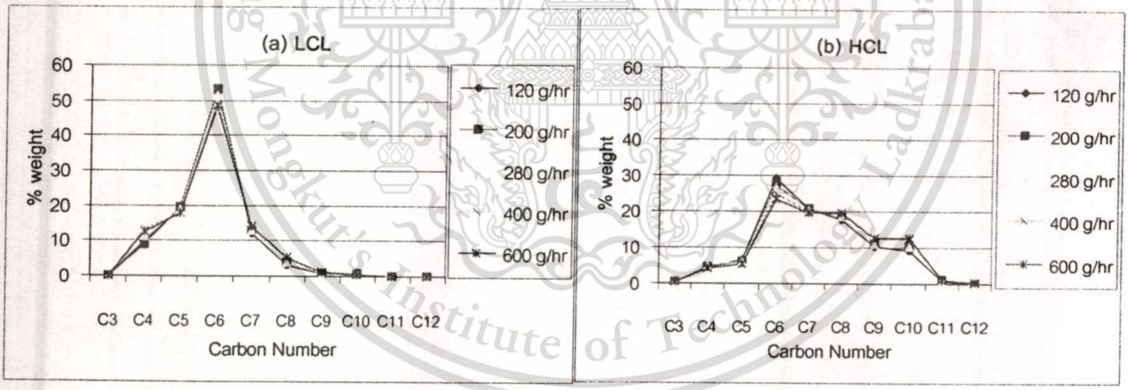


Figure 4.24 Product distribution of liquid product at different polymer feeding rates (a) light cracked liquid product (b) heavy cracked liquid product; reaction conditions : temperature, 430^{O}C; polymer feeding rate, ~120-600 g/hr; catalyst content, 1%; nitrogen, 50 ml/min

The gasoline selectivity with different of polymer feeding rates is shown in Figure 4.25. It is clear that increasing polymer feeding rate shall decrease residence times, which directly effects conversion and, hence, the amount of liquid products. Accordingly, yield of gasoline is proportionally decreased with an increase in polymer feeding rate. However, increasing polymer feeding rate does not effect gasoline selectivity because product distribution is virtually controlled by the catalyst pore size as suggested earlier. Although, the residence time is varied, only cracking activity is modified, no change in reaction pathway and selectivity can be observed. The liquid selectivity was increased from approximate polymer feeding rate of 280 to 400 g/hr. This is because long residence times would promote secondary cracking, resulting in increasing of gas product. In the case of high polymer feeding rate (~600 g/hr), the activity of the reaction was low, leading to a large amounts of heavy molecular weight in residue. This is because secondary cracking was slightly inhibited.

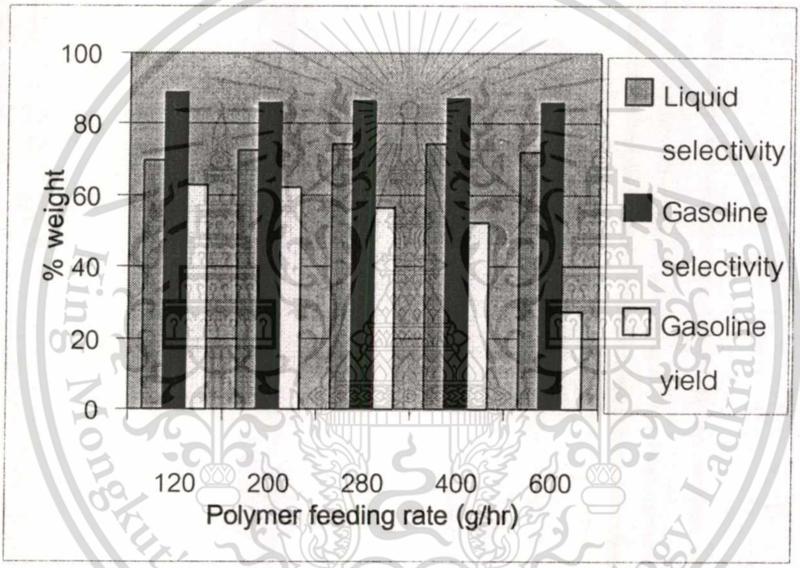


Figure 4.25 The selectivity of liquid product and gasoline fraction at different polymer feeding rates; reaction conditions: temperature, 430°C; polymer feeding rate, ~120-600 g/hr; catalyst content, 1%; nitrogen, 50 ml/min

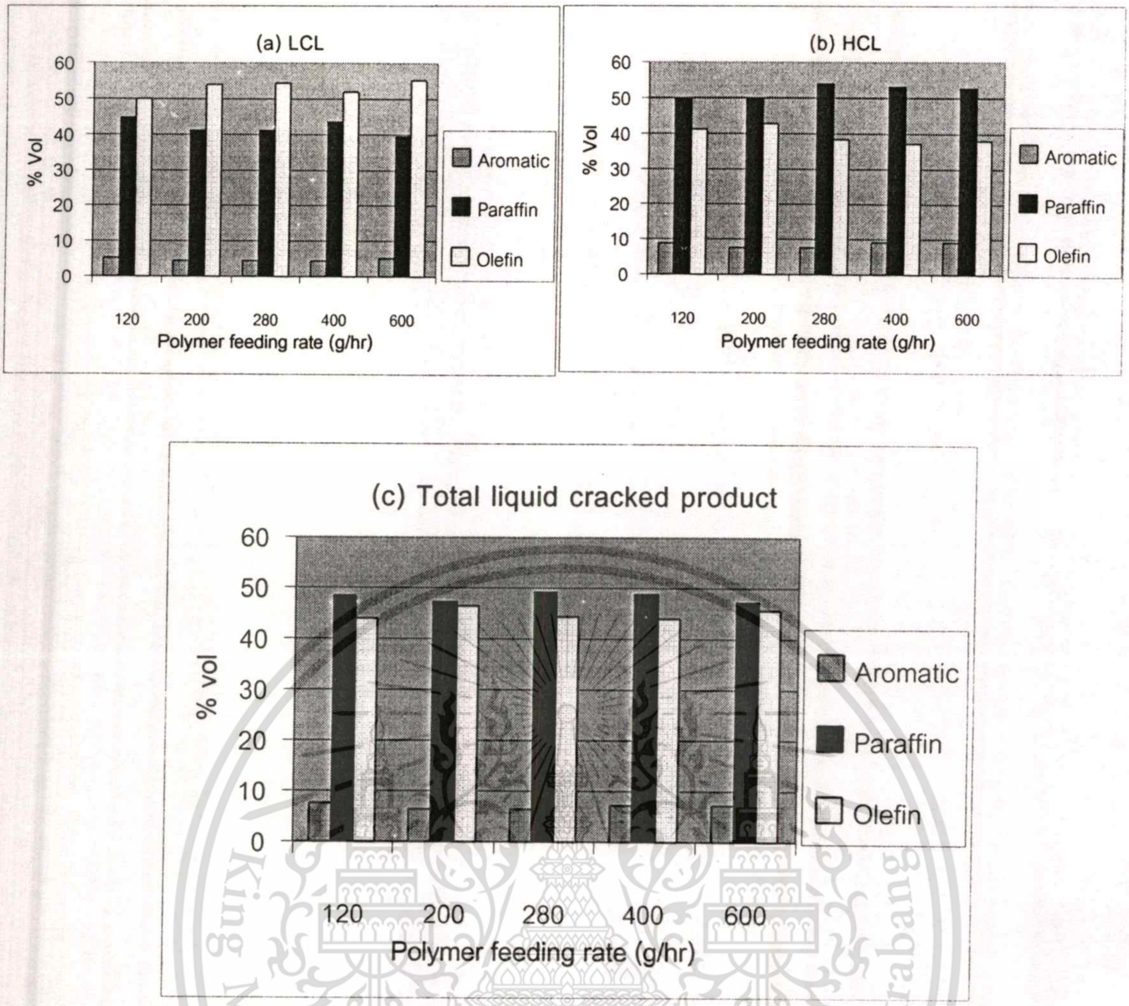


Figure 4.26 Hydrocarbon types of liquid products at different polymer feeding rates (a) light cracked liquid product, (b) heavy cracked liquid product and (c) total cracked liquid product; reaction conditions: temperature, 430°C; polymer feeding rate, ~120-600 g/hr; catalyst content, 1%; nitrogen, 50 ml/min

The contents of olefin, paraffin, and aromatics in the cracked liquid products with different polymer feeding rates are shown in Figure 4.26. It can be seen that the increasing of polymer feeding rate using the same catalyst content does not significantly modify the selectivity of olefin, paraffin and aromatic in liquid product. These results suggest that the hydrocarbon types can be largely influenced by catalyst content, rather than by the polymer feeding rate. This is because the catalyst determines pathway of the reaction. Nevertheless, the heavy cracked product contains higher amount of paraffinic hydrocarbons as compared to light cracked fraction, since hydrogen transfer was favorable over with high molecular weight of unsaturated cracked fragments.

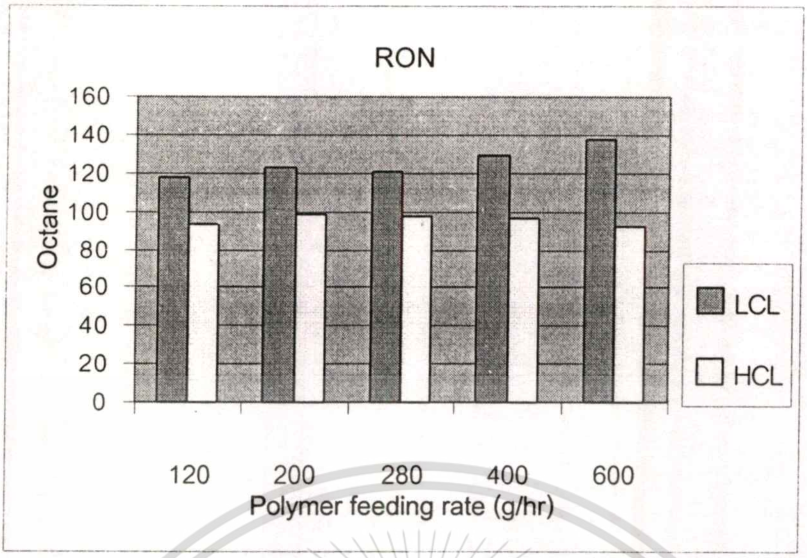


Figure 4.27 The Octane number of liquid product from catalytic cracking at different polymer feed rates; reaction conditions: temperature, 430°C; polymer feeding rate, ~120-600 g/hr; catalyst content, 1%; nitrogen, 50 ml/min

The effect of polymer feeding rate on the octane number of light and heavy cracked liquid products is shown in Figure 4.27. The light cracked liquid fraction has higher octane number than heavy fraction because it was consisted of small hydrocarbon molecules and high olefinic compounds. When polymer feeding rate was increased, more olefins were produced in light fraction which corresponded to the higher octane number. The octane number of light and heavy cracked fraction appears to depend upon the olefin content.

4.5 Study on cracking of waste polyethylene in continuous process

The yield of products from catalytic cracking of the waste polyethylene compared to the virgin polyethylene was investigated with 1 %wt. catalyst content. The nitrogen flow rate of 50 ml/min was used as a carrier gas with a constant polymer feed rate, approximately 400 g/hr at 430 °C. The result is shown in Figure 4.28.

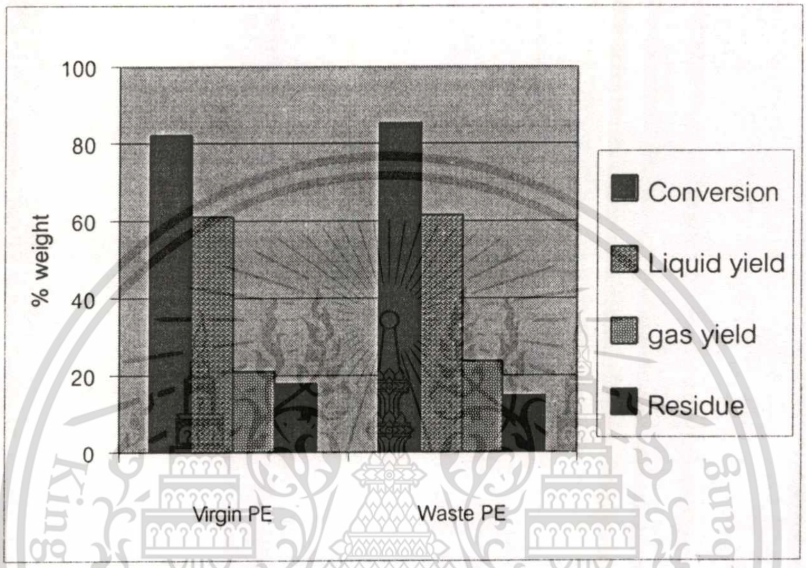


Figure 4.28 The average conversion and yield of products from catalytic cracking of virgin and waste polyethylene; reaction conditions: temperature,430 °C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen 50 ml/min

It was seen that cracking of waste polyethylene, primarily processed at high temperature, given higher conversion as compared to that of virgin polyethylene. These results suggested that the waste polyethylene may contain relatively higher unsaturation and branching on the polymer backbone which is evident by a higher melt flow index as compared to that of the virgin. Furthermore, the waste polyethylene required lower temperature for degradation, as confirmed by TGA (section 4.3). Therefore the waste polyethylene was easily cracked, leading to a higher gas yield and a lower residue yield as compared to the virgin polyethylene.

The carbon distribution of light and heavy cracked liquid products from catalytic cracking of waste polyethylene compared to virgin polyethylene shown in Figure 4.29.

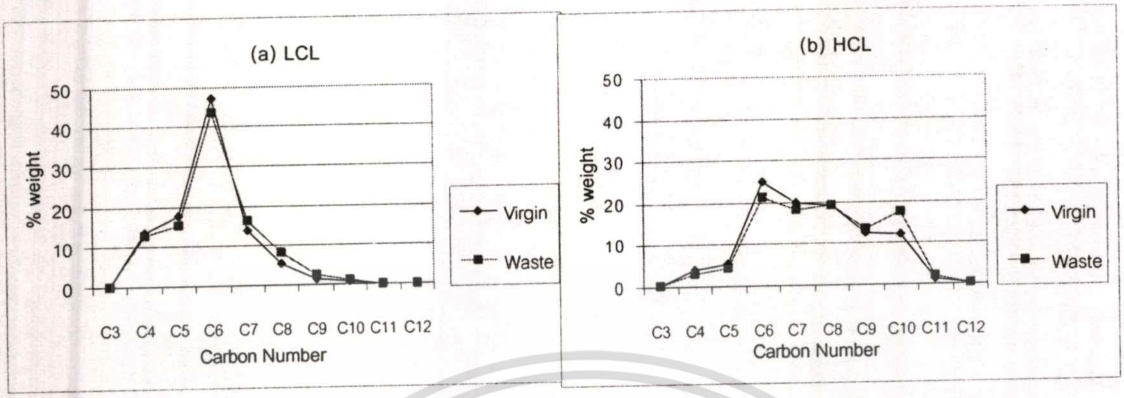


Figure 4.29 Product distribution of liquid product from catalytic cracking of waste and virgin polyethylene (a) light cracked liquid product (b) heavy cracked liquid product; reaction conditions : temperature, 430^{o}C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen, 50 ml/min

It was observed that higher molecular weight of liquid cracked product was obtained from cracking of the waste polyethylene. As mentioned earlier, waste polyethylene was easily cracked and its residue can be converted to high molecular weight products. Although different types of polyethylene were used as feed for catalytic cracking, the catalyst can control the product distribution in gasoline range.

The liquid selectivity of the virgin polyethylene was only slightly higher (~74 %wt.) than that of the waste polyethylene (~72 %wt.) as shown in Figure 4.30. Although a high conversion was obtained from catalytic cracking of waste polyethylene, gasoline yield was lower than that of the virgin polyethylene. These are because catalytic cracking of the waste polyethylene produce higher amounts of gaseous products than that of the virgin. However, the gasoline selectivity for the waste polyethylene was lower than that for the virgin because the heavy cracked liquid fraction composed of higher molecular weight hydrocarbon as discussed earlier. This leads to an out range distillation characteristic of the gasoline for the liquid products obtained from catalytic cracking of the waste polyethylene. Nevertheless, the liquid products from the catalytic cracking using developed continuous reactor provide gasoline fraction with high selectivity (> 80 %).

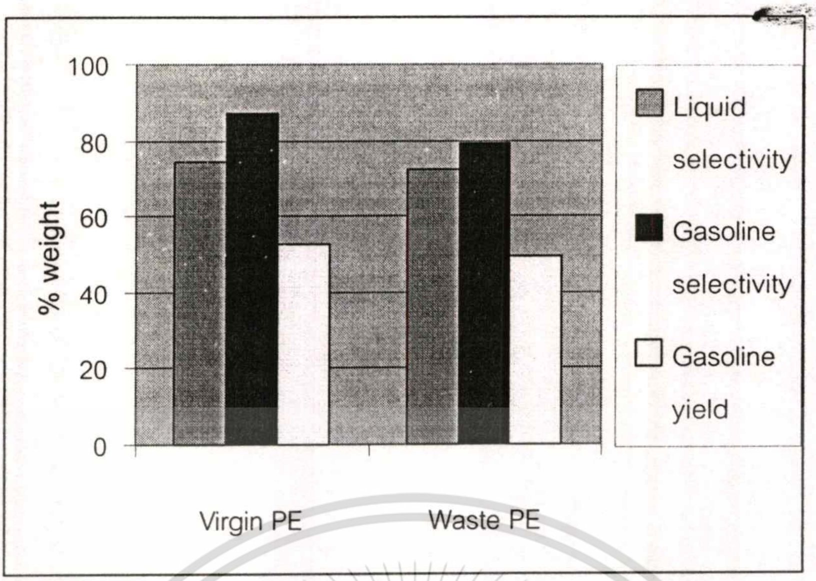


Figure 4.30 The selectivity of liquid product and gasoline fraction from catalytic cracking of waste and virgin polyethylene; reaction conditions: temperature, 430°C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen, 50 ml/min

Figure 4.31 shows the contents of olefin, paraffin, and aromatics in the liquid products from catalytic cracking of the waste polyethylene compared to the virgin polyethylene. It was seen that paraffin content from catalytic cracking of the virgin polyethylene was lower than that of the waste, while a higher olefin content was obtained. This is because the hydrogen transfer is facilitated over the cracking of unsaturated and branched hydrocarbons which is relatively abundance in the waste polyethylene.

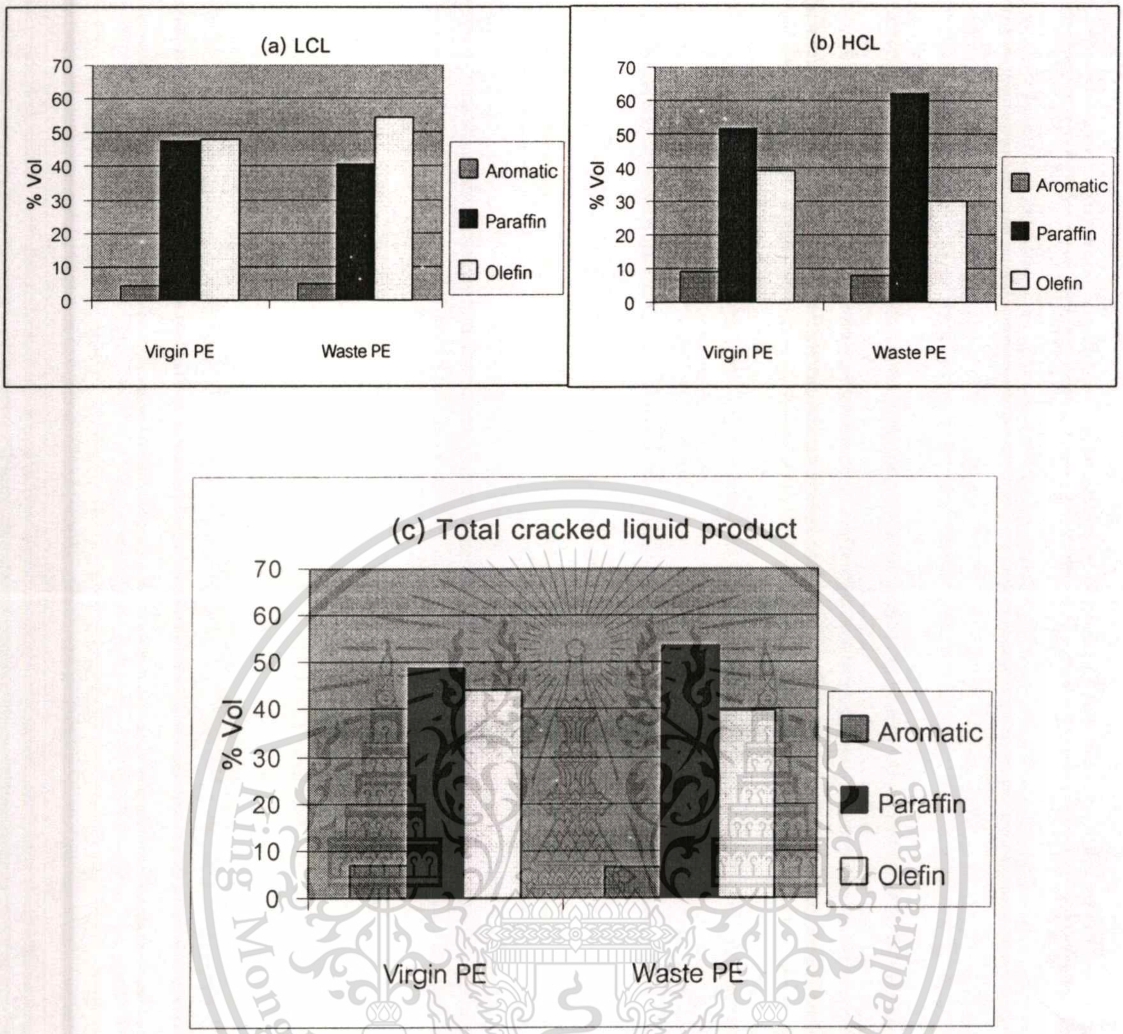


Figure 4.31 Hydrocarbon types of liquid products from catalytic cracking of waste and virgin polyethylene (a) light cracked liquid product, (b) heavy cracked liquid product and (c) total cracked liquid product; reaction conditions: temperature, 430°C; polymer feeding rate,~400 g/hr; catalyst content, 1 %; nitrogen, 50 ml/min

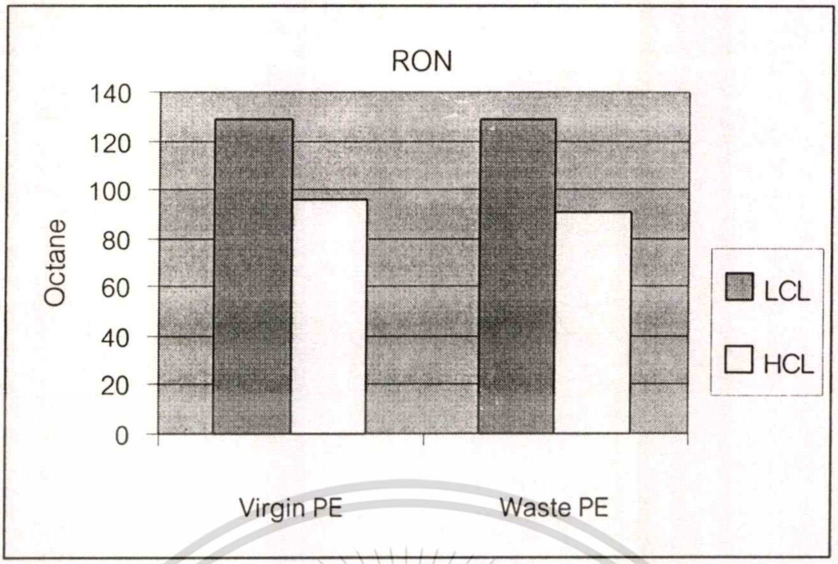


Figure 4.32 The Octane number of liquid product from catalytic cracking of waste and virgin polyethylene ; reaction conditions: temperature, 430^{O}C; polymer feeding rate, ~400 g/hr; catalyst content, 1%; nitrogen, 50 ml/min

Comparing the two types of polyethylene, the octane number of liquid products was not significantly different as shown in Figure 4.32. However, the octane number of heavy cracked liquid product from the waste polyethylene is slightly lower than that from the virgin due to a slightly higher content of heavier molecular weight hydrocarbons, as discussed earlier.

CHAPTER 5

CONCLUSIONS AND SUGGESTION

5.1 Conclusions

The designed reactor in this thesis can be used for continuous cracking of polyethylene. The polymer melt was continuously fed into the top of the reactor, whilst the residue was driven out of the reactor at the bottom end, together with the spent catalyst. This was collected by a residue chamber in a close system. Nitrogen gas can be used to carry the volatile products out of the reactor into a series of condensers. Catalytic cracking of polyethylene yielded mostly liquid products ranging from 40 to 72.5 %wt. The yield of gaseous products was approximately 4-35 %wt. The reaction approached a steady state after 4 hours on stream. Catalytic cracking with an approximate polymer feed of 200-600 g/hr can be readily operated in this system. From TGA, zeolite Beta shows excellent catalytic properties for cracking of polyethylene leading to a decrease in cracking temperature. This process is so efficient that only small amounts of catalyst loading (0.5-2 %wt.) can provide high activity and selectivity.

The reaction activity can be increased with increases in catalyst content and residence time. The higher catalyst contents also promote disproportination of the hydrocarbon fragments leading to higher gas products and large amounts of high molecular weight hydrocarbons in liquid products. Therefore, liquid and gasoline selectivity is decreased with an increase in catalyst content.

The rate of hydrogen transfer determines product selectivity. The hydrogen transfer can be promoted by higher catalyst content and residence time leading to an increase in the paraffin content in liquid products. Increasing carrier gas flow rate can decrease residence times, hence it directly effects rate of hydrogen transfer. However increasing residence time by reducing polymer feed rate does not significantly modify the selectivity of olefins, paraffins and aromatics.

The carrier gas flow rate indeed influences on the reaction activity. High carrier gas flow rate can reduce the reactor temperature resulting in a decreased activity. In addition, low carrier gas flow rate can facilitate oligomerisation of cracked hydrocarbons which reduces amounts of light cracked products.

It is interesting that the liquid products obtained from catalytic cracking of polyethylene are distributed in a narrow range of gasoline fraction (80-90 %wt.). The carbon distribution of the products can be controlled by the pore size of the catalyst. The gasoline products from the investigation were found to be more environmental friendly due to small aromatic content (3-7 %wt.), as compared to that of the commercial gasoline (30-33 %wt.). The liquid products show high octane number as well as the commercial gasoline. The octane number depends on olefin content which is varied by the rate of hydrogen transfer, secondary cracking and disproportination. The high octane products can be readily used for blending in a refinery gasoline pool to obtain a required octane level.

Cracking of waste polyethylene can be easily promoted in this system, leading to a higher gas yield, as compared to that from the virgin polyethylene. The hydrogen transfer can be largely facilitated in waste polyethylene corresponding to an observed higher paraffin content. However, the heavy cracked liquid product composed of higher molecular weight hydrocarbons resulting in a lower gasoline selectivity and products with relatively lower octane number.

The optimum operating conditions for highly selective production of gasoline from this study are shown as follows;

Optimum operating condition			Out put (from average 7-8 hours on stream)		
Feeding material	: Waste polyethylene		Conversion	: 89.0	%g/g polymer
MFI	: 3.68	g/10 min	Gas yield	: 25.2	%g/g polymer
Catalyst content	: 1	%wt.	Liquid yield	: 63.6	%g/g polymer
Polymer feeding rate	: ~400	g/hr	Residue yield	: 11.2	%g/g polymer
Carrier gas	: N_2		Liquid selectivity	: 72.2	%g/g product
Flow rate	: 50	ml/min	Gasoline yield	: 49.7	%g/g polymer
Temperature	: 430	°C	Gasoline selectivity	: 79.1	%g/g liquid product
Stir speed	: 50	rpm	Paraffin content	: 53.6	%vol.
Condenser 1, 2, 3	: ~ 40, -5, -5	°C	Olefin content	: 39.9	%vol.
Extruder			Aromatic content	: 6.6	%vol.
Temperature	:100, 150, 200, 220	°C	RON	: 105.0	
(Feeding, Metering, Transition, Die zone)			MON	: 98.6	
			IBP	: 24.5	°C
			FBP	: 337.2	°C

5.2 Suggestion for future studies

1. In this thesis, the high quality gasoline in liquid products can be obtained from catalytic cracking in continuous process. This process should be scaled up to a pilot plant for a study on effective cost and possibility for commercial. Additionally, the outlet gas stream should be simultaneously used for heat recovery to promote energy conservation and minimize the emissions.

2. Since the remaining half of the waste plastic generated from household is in the forms of plastic mixtures, a mixture of waste plastics, particularly the hydrocarbon polyolefin should be investigated to minimize separation cost for waste plastics in the future study.

3. In the study on polymer with high viscosity, the mixing speed of paddle cannot be controlled due to high torque of the viscous polymer melt. Particularly, the effect of stirring speed should be investigated when a high torque motor is equipped.

4. Catalyst deactivation is also an important indication for the catalyst performance in cracking reaction. Therefore, a study on coke and deactivation behavior should be carried out. This can be accomplished by recycling the catalyst without regeneration. However, in order to attain a benefit for solid catalyst, the catalyst regeneration should also be studied.

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APPENDICES

APPENDIX A

Calculation of the catalytic activity

Conversion

The conversion of product can be calculated as the fraction of the initial mass of polymer reacted to form gas and liquid products. It can be expressed as the following.

$$\%\ \text{Conversion} = \frac{\text{Initial mass of polymer} - \text{Mass of residue}}{\text{Initial mass of polymer}} \times 100$$

Liquid yield

The yield of liquid products was calculated as the mass of liquid collected divided by the initial amount of polymer. It can be expressed as the following.

$$\%\ \text{Yield of liquid product} = \frac{\text{Mass of liquid product}}{\text{Initial mass of polymer}} \times 100$$

Gas yield

The yield of gas products was determined by subtracting the weight of all of liquids and residue. Yield of gas can be defined by the relation.;

$$\text{Gas (wt\%)} = 100 - [\ \text{LCL (wt\%)} + \text{HCL (wt\%)} + \text{residue (wt\%)}\ ]$$

Selectivity

The selectivity of liquid product is the ratio of mass of polymer that converted to liquid product over mass of polymer that converted to all of products. It can be expressed as the following.

$$\%\ \text{Selectivity of liquid product} = \frac{\%\ \text{Yield of the liquid product}}{\%\ \text{Conversion of the product}} \times 100$$

APPENDIX B

X-RAY DIFFRACTION OF STANDARD PATTERN

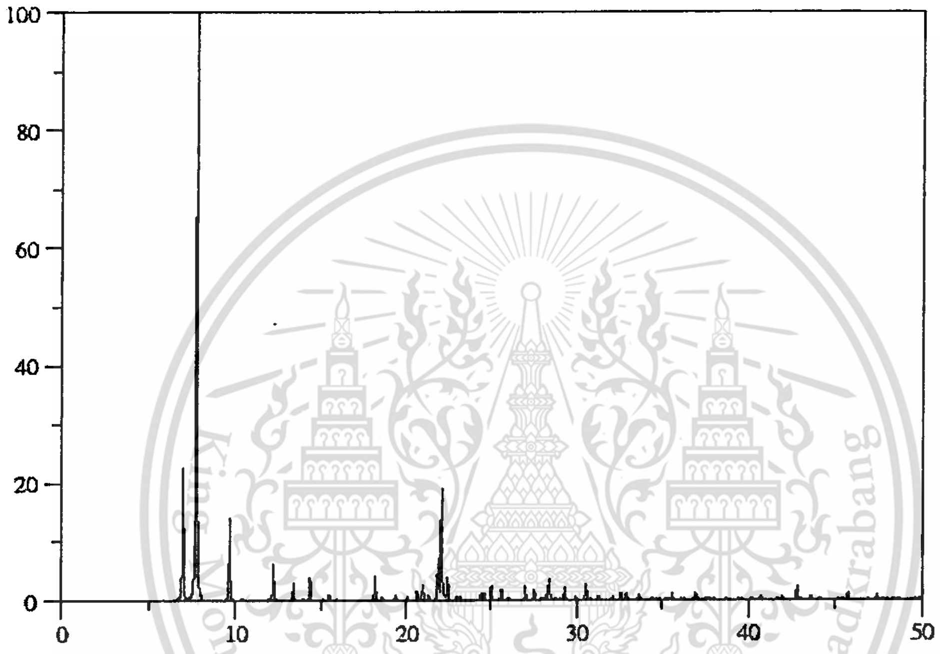


Figure B.1 X-ray diffraction pattern of standard Beta

APPENDIX C

REACTION DATA

Table C.1 Yield, selectivity and properties of products form cracking of polyethylene at 430 °C under nitrogen flow

Reaction			Time (hours)							Total		LCL	HCL
Condition			**2**	**3**	**4**	**5**	**6**	**7**	**8**	average*	Aromatic content	-	4.22
Virgin PE	LCL	%	-	-	-	-	-	-	-	-	RON***	-	82.87
Catalyst	HCL	%	3.16	2.00	2.17	2.03	2.06	2.18	2.07	2.08	MON***	-	73.72
0 (%w/w)	Liquid yield		3.16	2.00	2.17	2.03	2.06	2.18	2.07	2.08	IBP****	-	-
Feed rate	Gas yield		3.22	5.41	0.99	0.91	1.25	1.63	0.84	1.16	FBP****	-	-
116 g/hr	Residue yield		95.08	94.03	98.35	98.57	98.20	97.69	98.60	98.27	Liquid selectivity	64.90	
Gas flow rate	Conversion		6.38	7.41	3.16	2.94	3.31	3.81	2.91	3.24	Gasoline selectivity**	-	
50 ml/min	Density (HCL)		-	-	-	-	-	-	-	-	Gasoline yield	-	
											%Catalyst*****	-	

* The result calculated average values from 4th to 8th hour

** The result calculated from gasoline in total liquid product

*** The result calculated from NMR analysis

**** The result obtained from Automatic distillation analyzer

***** The used catalyst obtained from the bottom reactor at 8th hour

Table C.2 Yield, selectivity, and properties of products form cracking of polyethylene at 430 ^{o}C under nitrogen flow

Reaction			**Time (hours)**							**Total**		**LCL**	**HCL**
Condition			**2**	**3**	**4**	**5**	**6**	**7**	**8**	**average***	Aromatic content	5.49	7.11
Virgin PE	LCL	%	8.35	9.59	11.24	12.86	12.12	9.80	8.29	10.77	RON***	104.30	90.14
Catalyst	HCL	%	53.30	56.04	58.21	57.20	55.50	53.69	57.11	55.87	MON***	97.77	81.83
0.25 (%w/w)	Liquid yield		61.65	65.63	69.45	70.06	67.62	63.49	65.40	66.64	IBP****	27.8	35.5
Feed rate	Gas yield		38.30	38.30	30.55	29.94	32.38	36.51	34.60	33.36	FBP****	126.8	317.9
121 g/hr	Residue yield		0.05	0	0	0	0	0	0	0	Liquid selectivity	66.64	
Gas flow rate	Conversion		99.95	100	100	100	100	100	100	100	Gasoline selectivity**	78.78	
50 ml/min	Density (HCL)		0.727	0.725	0.728	0.731	0.732	0.732	0.730	0.731	Gasoline yield	51.56	
											%Catalyst*****	30.6	

Table C.3 Yield, selectivity, and properties of products form cracking of polyethylene at 430 ^{o}C under nitrogen flow

Reaction			Time (hours)							Total		**LCL**	**HCL**
Condition			**2**	**3**	**4**	**5**	**6**	**7**	**8**	average*	Aromatic content	4.89	7.60
Virgin PE	LCL	%	8.35	9.59	11.24	12.86	12.12	9.80	8.29	13.63	RON***	104.25	91.37
Catalyst	HCL	%	53.30	56.04	58.21	57.20	55.50	53.69	57.11	51.65	MON***	97.73	83.20
0.5 (%w/w)	Liquid yield		61.65	65.63	69.45	70.06	67.62	63.49	65.40	65.28	IBP****	26.1	30.6
Feed rate	Gas yield		38.30	38.30	30.55	29.94	32.38	36.51	34.60	34.72	FBP****	119.3	316.6
124 g/hr	Residue yield		6.67	0	0	0	0	0	0	0	Liquid selectivity	65.28	
Gas flow rate	Conversion		93.33	100	100	100	100	100	100	100	Gasoline selectivity**	85.51	
50 ml/min	Density (HCL)		0.723	0.720	0.720	0.721	0.722	0.723	0.724	0.723	Gasoline yield	56.14	
											%Catalyst*****	72.2	

Table C.4 Yield, selectivity, and properties of products form cracking of polyethylene at 430 ^{o}C under nitrogen flow

Reaction Condition			Time (hours)							Total		LCL	HCL
			2	3	4	5	6	7	8	average*	Aromatic content	5.36	8.62
Virgin PE	LCL	%	23.42	23.46	20.51	20.44	20.52	19.00	18.25	19.55	RON***	117.82	93.77
Catalyst	HCL	%	51.05	49.80	50.96	49.31	50.45	51.24	50.85	50.46	MON***	112.97	85.88
1 (%w/w)	Liquid yield		74.47	73.26	71.47	69.75	70.97	70.24	69.1	70.01	IBP****	26.8	34.2
Feed rate	Gas yield		25.29	26.74	28.54	30.25	29.03	29.76	30.90	29.99	FBP****	119.4	297.4
124 g/hr	Residue yield		0.24	0	0	0	0	0	0	0	Liquid selectivity	70.01	
Gas flow rate	Conversion		99.76	100	100	100	100	100	100	100	Gasoline selectivity**	89.21	
50 ml/min	Density (HCL)		0.726	0.726	0.722	0.723	0.722	0.724	0.722	0.723	Gasoline yield	62.74	
											%Catalyst*****	76.8	

Table C.5 Yield, selectivity, and properties of products form cracking of polyethylene at 430 ^{o}C under nitrogen flow

Reaction Condition			Time (hours)							Total		LCL	HCL
			2	3	4	5	6	7	8	average*	Aromatic content	3.99	9.64
Virgin PE	LCL	%	43.96	32.08	26.10	25.62	24.76	20.70	21.18	23.06	RON***	103.39	93.44
Catalyst	HCL	%	53.47	50.74	43.16	42.78	44.98	47.45	48.64	45.97	MON***	96.78	85.49
2 (%w/w)	Liquid yield		97.43	82.82	69.26	68.4	69.74	68.15	69.82	69.03	IBP****	27.0	34.0
Feed rate	Gas yield		2.22	17.18	30.74	31.60	30.25	31.85	30.18	30.97	FBP****	122.1	304.4
128 g/hr	Residue yield		0.35	0	0	0	0	0	0	0	Liquid selectivity	69.03	
Gas flow rate	Conversion		99.65	100	100	100	100	100	100	100	Gasoline selectivity**	87.06	
50 ml/min	Density (HCL)		0.729	0.730	0.731	0.734	0.731	0.734	0.732	0.733	Gasoline yield	61.50	
											%Catalyst*****	73.76	

Table C.6 Yield, selectivity, and properties of products form cracking of polyethylene at 430 ^{o}C under nitrogen flow

Reaction			**Time (hours)**							**Total**		**LCL**	**HCL**
Condition			**2**	**3**	**4**	**5**	**6**	**7**	**8**	**average***	Aromatic content	4.23	15.99
Virgin PE	LCL	%	29.53	27.71	28.88	26.66	27.62	27.41	27.42	27.28	RON***	100.64	93.23
Catalyst	HCL	%	50.99	49.95	46.89	40.72	42.18	43.13	45.41	42.86	MON***	93.69	85.14
5 (%w/w)	Liquid yield		80.52	77.66	75.77	67.38	69.8	70.54	72.83	70.14	IBP****	30.0	38.8
Feed rate	Gas yield		19.48	22.33	24.23	32.62	30.19	29.46	27.17	29.86	FBP****	133.0	326.0
110 g/hr	Residue yield		0	0	0	0	0	0	0	0	Liquid selectivity	70.14	
Gas flow rate	Conversion		100	100	100	100	100	100	100	100	Gasoline selectivity**	83.99	
50 ml/min	Density (HCL)		0.739	0.741	0.742	0.741	0.742	0.742	0.740	0.741	Gasoline yield	60.05	
											%Catalyst*****	46.47	

Table C.7 Yield, selectivity, and properties of products form cracking of polyethylene at 430 ^{o}C under nitrogen flow

Reaction			Time (hours)							Total		**LCL**	**HCL**
Condition			2	3	4	5	6	7	8	average*	Aromatic content	4.64	2.37
Virgin PE	LCL	%	7.34	9.25	7.89	11.15	11.76	11.24	11.92	11.52	RON***	101.90	93.23
Catalyst	HCL	%	22.95	25.70	27.19	28.64	29.08	28.31	29.12	28.79	MON***	95.09	85.40
0.5 (%w/w)	Liquid yield		30.29	34.95	35.08	39.79	40.84	39.55	41.04	40.31	IBP****	23.6	35.6
Feed rate	Gas yield		18.50	16.02	14.21	13.19	12.98	14.18	13.30	13.57	FBP****	126.0	305.9
385 g/hr	Residue yield		51.22	49.03	50.71	47.02	46.18	46.26	45.66	46.28	Liquid selectivity	75.03	
Gas flow rate	Conversion		48.78	50.97	49.29	52.98	53.82	53.74	54.34	53.72	Gasoline selectivity**	85.56	
50 ml/min	Density (HCL)		0.730	0.730	0.729	0.729	0.728	0.728	0.729	0.729	Gasoline yield	34.49	
											%Catalyst*****	0.6	

Table C.8 Yield, selectivity, and properties of products form cracking of polyethylene at 430 °C under nitrogen flow

Reaction			Time (hours)							Total		LCL	HCL
Condition			2	3	4	5	6	7	8	average*	Aromatic content	4.25	9.34
Virgin PE	LCL	%	15.90	23.82	26.02	26.55	25.03	26.16	25.61	25.84	RON***	128.85	95.94
Catalyst	HCL	%	34.05	33.68	35.01	34.49	34.80	34.18	36.48	34.99	MON***	125.38	88.31
1 (%w/w)	Liquid yield		49.95	57.5	61.03	61.04	59.83	60.34	62.09	60.83	IBP****	26.4	37.4
Feed rate	Gas yield		20.78	21.01	20.72	20.78	21.96	21.53	19.99	21.06	FBP****	142.8	309.6
382 g/hr	Residue yield		29.27	21.49	18.25	18.19	18.21	18.13	17.92	18.11	Liquid selectivity	74.28	
Gas flow rate	Conversion		70.73	78.51	81.75	81.81	81.79	81.87	82.08	81.89	Gasoline selectivity**	87.24	
50 ml/min	Density (HCL)		0.734	0.736	0.735	0.737	0.739	0.737	0.739	0.738	Gasoline yield	52.50	
											%Catalyst*****	6.7	

Table C.9 Yield, selectivity, and properties of products form cracking of polyethylene at 430 °C under nitrogen flow

Reaction			Time (hours)							Total		LCL	HCL
Condition			2	3	4	5	6	7	8	average*	Aromatic content	5.30	9.24
Virgin PE	LCL	%	28.70	28.55	31.21	30.01	29.09	29.29	30.56	29.74	RON***	120.53	92.03
Catalyst	HCL	%	29.72	30.35	39.02	37.51	39.89	39.53	38.42	38.84	MON***	116.1	83.91
2 (%w/w)	Liquid yield		58.42	58.9	70.23	67.52	68.98	68.82	68.98	68.58	IBP****	26.1	39.0
Feed rate	Gas yield		20.92	28.21	26.89	28.72	26.82	27.86	27.40	27.70	FBP****	160.6	330.0
381 g/hr	Residue yield		20.66	12.89	2.88	3.76	4.20	3.32	3.62	3.72	Liquid selectivity	71.23	
Gas flow rate	Conversion		79.34	87.11	97.12	96.24	95.80	96.68	96.38	96.27	Gasoline selectivity**	81.19	
50 ml/min	Density (HCL)		0.743	0.742	0.744	0.748	0.747	0.749	0.713	0.749	Gasoline yield	55.67	
											%Catalyst*****	30.3	

Table C.10 Yield, selectivity, and properties of products form cracking of polyethylene at 430 $^{\circ}$C under nitrogen flow

Reaction Condition			Time (hours) 2	3	4	5	6	7	8	Total average*		LCL	HCL
Virgin PE	LCL	%	12.69	15.50	17.51	15.63	-	-	-	15.63	Aromatic content	4.34	3.30
Catalyst	HCL	%	36.75	37.76	39.17	29.40	-	-	-	29.40	RON***	103.69	90.46
1 (%w/w)	Liquid yield		49.44	53.26	56.68	45.03	-	-	-	45.03	MON***	97.11	82.26
Feed rate	Gas yield		9.68	11.91	8.87	4.57	-	-	-	4.57	IBP****	26.8	35.3
387 g/hr	Residue yield		40.88	34.83	34.45	50.40	-	-	-	50.40	FBP****	141.7	321.9
Gas flow rate	Conversion		59.12	65.17	65.55	49.60	-	-	-	49.60	Liquid selectivity	90.79	
10 ml/min	Density (HCL)		0.737	0.741	0.740	0.737	-	-	-	0.737	Gasoline selectivity**	79.98	
											Gasoline yield	43.96	
											%Catalyst*****	1.5	

Table C.11 Yield, selectivity, and properties of products form cracking of polyethylene at 430 $^{\circ}$C under nitrogen flow

Reaction Condition			Time (hours) 2	3	4	5	6	7	8	Total average*		LCL	HCL
Virgin PE	LCL	%	13.44	14.37	15.80	15.09	-	-	-	15.09	Aromatic content	4.41	8.01
Catalyst	HCL	%	37.23	37.70	40.59	39.15	-	-	-	39.15	RON***	115.21	94.87
1 (%w/w)	Liquid yield		50.67	52.07	56.39	54.24	-	-	-	54.24	MON***	110.06	87.13
Feed rate	Gas yield		17.73	19.37	14.86	17.11	-	-	-	17.11	IBP****	27.5	36.2
392 g/hr	Residue yield		31.61	28.56	28.75	28.65	-	-	-	28.65	FBP****	136.6	322.4
Gas flow rate	Conversion		68.39	71.44	71.25	71.35	-	-	-	71.35	Liquid selectivity	76.01	
20 ml/min	Density (HCL)		0.737	0.737	0.738	0.738	-	-	-	0.738	Gasoline selectivity**	82.10	
											Gasoline yield	44.53	
											%Catalyst*****	1.7	

Table C.12 Yield, selectivity, and properties of products form cracking of polyethylene at 430 ^{o}C under nitrogen flow

Reaction			Time (hours)							Total		LCL	HCL
Condition			2	3	4	5	6	7	8	average*	Aromatic content	4.87	9.72
Virgin PE	LCL	%	8.37	11.03	11.58	14.25	16.12	15.88	15.43	15.42	RON***	123.29	95.27
Catalyst	HCL	%	19.12	18.97	21.63	24.55	24.50	24.94	25.19	24.79	MON***	119.13	87.55
1 (%w/w)	Liquid yield		27.49	30.00	33.21	38.80	40.62	40.82	40.62	40.21	IBP****	29.1	37.1
Feed rate	Gas yield		15.62	14.13	11.44	13.87	15.30	13.24	14.39	14.20	FBP****	138.6	304.0
396 g/hr	Residue yield		56.89	55.87	55.35	47.32	44.08	45.95	45.00	45.59	Liquid selectivity	73.91	
Gas flow rate	Conversion		43.11	44.13	44.65	52.68	55.92	54.05	55.00	54.41	Gasoline selectivity**	86.38	
100 ml/min	Density (HCL)		0.732	0.733	0.735	0.736	0.737	0.739	0.739	0.738	Gasoline yield	34.74	
											%Catalyst*****	1.8	

Table C.13 Yield, selectivity, and properties of products form cracking of polyethylene at 430 ^{o}C under nitrogen flow

Reaction			Time (hours)							Total		LCL	HCL
Condition			2	3	4	5	6	7	8	average*	Aromatic content	4.44	7.49
Virgin PE	LCL	%	20.98	21.69	21.23	22.51	21.00	21.18	21.42	21.53	RON***	122.78	98.63
Catalyst	HCL	%	46.97	48.65	50.05	50.49	50.60	51.53	51.26	50.97	MON***	118.55	91.36
1 (%w/w)	Liquid yield		67.95	70.34	71.28	73.00	71.60	72.71	72.68	72.50	IBP****	27.2	36.1
Feed rate	Gas yield		32.05	29.66	28.72	27.00	28.40	27.29	27.32	27.50	FBP****	118.9	310.5
187 g/hr	Residue yield		0	0	0	0	0	0	0	0	Liquid selectivity	72.50	
Gas flow rate	Conversion		100	100	100	100	100	100	100	100	Gasoline selectivity**	85.79	
50 ml/min	Density (HCL)		0.726	0.727	0.726	0.728	0.731	0.732	0.731	0.731	Gasoline yield	62.04	
	%Catalyst		11.6	12.8	19.8	16.3	19.2	16.8	20.0	18.1			

Table C.14 Yield, selectivity, and properties of products form cracking of polyethylene at 430 °C under nitrogen flow

Reaction			Time (hours)							Total		LCL	HCL
Condition			2	3	4	5	6	7	8	average*	Aromatic content	4.59	7.70
Virgin PE	LCL	%	18.40	22.46	22.78	21.62	23.17	22.79	23.05	22.66	RON***	120.88	97.52
Catalyst	HCL	%	39.87	39.19	43.51	43.00	42.22	43.12	43.93	43.06	MON***	116.42	90.11
1 (%w/w)	Liquid yield		58.27	61.65	66.29	64.62	65.39	65.91	66.97	65.72	IBP****	25.9	34.2
Feed rate	Gas yield		10.11	14.53	17.99	22.95	23.67	22.45	21.29	22.59	FBP****	123.3	311.4
276 g/hr	Residue yield		31.62	23.81	15.73	12.43	10.94	11.64	11.75	11.69	Liquid selectivity		74.42
Gas flow rate	Conversion		68.38	76.19	84.27	87.57	89.06	88.36	88.25	88.31	Gasoline selectivity**		86.88
50 ml/min	Density (HCL)		0.744	0.738	0.731	0.730	0.730	0.731	0.732	0.731	Gasoline yield		56.59
											%Catalyst*****		2.9

Table C.15 Yield, selectivity, and properties of products form cracking of polyethylene at 430 °C under nitrogen flow

Reaction			Time (hours)							Total		LCL	HCL
Condition			2	3	4	5	6	7	8	average*	Aromatic content	5.09	9.06
Virgin PE	LCL	%	15.95	16.68	14.98	13.15	13.06	12.89	13.59	13.17	RON***	137.34	92.19
Catalyst	HCL	%	20.80	19.19	17.94	18.12	18.08	19.01	18.26	18.37	MON***	134.91	84.09
1 (%w/w)	Liquid yield		36.75	35.87	32.92	31.27	31.14	31.9	31.85	31.54	IBP****	26.3	37.4
Feed rate	Gas yield		25.25	20.02	16.29	12.39	11.90	12.47	11.69	12.11	FBP****	142.3	310.6
587 g/hr	Residue yield		38.00	44.10	50.79	56.33	56.97	55.63	56.46	56.35	Liquid selectivity		72.26
Gas flow rate	Conversion		62.00	55.90	49.21	43.67	43.03	44.37	43.54	43.65	Gasoline selectivity**		86.32
50 ml/min	Density (HCL)		0.734	0.735	0.736	0.733	0.735	0.733	0.737	0.735	Gasoline yield		27.20
											%Catalyst*****		1.1

Table C.16 Yield, selectivity, and properties of products form cracking of polyethylene at 430 ^{o}C under nitrogen flow

Reaction			Time (hours)							Total		LCL	HCL
Condition			2	3	4	5	6	7	8	average*	Aromatic content	4.70	7.81
Waste PE	LCL	%	4.99	9.02	14.77	20.89	22.44	24.35	23.15	22.71	RON***	128.73	91.10
Catalyst	HCL	%	11.11	14.44	28.55	35.86	38.86	40.38	39.40	38.63	MON***	125.24	82.90
1 (%w/w)	Liquid yield		16.1	23.46	43.32	56.75	61.3	64.73	62.55	61.34	IBP****	24.5	39.2
Feed rate	Gas yield		4.02	4.07	6.69	19.06	25.32	23.79	26.59	23.69	FBP****	163.8	337.2
393 g/hr	Residue yield		79.88	72.48	49.99	24.19	13.39	11.47	10.86	14.98	Liquid selectivity	72.23	
Gas flow rate	Conversion		20.12	27.52	50.01	75.81	86.61	88.53	89.14	85.02	Gasoline selectivity**	79.09	
50 ml/min	Density (HCL)		0.738	0.737	0.734	0.736	0.738	0.747	0.749	0.743	Gasoline yield	49.70	
											%Catalyst*****	2.9	

APPENDIX D

GAS CHROMATOGRAPH CONDITION AND DATA

D.1 Condition for gaseous and liquid products

Column parameter

Type : Equity-1 capillary column

Length (meters) : 30

I.D. (mm) : 0.53

Film thickness (μm) : 0.3

Carrier gas : Helium

Linear velocity : 20.3 cm/sec

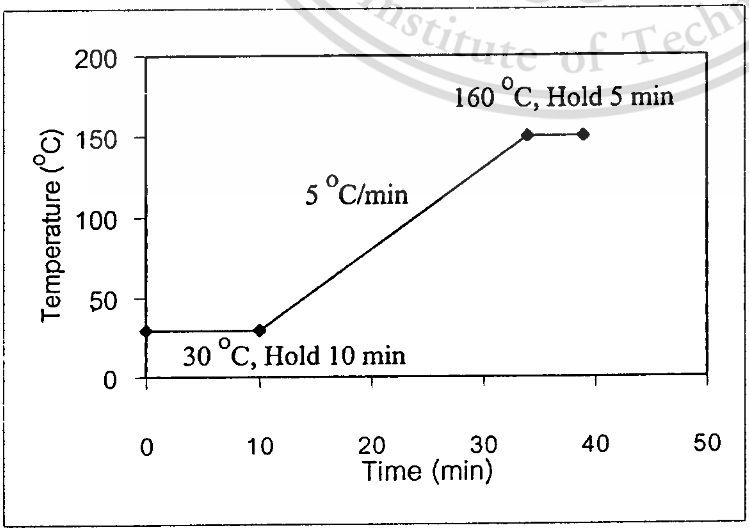
Injector temperature : 220°C

FID detector temperature : 220°C

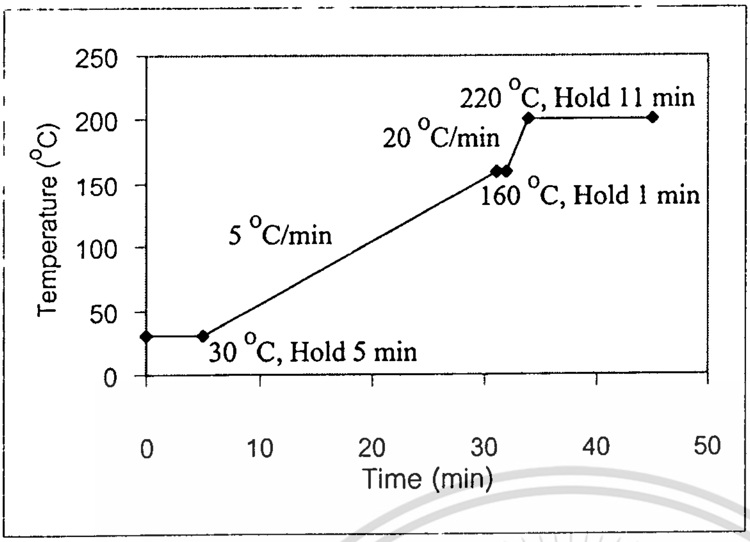
Split ratio : 100

Amount injected (μl) : 0.1

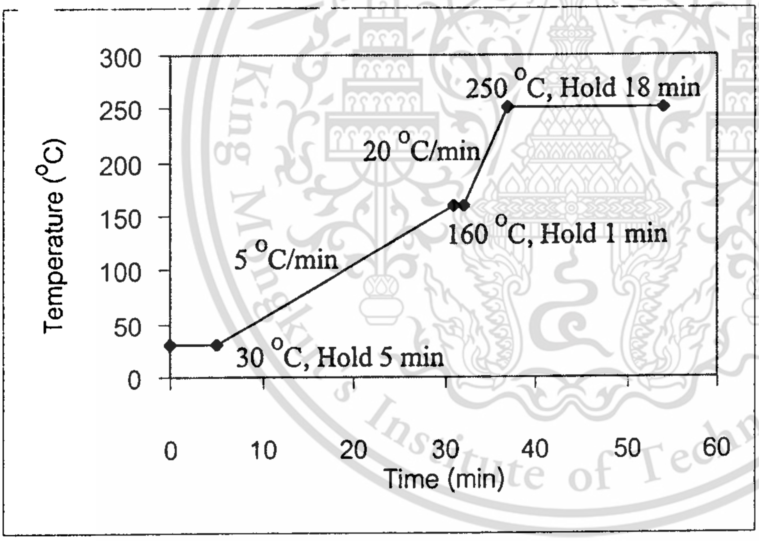
Column oven condition for gaseous products



Column oven condition for light cracked liquid products



Column oven condition for heavy cracked liquid products



D.2 Chromatogram of liquid product (heavy fraction) from cracking of virgin polyethylene using catalyst content of 1 %wt, polymer feeding rate of ~400 g/hr, N_2 feed rate 50 ml/min, and reaction temperature at 430 °C

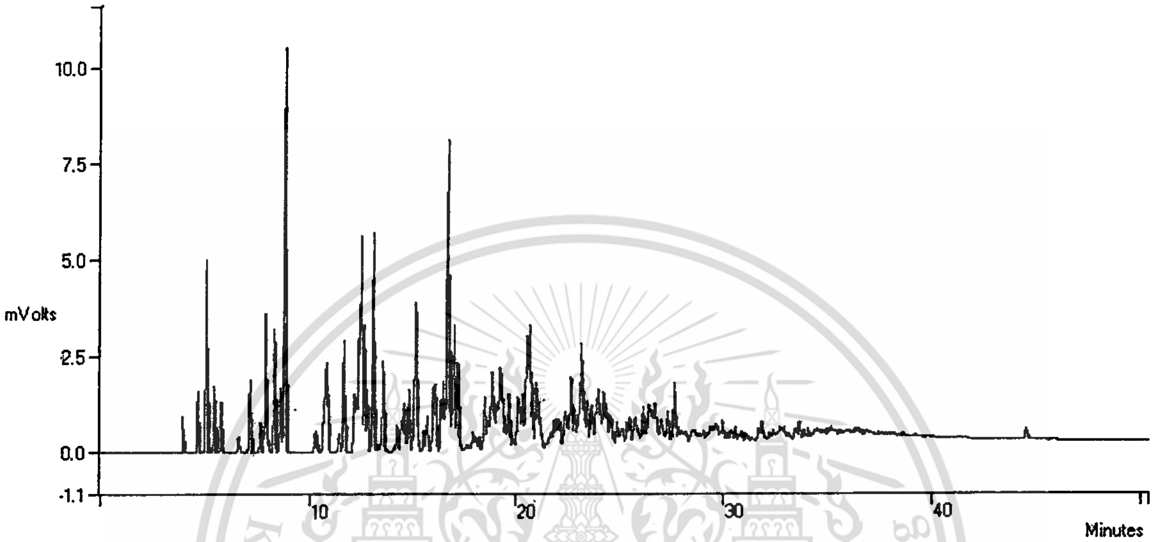


Figure D.1 Chromatogram of heavy cracked liquid hydrocarbons product

The composition list of heavy cracked liquid hydrocarbons product

Peak	Retention time	Area%	Name
1.	3.89	0.2731	Propene
2.	4.60	0.6430	Isobutane
3.	5.00	2.1203	Isobutene
4.	5.17	0.0553	Butene
5.	5.14	0.6877	*cis*-Butene
6.	5.39	0.5693	*cis*-Butene
7.	6.55	0.2235	2-Methyl-1-butene
8.	7.08	1.0527	Isopentane
9.	7.57	0.3896	1-Pentene
10.	7.81	2.0640	2-Pentene
11.	8.24	1.6077	*cis*-2-Pentene
12.	8.54	0.8758	*cis*-1,2-Dimethylcyclopropane
13.	8.73	5.6094	3-Methyl-1-pentene

Peak	Retention time	Area%	Name
14.	10.25	0.4904	2,3-Dimethyl-1-butene
15.	10.76	2.6153	2,3-Dimethyl-1-butene
16.	11.36	0.2797	3-Methylpentane
17.	11.59	1.7135	2-Methyl-1-pentene
18.	12.09	0.8170	3-Methylenepentane
19.	12.19	0.6552	3-Hexene
20.	12.32	1.4696	3-Hexene
21.	12.42	3.1387	2-Methyl-2-pentene
22.	12.59	2.0813	3-Methyl-2-pentene
23.	12.74	0.4991	*cis*-2-Hexene
24.	13.01	3.0366	3-Methyl-*cis*-2-pentene
25.	13.21	0.0674	2,3-Dimethyl-2-pentene
26.	13.50	1.3532	4-Methyl-2-*cis*-pentene
27.	14.02	0.0573	3,4-Dimethyl-1-pentene
28.	14.18	0.3848	2,4-Dimethyl-1-pentene/1-Methylcyclopentene/ 3-Methyl-1-hexene/2-Methyl-*trans*-3-hexene
29.	14.37	0.4516	4,4-Dimethyl-(E)-2-pentene
30.	14.50	0.7673	2,3-Dimethyl-1-pentene
31.	14.74	0.9561	*cis*-3-Methyl-3-hexene/5-Methyl-2-hexene
32.	15.07	2.9350	*cis*-4-Methyl-2-hexene/2-Methylhexane
33.	15.47	0.3095	3-Methylhexane
34.	15.65	0.5002	Methylcyclohexane
35.	15.92	0.8912	2-Methyl-1-hexene
36.	16.02	1.2372	3,4-Dimethyl-2-pentene/2,4-Dimethyl-2-pentene
37.	16.30	0.6808	3-Methyl-3-hexene
38.	16.41	0.9961	3-Heptene
39.	16.62	7.2131	2-Methyl-2-hexene
40.	16.82	0.1356	*trans*-2-heptene
41.	16.93	1.1898	*cis*-3-methyl-2-hexene
42.	17.11	1.0993	1,1,2,3-Tetramethylcyclopropane
43.	17.55	0.0900	*trans*-4,4-Dimethyl-2-hexene

Peak	Retention time	Area%	Name
44.	17.85	0.2477	1,3-Dimethylcyclohexene/ 1,3,3,4-Tetramethylcyclobutene
45.	17.98	0.2272	2,5-Dimethylhexane
46.	18.16	0.1795	2,4-Dimethyl-2-hexene
47.	18.43	0.9307	Ethylcyclohexane
48.	18.57	0.3749	Ethylcyclohexane
49.	18.77	2.1782	4-Methylcyclohexene
50.	19.01	0.6741	Toluene
51.	19.14	1.4241	2,3-Dimethyl-3-hexene/2-Propyl-1-pentene
52.	19.26	1.5051	*trans*-4-Methyl-2-heptene/ 2,5-Dimethyl-2-hexene
53.	19.44	0.1020	2-Methylheptane
54.	19.59	1.0171	2,3-Dimethyl-2-hexene/3-Methylheptane/ 5-Methyl-2-heptane
55.	19.78	0.1316	6-Methyl-2-heptene
56.	20.03	1.2955	4-Methyl-3-heptane/2-Ethyl-1-hexene
57.	20.27	0.9707	3-Ethyl-3-hexene
58.	20.49	2.2453	4-Methyl-3-heptene/3-Ethyl-2-hexene
59.	20.60	1.8167	2,3-Dimethyl-3-hexene
60.	20.74	0.8446	2,5-Dimethyl -3-hexene
61.	20.92	0.9530	2,3-Dimethyl -1,4-hexadiene
62.	20.99	1.0376	2-Ethyl-1-hexane
63.	21.38	0.0640	2-Octene
64.	21.64	0.3849	2,6-Dimethyl-3-heptene/ 3,5-Dimethylcyclohexene
65.	21.77	0.4241	2,5-Dimethyl-2,4-hexadiene
66.	21.91	0.4991	2,6-Dimethylheptane
67.	22.05	0.4626	2,4-Dimethylheptane/2,5-Dimethylheptane/ 2,6-Dimethylhepta-2,4-diene
68.	22.33	0.9653	C_9 Brach olefin derivative
69.	22.59	1.4693	C_9 Cyclic paraffin derivative

Peak	Retention time	Area%	Name
70.	22.78	0.5801	4-Ethyl-3- heptene
71.	23.10	3.6864	Xylene
72.	23.22	0.1189	Xylene
73.	23.37	0.3514	Isopropylcyclohexane
74.	23.58	0.5168	2,3-Dimethyl-2-heptene
75.	23.90	1.8231	C_9 Oxygenate paraffin derivative/ C_9 Cyclic paraffin derivative
76.	24.17	0.9807	*cis,cis,cis*-1,2,3-Trimethylcyclohexane/ 1,2,3- Trimethylcyclohexane
77.	24.26	0.7714	C_9 Brach oxygenate olefin derivative/ C_9 Brach oxygenate olefin derivative
78.	24.47	0.4080	C_9 Cyclic olefin derivative
79.	24.55	0.3767	C_9 Cyclic paraffin derivative/ 2,6-Dimethyl-3-heptene
80.	24.82	0.3676	6-Methyl-1-octene/C_9 Brach paraffin derivative/*trans*-2-methyl-3-octene
81.	25.06	0.4971	nonane
82.	25.29	0.3385	5-Decene
83.	25.43	0.4397	C_9 Oxygenate paraffin derivative/ C_{10} Brach cyclic olefin derivative
84.	25.70	0.6980	2,4,6-Trimethyl-3-heptene
85.	25.84	0.2471	2,7-Dimethyl octane
86.	26.09	0.8493	C_{10} Olefin derivative/2-Methyl-3-ethyl-2-heptene
87.	26.36	0.9608	C_{10} Aromatic derivative
88.	26.50	0.4769	C_{10} Cyclic olefin derivative/2-Methyl-2-nonene
89.	26.65	1.0645	C_{10} Aromatic derivative/ C_{10} Cyclic paraffin derivative
90.	26.97	0.6651	C_{10} Cyclic paraffin derivative/ C_{10} Oxygenate paraffin derivative
91.	27.29	0.6244	2-Methylnonane

Peak	Retention time	Area%	Name
92.	27.60	1.4781	C_{10} Brach olefin derivative/ 1,2,3-Trimethylbenzene
93.	27.82	0.0965	C_{10} Brach olefin derivative
94.	27.97	0.1210	2,6-Dimethyl-4-octene
95.	28.17	0.2258	2,6-Dimethyl-4-octene
96.	28.50	0.2559	2-Methyl-3-nonene
97.	28.60	0.1953	2-Methyl-3-nonene
98.	28.81	0.1169	Decane
99.	29.03	0.1370	3,7-Dimethyl-2-octene
100.	29.19	0.0703	2,3,6-Trimethyl-4-octene
101.	29.35	0.1710	C_{10} Oxygenate derivative
102.	29.48	0.1394	3,3,5,5-Tetramethylcyclohexanone
103.	29.63	0.2135	C_{10} Aromatic derivative
104.	29.70	0.0874	C_{10} Aromatic derivative
105.	29.94	0.2392	C_{10} Aromatic derivative
106.	30.17	0.0678	4-Ethyl-o-xylene
107.	30.36	0.1611	5,6-Methylenedecane/ 1-Methyl-2-(1-methylethyl)-benzene
108.	30.57	0.2237	2-Methyl-decane
109.	30.74	0.0338	4-Ethyl-*m*-xylene
110.	30.86	0.1378	5-Undecene
111.	31.05	0.2557	5-Methyl-1-decene
112.	31.69	0.1866	2-Ethyl-*m*-xylene
113.	31.82	0.3449	1,2,3,5-Tetramethylbenzene
114.	32.71	0.9575	C_{10} Aromatic derivative
115.	33.49	0.1517	Pentamethylbenzene
116.	33.64	0.1788	1-Methyl-4-(1-methylpropyl)-benzene
117.	34.05	0.2026	C_{12} Aromatic derivative

D.3 Distribution of gaseous and liquid products (light and heavy fraction) from cracking of polyethylene at 430 °C under nitrogen flow

Table D.1 Distribution of heavy cracked liquid products from cracking of polyethylene at 430 °C using approximate polymer feeding rate of 400 g/hr, catalyst content 1%wt, and N_2 flow rate 50 ml/min

Hour	Product Distribution (%)									
	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
2	2.72	4.15	2.71	24.28	21.84	19.25	13.02	10.62	1.20	0.21
3	0.19	3.89	5.88	24.28	20.61	19.25	13.50	11.00	1.21	0.19
4	0.12	4.25	6.49	25.29	19.72	18.19	13.00	11.49	1.23	0.22
5	0.15	4.29	5.94	24.93	20.26	18.93	12.39	11.61	1.26	0.23
6	0.21	3.87	6.16	24.86	20.29	18.94	12.45	11.80	1.18	0.24
7	0.16	4.24	5.87	24.75	20.07	19.16	12.35	11.80	1.35	0.25
8	0.22	4.51	6.06	24.84	20.08	19.20	12.37	11.56	0.98	0.18

Table D.2 Distribution of gaseous products from cracking of polyethylene at 430 °C using approximate polymer feeding rate of 400 g/hr, catalyst content 1%wt, and N_2 flow rate 50 ml/min (The result from 8th hour)

Reaction condition (N_2, 50 ml/min)	Product Distribution (%)				
	C2	C3	C4	C5	C6
PE + Cat. 1% (%w/w)	0.58	25.72	59.63	8.16	5.91

Table D.3 Distribution of light cracked liquid hydrocarbons product from cracking of polyethylene at 430 ^{o}C (The result from 8th hour)

Sample	Catalyst content (%)	N_2 Flow rate (ml/min)	Feed rate (g/hr)	Product Distribution (%)									
				C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
PE	0.25	50	121	0.14	8.57	15.83	53.32	15.23	4.67	1.04	1.02	0.11	0.07
PE	0.5	50	124	0.07	9.44	18.08	54.13	13.25	3.73	0.70	0.50	0.06	0.03
PE	1	50	124	-	9.83	19.39	53.16	12.34	3.41	0.79	0.91	0.10	0.07
PE	2	50	128	1.13	8.44	21.27	53.69	11.16	3.03	0.53	0.62	0.06	0.06
PE	5	50	110	-	0.36	16.05	55.08	17.93	6.74	2.54	1.25	0.06	
PE	0.5	50	385	-	9.80	19.17	51.52	13.64	4.34	1.10	0.44	-	-
PE	1	50	382	0.11	13.38	17.73	47.31	13.91	5.41	1.41	0.66	0.06	0.03
PE	2	50	381	-	6.21	18.77	48.59	16.78	7.30	1.86	0.49	-	-
PE	1	10	387	-	7.92	19.05	49.52	15.74	5.79	1.47	0.51	-	-
PE	1	20	392	0.07	11.25	19.59	49.62	13.60	4.58	1.00	0.31	-	-
PE	1	100	396	0.07	9.17	16.87	51.44	15.33	5.41	1.22	0.49	-	-
PE	1	50	187	-	9.10	19.30	53.03	13.13	3.89	0.83	0.63	0.07	0.04
PE	1	50	276	-	11.45	19.06	51.30	13.05	4.01	0.87	0.27	-	-
PE	1	50	382	0.09	12.38	17.73	48.66	14.06	5.40	1.31	0.38	-	-
Waste PE	1	50	393	0.15	12.74	15.23	43.71	16.37	8.00	2.61	1.15	0.05	

Table D.4 Distribution of heavy cracked liquid hydrocarbons product from cracking of polyethylene at 430 °C (The result from 8th hour)

Sample	Catalyst content (%)	N_2 Flow rate (ml/min)	Feed rate (g/hr)	Product Distribution (%)									
				C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
PE	0.25	50	121	0.27	4.57	5.63	25.10	20.14	18.73	12.43	11.64	1.29	0.21
PE	0.5	50	124	0.32	5.40	6.55	28.60	20.65	17.51	10.65	9.39	0.80	0.15
PE	1	50	124	0.33	4.77	6.41	29.11	20.95	17.81	10.58	9.08	0.83	0.14
PE	2	50	128	0.30	5.94	8.04	31.94	19.97	15.49	9.25	8.13	0.78	0.15
PE	5	50	110	0.18	4.32	7.35	27.86	17.22	15.16	10.81	14.71	2.04	0.36
PE	0.5	50	385	0.16	3.87	5.73	27.22	21.45	18.67	11.35	10.38	0.98	0.18
PE	1	50	382	0.28	4.11	5.41	24.87	20.09	19.26	12.41	12.18	1.18	0.21
PE	2	50	381	-	0.89	2.60	17.61	18.73	22.37	17.00	18.44	2.04	0.33
PE	1	10	387	0.24	4.41	5.71	22.25	18.69	19.09	13.09	14.53	1.67	0.32
PE	1	20	392	0.31	4.44	5.96	24.66	19.68	18.92	11.97	12.57	1.27	0.24
PE	1	100	396	0.36	5.03	6.05	25.83	18.41	16.49	10.06	15.37	2.05	0.35
PE	1	50	187	0.22	4.51	6.06	27.34	20.88	18.40	11.17	10.26	0.98	0.18
PE	1	50	276	0.34	5.00	6.07	26.85	20.39	18.61	11.19	10.40	0.98	0.17
PE	1	50	382	0.30	4.33	5.26	23.56	19.76	19.74	12.73	12.79	1.30	0.24
Waste PE	1	50	393	0.20	3.18	4.51	21.24	18.08	19.26	13.68	17.54	1.90	0.41

APPENDIX E

GAS CHROMATOGRAPH/MASS SPECTROMETER CONDITION

E.1 Condition for heavy liquid products

Column parameters

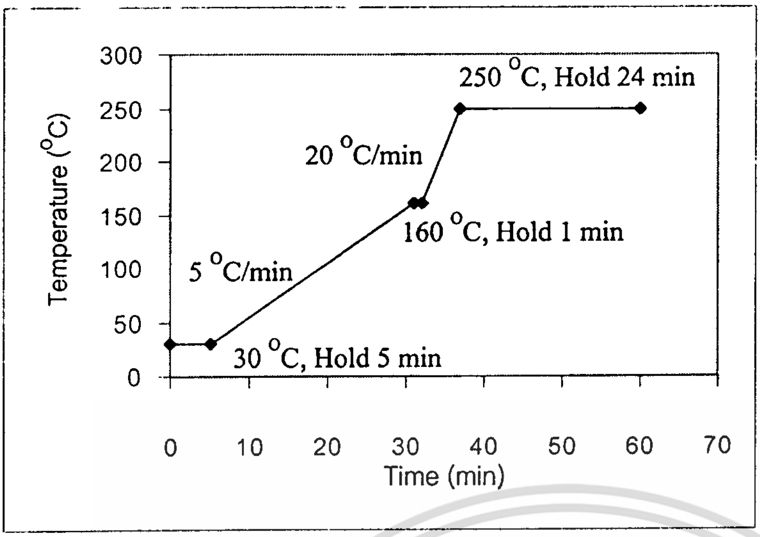
- Type : HP-1 capillary column
- Length (meters) : 30
- I.D. (mm) : 0.25
- Film thickness (μm) : 0.25

Carrier gas : Helium
Average velocity : 28 cm/sec
Injector temperature : 220°C
FID detector temperature : 220°C
Split ratio : 100
Amount injected (μl) : 0.1

Scan parameters

- Low Mass : 30
- High Mass : 350

Column oven condition



E.2 Composition of heavy cracked liquid products from cracking of virgin polyethylene using catalyst content of 1% (w/w), polymer feeding rate of ~400 g/hr, N_2 feed rate 50 ml/min, and reaction temperature at 430 °C

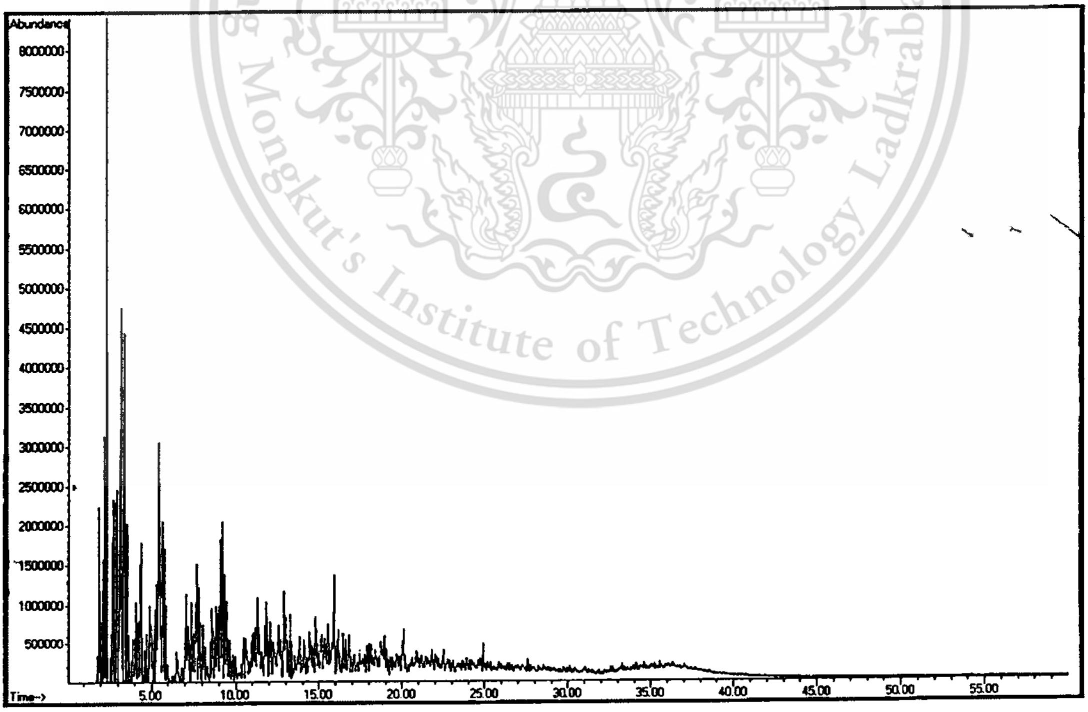


Figure E.1 Chromatogram of heavy cracked liquid hydrocarbon products

The composition list of heavy cracked liquid hydrocarbons product

Peak	Retention time	Area%	Name
1.	1.77	0.033	Propene
2.	1.84	0.211	Isobutane
3.	1.89	0.719	Isobutene
4.	1.92	0.238	*cis*-Butene
5.	1.95	0.199	*cis*-Butene
6.	2.04	0.114	2-Methyl-1-butene
7.	2.10	0.513	Isopentane
8.	2.16	0.187	1-Pentene
9.	2.19	1.148	2-Pentene
10.	2.26	0.896	*cis*-2-Pentene
11.	2.33	3.652	*cis*-1,2-Dimethylcyclopropane
12.	2.60	0.324	3-Methyl-1-pentene
13.	2.69	0.606	2,3-Dimethyl-1-butene
14.	2.73	1.265	2,3-Dimethyl-1-butene
15.	2.87	0.194	3-Methylpentane
16.	2.93	1.188	2-Methyl-1-pentene
17.	3.07	0.558	3-Methylenepentane
18.	3.11	0.562	3-Hexene
19.	3.15	0.983	3-Hexene
20.	3.18	2.443	2-Methyl-2-pentene
21.	3.22	1.359	3-Methyl-2-pentene
22.	3.28	0.548	*cis*-2-Hexene
23.	3.38	2.288	3-Methyl-cis-2-pentene
24.	3.48	0.154	2,3-Dimethyl-2-pentene
25.	3.55	1.130	4-Methyl-2-cis-pentene
26.	3.77	0.066	3,4-Dimethyl-1-pentene
27.	3.86	0.338	2,4-Dimethyl-1-pentene
28.	3.90	0.209	1-Methylcyclopentene
29.	3.96	0.117	3-Methyl-1-hexene
30.	4.01	0.101	2-Methyl-*trans*-3-hexene

Peak	Retention time	Area%	Name
31.	4.06	0.663	4,4-Dimethyl-(E)-2-pentene
32.	4.12	0.387	2,3-Dimethyl-1-pentene
33.	4.20	0.496	*cis*-3-Methyl-3-hexene
34.	4.27	0.129	5-Methyl-2-hexene
35.	4.33	0.985	*cis*-4-Methyl-2-hexene
36.	4.38	1.399	2-Methylhexane
37.	4.59	0.274	3-Methylhexane
38.	4.69	0.482	Methylcyclohexane
39.	4.90	0.713	2-Methyl-1-hexene
40.	4.96	0.572	3,4-Dimethyl-2-pentene
41.	5.00	0.564	2,4-Dimethyl-2-pentene
42.	5.19	0.705	3-Methyl-3-hexene
43.	5.31	1.300	3-Heptene
44.	5.44	4.433	2-Methyl-2-hexene
45.	5.54	1.275	*trans*-2-Heptene
46.	5.68	1.770	*cis*-3-Methyl-2-hexene
47.	5.81	1.439	1,1,2,3-Tetramethylcyclopropane
48.	5.95	0.228	*trans*-4,4-Dimethyl-2-hexene
49.	6.26	0.072	1,3-Dimethylcyclohexene
50.	6.32	0.073	1,3,3,4-Tetramethylcyclobutene
51.	6.51	0.430	2,5-Dimethylhexane
52.	6.81	0.152	2,4-Dimethyl-2-hexene
53.	7.04	1.460	Ethylcyclohexane
54.	7.14	0.630	4-Methylcyclohexene
55.	7.21	0.812	Toluene
56.	7.38	1.058	2,3-Dimethyl-3-hexene
57.	7.49	0.666	2-Propyl-1-pentene
58.	7.59	0.437	*trans*-4-Methyl-2-heptene
59.	7.68	1.574	2,5-Dimethyl-2-hexene
60.	7.85	1.362	2-Methylheptane
61.	8.05	0.589	2,3-Dimethyl-2-hexene

Peak	Retention time	Area%	Name
62.	8.13	0.272	3-Methylheptane
63.	8.17	0.340	5-Methyl-2-heptane
64.	8.32	0.202	6-Methyl-2-heptene
65.	8.58	0.978	4-Methyl-3-heptane
66.	8.64	0.460	2-Ethyl-1-hexene
67.	8.77	0.495	3-Ethyl-3-hexene
68.	8.85	1.542	4-Methyl-3-heptene
69.	8.97	0.461	3-Ethyl-2-hexene
70.	9.08	2.140	2,3-Dimethyl-3-hexene
71.	9.21	1.696	2,5-Dimethyl -3-hexene
72.	9.37	1.400	2,3-Dimethyl -1,4-hexadiene
73.	9.47	0.889	2-Ethyl-1-hexane
74.	9.66	0.520	2-Octene
75.	9.78	0.110	2,6-Dimethyl-3-heptene
76.	9.86	0.323	3,5-Dimethylcyclohexene
77.	9.96	0.258	2,5-Dimethyl-2,4-hexadiene
78.	10.40	0.255	2,6-Dimethylheptane
79.	10.59	0.708	C_9 Brach olefin derivative
80.	10.71	0.165	2,5-Dimethylheptane
81.	10.77	0.129	2,6-Dimethylhepta-2,4-diene
82.	10.96	0.844	C_9 Brach olefin derivative
83.	11.08	0.815	C_9 Cyclic paraffin derivative
84.	11.19	0.654	4-Ethyl-3- heptene
85.	11.31	1.437	*p*-Xylene
86.	11.41	0.854	Isopropylcyclohexane
87.	11.58	0.662	2,3-Dimethyl-2-heptene
88.	11.77	0.971	C_9 Oxygenate paraffin derivative
89.	11.82	1.177	C_9 Cyclic paraffin derivative
90.	12.01	0.333	*cis,cis,cis*-1,2,3-Trimethylcyclohexane
91.	12.06	1.020	1,2,3- Trimethylcyclohexane
92.	12.25	0.656	C_9 Brach oxygenate olefin derivative

93.	12.34	0.568	C_9 Brach oxygenate olefin derivative
94.	12.50	0.744	C_9 Cyclic olefin derivative
95.	12.59	0.662	C_9 Cyclic paraffin derivative
96.	12.67	0.768	2,6-Dimethyl-3-heptene
97.	12.90	1.121	6-Methyl-1-octene
98.	12.98	0.520	C_9 Brach paraffin derivative
99.	13.04	0.737	*trans*-2-Methyl-3-octene
100.	13.14	1.217	nonane
101.	13.54	0.560	5-Decene
102.	13.72	0.397	C_9 Oxygenate paraffin derivative
103.	13.82	0.710	C_{10} Brach cyclic olefin derivative
104.	14.12	1.022	2,4,6-Trimethyl-3-heptene
105.	14.27	0.225	2,7-Dimethyl octane
106.	14.43	1.060	C_{10} Olefin derivative
107.	14.57	0.579	2-Methyl-3-ethyl-2-heptene
108.	14.78	0.731	C_{10} Aromatic derivative
109.	14.87	0.684	C_{10} Cyclic olefin derivative
110.	14.97	0.236	2-Methyl-2-nonene
111.	15.07	0.378	C_{10} Aromatic derivative
112.	15.14	0.911	C_{10} Cyclic paraffin derivative
113.	15.30	0.357	C_{10} Cyclic paraffin derivative
114.	15.36	0.727	C_{10} Oxygenate paraffin derivative
115.	15.54	0.881	2-Methylnonane
116.	15.77	1.018	C_{10} Brach olefin derivative
117.	15.90	1.096	1,2,3-Trimethylbenzene
118.	16.16	1.037	C_{10} Brach olefin derivative
119.	16.45	0.574	2,6-Dimethyl-4-octene
120.	16.59	0.550	2-Methyl-3-nonene
121.	16.75	0.254	Decane
122.	16.83	0.517	3,7-Dimethyl-2-octene
123.	16.95	0.180	2,3,6-Trimethyl-4-octene
124.	17.10	0.323	C_{10} Oxygenate derivative

Peak	**Retention time**	**Area%**	**Name**
125.	17.44	0.247	3,3,5,5-Tetramethylcyclohexanone
126.	17.91	0.581	C_{10} Aromatic derivative
127.	18.04	0.391	C_{10} Aromatic derivative
128.	18.15	0.369	4-Ethyl-o-xylene
129.	18.73	0.683	5,6-Methylenedecane
130.	18.80	0.549	1-Methyl-2-(1-methylethyl)-benzene
131.	18.91	0.455	2-Methyl-decane
132.	18.98	0.510	4-Ethyl-m-xylene
133.	19.09	0.403	5-Undecene
134.	19.27	0.107	5-Methyl-1-decene
135.	20.01	0.512	2-Ethyl-m-xylene
136.	20.08	0.442	1,2,3,5-Tetramethylbenzene
137.	21.78	0.440	Pentamethylbenzene
138.	22.48	0.385	1-Methyl-4-(1-methylpropyl)-benzene
139.	24.89	0.360	C_{12} Indane derivative

APPENDIX F

NMR DATA

A nuclear magnetic resonance (NMR) technique has been developed for determining the octane number from the composition of gasoline. Since the determination of gasoline octane number using the ASTM test engine required large quantities of the samples. The NMR technique can be used for limited amounts of samples. These measurements are performed using a Bruker AVANCE DPX300 NMR spectrometer with 300-MHz proton resonance frequency. A typical NMR spectrum of light fraction, heavy fraction and a gasoline fraction is shown in Figures F.1, F.2 and F.3, respectively.

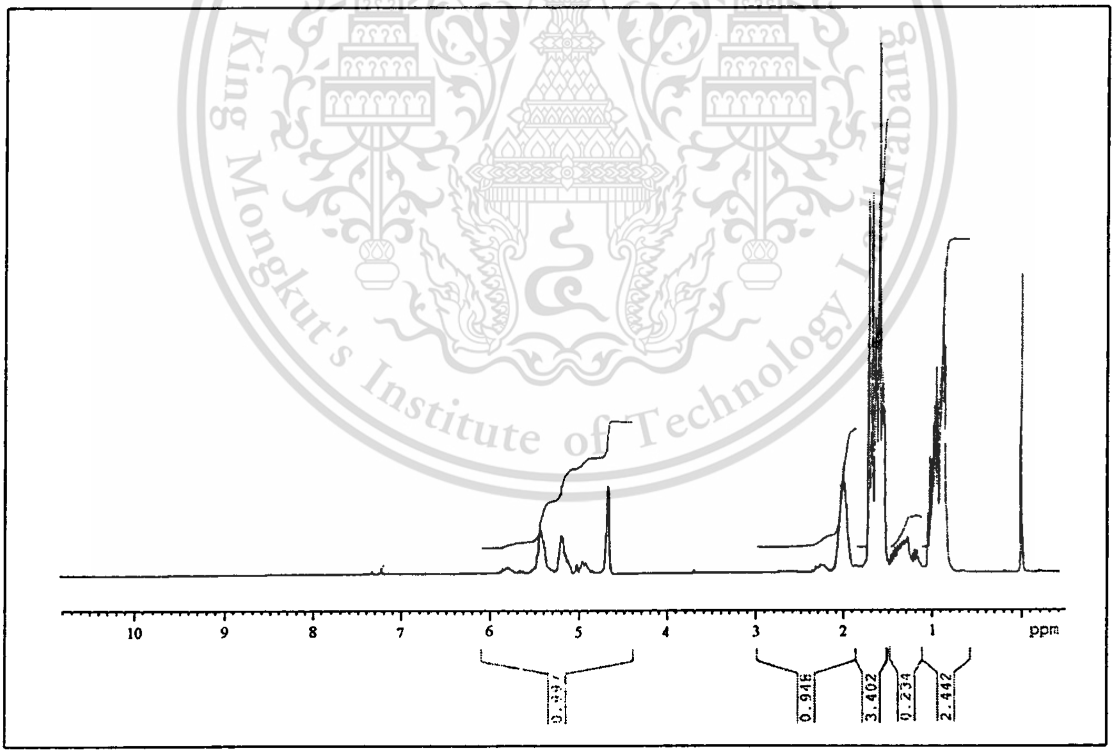


Figure F.1 NMR spectrum of light product fraction

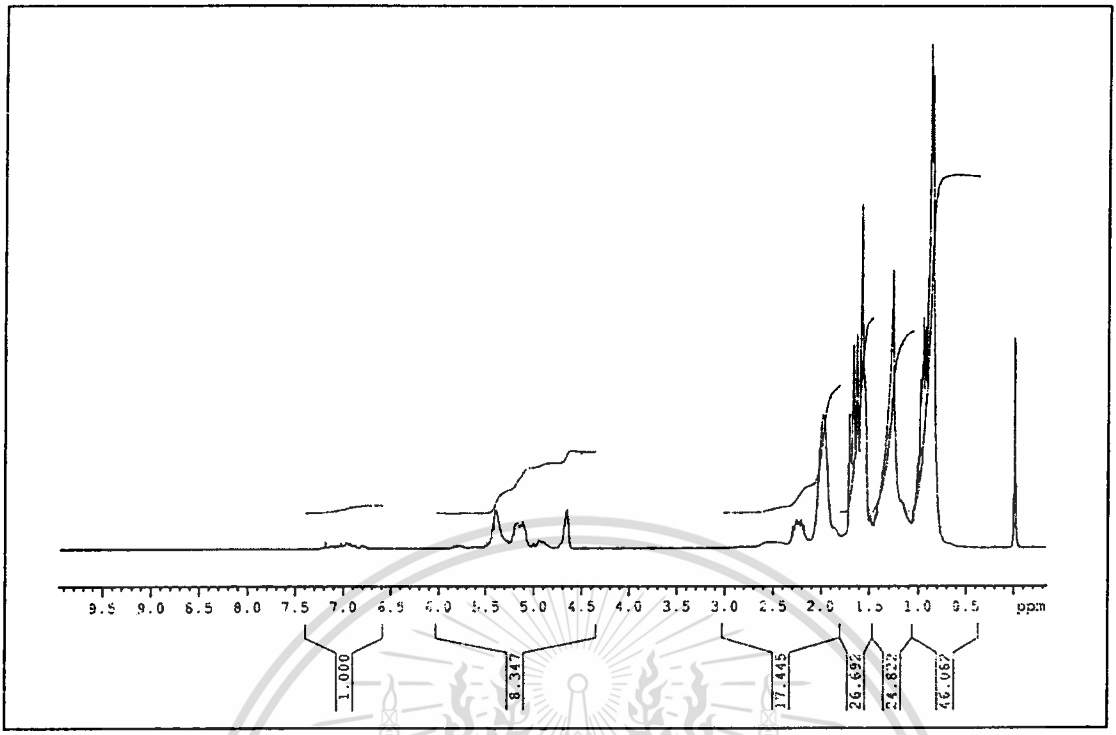


Figure F.2 NMR spectrum of heavy product sample

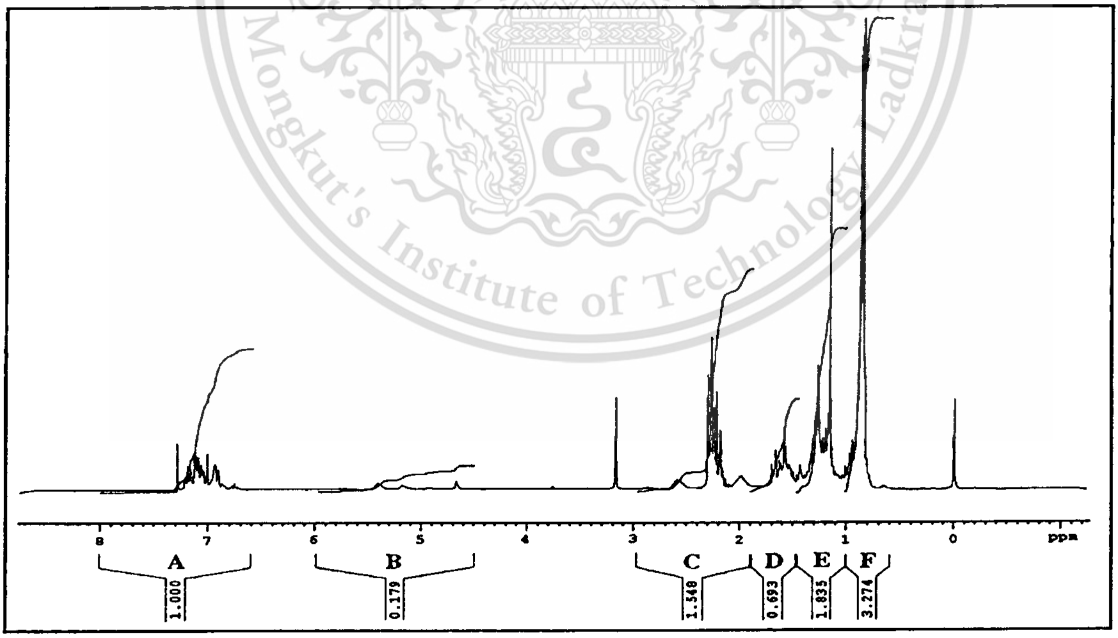


Figure F.3 NMR spectrum of gasoline fraction

The hydrocarbon species including aromatics, paraffins and olefins which are major components of petroleum products are estimated using literature correlations developed by Myers *et at.* [37]. In these equations, the chemical shift scale is divided into 6 regions (Figure F.3), marked as A to F. A, B, C, D, E and F representing the integrated area of the spectral regions are used for the octane number prediction as shown in Table F.1.

Table F.1 NMR spectral regions

Regions	**Proton type**	**Chemical shift region (ppm)**
A	Ring aromatics	6.6-8.0
B	Olefin	4.5-6.0
C	α-methyl	2.0-3.0
D	Methine (paraffins)	1.5-2.0
E	Methylene (paraffins)	1.0-1.5
F	Methyl (paraffins)	0.6-1.0

These equations include correction factors for the varying densities of the different hydrocarbon types which can be defined by the relations:

$$\text{Aromatics, vol.\%} = \left[\frac{0.97\left(A+\frac{C}{3}\right)\times 100}{0.97\left(A+\frac{C}{3}\right)+1.02\left(D-2B+\frac{E}{2}+\frac{F}{3}\right)+3.33B}\right] \text{------(1)}$$

$$\text{Paraffins, vol.\%} = \left[\frac{1.02\left(D-2B+\frac{E}{2}+\frac{F}{3}\right)\times 100}{0.97\left(A+\frac{C}{3}\right)+1.02\left(D-2B+\frac{E}{2}+\frac{F}{3}\right)+3.33B}\right] \text{------(2)}$$

$$\text{Olefins, vol.\%} = \left[\frac{3.33B\times 100}{0.97\left(A+\frac{C}{3}\right)+1.02\left(D-2B+\frac{E}{2}+\frac{F}{3}\right)+3.33B}\right] \text{------(3)}$$

In addition, Myers *et al.* [38] also developed correlations for an 'isoparaffin index', and octane number. The isoparaffin index represents the estimated yields of branching which are the measured ratios of CH_3/CH_2 in the paraffins. The CH_3/CH_2 ratio is thus taken as a principal entry in an equation to calculate the octane number. The octane rating of gasoline (sample) is primarily arised from its isoparaffin and aromatic contents. By increasing the aromatic content, the blender can increase the octane quality to the required level. Aromatics are used because their individual octane ratings tend to be high. Another possible contributor to the high octane number would be the olefins. However, among the three hydrocarbon types (paraffins, aromatics, and olefins), olefin concentration is usually low (~10%) in petroleum fraction, which is fortunate because the olefin groups are determined with the least precision. Thus, olefin concentration is ignored in the linear regression analysis. A multiple linear equation is developed to express the octane number as a linear combination of the isoparaffin index, the aromatic content (vol%), the lead content (g/gal), and the sulfur content (wt%)

$$\text{Isoparaffin index} = CH_3/CH_2 = (F/3)\,/\,(E/2) \qquad \text{--------(4)}$$

$$\begin{aligned} \text{RON} &= 80.2 + 8.9\ (\text{isoparaffin index}) + 0.107\ \text{aromatics (vol.\%)} \\ &\quad + 2.93\ \text{lead (g/gal)} - 13.4\ \text{sulfur (wt\%)} \qquad \text{--------(5)} \\ \text{MON} &= 70.8 + 10.0\ (\text{isoparaffin index}) + 0.101\ \text{aromatics (vol.\%)} \\ &\quad + 3.27\ \text{lead (g/gal)} - 11.1\ \text{sulfur (wt\%)} \qquad \text{--------(6)} \end{aligned}$$

In the case of cracking of polyethylene, lead and sulfur contents are assumed to be negligible in the final gasoline range products. Therefore, equations (5) and (6) can be rewritten as:

$$\text{RON} = 80.2 + 8.9\ (\text{isoparaffin index}) + 0.107\ \text{aromatics (vol.\%} \qquad \text{--------(7)}$$

$$\text{MON} = 70.8 + 10.0\ (\text{isoparaffin index}) + 0.101\ \text{aromatics (vol.\%)} \qquad \text{--------(8)}$$

Table F.2 Intergrated area of the spectral regions of light liquid product fractions

Sample	% Catalyst	N_2 Flow rate (ml/min)	Feed rate (rpm)	Hour	A	B	C	D	E	F
PE	0.25	50	121	8	0	1	0.941	2.958	0.502	1.989
PE	0.5	50	124	8	0	1	0.852	3.088	0.496	1.967
PE	1	50	124	8	0	17.839	19.707	67.388	7.899	49.323
PE	2	50	128	8	0	1	0.768	3.415	0.663	2.544
PE	5	50	110	8	0	1	0.910	3.524	1.071	3.608
PE	0.5	50	385	8	0	15.355	13.557	52.150	9.876	35.291
PE	1	50	382	8	0	82	68.972	301.351	27.261	221.440
PE	2	50	381	8	0	0.902	1.029	3.445	0.456	3.056
PE	1	10	387	8	0	24.720	20.906	80.744	19.041	73.893
PE	1	20	392	8	0	15.363	14.675	60.968	8.398	48.890
PE	1	100	396	8	1	117.602	118.608	458.991	50.024	358.933
PE	1	50	187	8	0	37.078	29.887	126.252	11.443	81.206
PE	1	50	276	8	0	1.019	0.886	3.173	0.498	3.373
PE	1	50	382	8	0	0.997	0.948	3.402	0.256	2.442
Waste PE	1	50	393	8	0	21.999	19.472	74.903	7.056	57.113

Table F.3 Intergrated area of the spectral regions of heavy liquid product fractions with commercial gasoline

Sample	% Catalyst	N_2 Flow rate (ml/min)	Feed rate (rpm)	Hour	A	B	C	D	E	F
PE	0	50	115	8	0	1	1.215	0.778	10.724	4.015
PE	0.25	50	121	8	0	1	1.610	2.676	2.680	4.146
PE	0.5	50	124	8	1	17.368	26.703	49.212	40.023	69.861
PE	1	50	124	8	1	9.503	17.479	29.272	22.712	48.407
PE	2	50	128	8	1	6.042	11.496	20.039	12.982	26.710
PE	5	50	110	8	1	1.462	4.324	5.483	4.286	8.180
PE	0.5	50	385	8	1	15.016	4.720	42.435	32.468	69.922
PE	1	50	382	8	1	6.7	14.249	24.213	15.338	38.116
PE	2	50	381	8	1	5.429	11.156	12.779	22.046	40.285
PE	1	10	387	8	1	6.721	3.609	24.778	26.605	44.403
PE	1	20	392	8	1	9.668	19.772	35.403	27.619	64.318
PE	1	100	396	8	1	4.486	8.969	15.348	11.031	26.084
PE	1	50	187	8	1	14.400	21.400	39.000	22.200	65.800
PE	1	50	276	8	1	10.760	19.181	38.331	22.653	62.976
PE	1	50	382	8	1	8.347	17.445	26.692	24.822	46.082

Table F.3 (continued)

Sample	Catalyst %	N_2 Flow rate (ml/min)	Feed rate (rpm)	Hour	A	B	C	D	E	F
Waste PE	1	50	393	8	1	9.538	22.489	35.738	44.606	75.694
Octane91	-	-	-	-	1	0.055	1.001	0.681	1.585	3.118
Octane95	-	-	-	-	1	0.102	1.201	0.797	1.577	3.552

Table F.4 Hydrocarbon types and octane number of light liquid product fractions

Sample	% Catalyst	N_2 Flow rate (ml/min)	Feed rate (rpm)	Hour	Aromatic %	Paraffin %	Olefin %	Isoparaffin %	RON	MON
PE	0.25	50	121	8	5.49	34.44	60.07	2.64	104.30	97.77
PE	0.5	50	124	8	4.89	36.04	59.07	2.64	104.25	97.73
PE	1	50	124	8	5.36	44.69	49.95	4.16	117.82	112.97
PE	2	50	128	8	3.99	42.51	53.50	2.56	103.39	96.78
PE	5	50	110	8	4.23	47.87	47.90	2.25	100.64	93.69
PE	0.5	50	385	8	4.64	41.20	54.15	2.38	101.90	95.09
PE	1	50	382	8	4.25	43.70	52.05	5.42	128.86	125.39
PE	2	50	381	8	5.30	46.89	47.82	4.47	120.53	116.01
PE	1	10	387	8	4.34	42.84	52.82	2.59	103.69	97.11
PE	1	20	392	8	4.41	48.07	47.52	3.88	115.21	110.06
PE	1	100	396	8	4.87	46.58	48.54	4.78	123.29	119.13
PE	1	50	187	8	4.40	39.41	56.19	4.73	122.78	118.55
PE	1	50	276	8	4.59	41.01	54.39	4.52	120.88	116.42
PE	1	50	382	8	5.09	39.79	55.12	6.36	137.34	134.91
Waste PE	1	50	393	8	4.70	40.67	54.63	5.40	128.73	125.24

Table F.5 Hydrocarbon types and octane number of heavy liquid product fractions with commercial gasoline

Sample	% Catalyst	N_2 Flow rate (ml/min)	Feed rate (rpm)	Hour	Aromatic %	Paraffin %	Olefin %	Isoparaffin %	RON	MON
PE	0	50	115	8	4.22	60.02	35.77	0.25	82.87	73.72
PE	0.25	50	121	8	7.11	47.37	45.51	1.03	90.14	81.83
PE	0.5	50	124	8	7.60	46.63	45.77	1.16	91.37	83.20
PE	1	50	124	8	8.62	50.16	41.22	1.42	93.77	85.88
PE	2	50	128	8	9.64	48.98	41.38	1.37	93.44	85.49
PE	5	50	110	8	15.99	51.15	32.86	1.27	93.23	85.14
PE	0.5	50	385	8	2.37	50.23	47.40	1.44	93.23	85.40
PE	1	50	382	8	9.34	53.29	37.37	1.66	95.94	88.30
PE	2	50	381	8	9.24	54.28	36.48	1.22	92.03	83.91
PE	1	10	387	8	3.30	62.13	34.57	1.11	90.46	82.26
PE	1	20	392	8	8.01	56.95	35.03	1.55	94.87	87.13
PE	1	100	396	8	9.72	52.75	37.53	1.58	95.27	87.55
PE	1	50	187	8	7.89	44.12	47.98	1.98	98.63	91.36
PE	1	50	276	8	7.70	53.82	38.48	1.85	97.52	90.11
PE	1	50	382	8	9.06	52.82	38.11	1.24	92.19	84.09

Table F.5 (Continued)

Sample	Catalyst %	N_2 Flow rate (ml/min)	Feed rate (rpm)	Hour	Aromatic %	Paraffin %	Olefin %	Isoparaffin %	RON	MON
Waste PE	1	50	393	8	7.81	62.08	30.11	1.13	91.10	82.90
Octane91	-	-	-	-	29.70	62.90	7.40	1.14	93.48	85.15
Octane95	-	-	-	-	32.93	62.40	4.67	1.31	95.40	87.24

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