LIQUID FUEL FROM CO-PROCESSING OF PLASTIC WASTE

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE
(APPROPRIATE TECHNOLOGY FOR RESOURCES
AND ENVIRONMENTAL DEVELOPMENT)
FACULTY OF GRADUATE STUDIES
MAHIDOL UNIVERSITY
2005

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Thesis

Entitled

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was submitted to the Faculty of Graduate Studies, Mahidol University
for the degree of Master of Science (Appropriate Technology
for Resources and Environmental development)
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ACKNOWLEDGEMENTS

I would like to express my profound appreciation, wholehearted sense of gratitude and indebtedness to my thesis advisor, Asst. Prof. Dr. Aurapin Eamsiri, Dr. Kandis Sudsakorn. Who gave invaluable suggestions and comments and also gave me an opportunity to meet with invaluable experience in making thesis.

I gratefully thank Asst. Prof. Kanit Sanguantrakul for serving as a member of the thesis examination committee and his valuable comments and advice

I wish to thank the Department of Chemical Engineering, Faculty of Engineering, Kasetsart University for supporting the experimental location and equipments to carry out this thesis. I am also grateful to Miss Chompunut Hunsaworapong and Miss Monnut Chevakidakarn for providing me with a kindness, assistance and useful suggestion in may techniques for my experiment.

I am especially grateful to Thai Petrochemical Industry Public Company Limited (TPI), who kindly offered all polymers used in this study.

My special thank to all friends, AT 16, for their helpful, grateful friendship, happiness and all enjoyable thing that we have ever done throughout my study. These would be in my memory forever

I wish to express my appreciation to Mr. Parinya Choosub, for his helpful advice, and encouragement especially, during experimental period.

Most of all, I wish to express my deepest love and sincere gratitude to my family; father mother and sisters for their insight, support, trustfulness, understanding, supervision assistance and continuous encouragement throughout my study time.

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LIQUID FUEL FROM CO-PROCESSING OF PLASTIC WASTE

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ABSTRACT

The objective of this research is to study the effect of reaction temperatures on mixed plastic with polyethylene (high density), polypropylene and polystyrene at the ratio of 1:1:1. Polymers used were analyzed by the thermogravimetric analysis technique. The pyrolysis of plastic mixture to liquid fuel was carried out both with and without HZSM-5 catalyst. The thermal cracking conditions which provide optimal conditions enabling a maximum liquid hydrocarbon yield are: a temperature range 400-500°C under atmospheric pressure, nitrogen flow rate 60 ml min^{-1}, and 90 min. of reaction time. Catalytic temperatures were studied at 300-500°C in a packed bed reactor with mixed plastic to catalyst ratio 100:1. Liquid hydrocarbon from both cracking processes was then fractional distillated and gasoline was analyzed for amounts of Benzene, Toluene, and Xylene (BTX) using the Gas chromatography technique.

Based on all the results of these experiments, it can be concluded that the highest liquid hydrocarbon yields of 65.12% with 67.24% of gasoline, 8.78%of kerosene and 12.68% of gas oil are obtained from thermal degradation of mixed plastic at 500°C. In case of using HZSM-5 catalyst, development of thermal cracking can give the maximum liquid hydrocarbon yield of 80.43% at catalytic reactor 400°C with 63.65 % of gasoline, 7.74%of kerosene and 8.25% of gas oil. The amount of benzene, toluene and xylene from gasoline fraction in all cracking processes (BTX) are exceeds amounts allowed by environmental regulation. Therefore, the synthesized gasoline has to be purified before use.

KEYWORDS: MIXED PLASTIC/ HZSM-5 CATALYST/ DEGRADATION

67 P. ISBN 974-04-6333-9

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เชื้อเพลิงเหลวจากขยะพลาสติก
(LIQUID FUEL FROM CO-PROCESSING OF PLASTIC WASTE)

ธนาภรณ์ เอกคณาลักษมี 4436175 ENAT/M

วท.ม. (เทคโนโลยีที่เหมาะสมเพื่อการพัฒนาทรัพยากรและสิ่งแวดล้อม)

คณะกรรมการควบคุมวิทยานิพนธ์ : อรพินท์ เอี่ยมศิริ, Ph.D., กานดิส สุดสาคร Ph.D.

บทคัดย่อ

งานวิจัยในครั้งนี้มีวัตถุประสงค์หลักเพื่อศึกษาผลของอุณหภูมิของการทำปฏิกิริยาการเปลี่ยนพลาสติกผสมให้เป็นเชื้อเพลิงเหลวโดยใช้และไม่ใช้ตัวเร่งปฏิกิริยา HZSM-5 พลาสติกที่ใช้ในการทดลองคือ พอลิเอธิลีนความหนาแน่นสูง พอลิโพรพิลีน และ พอลิสไตรีน ซึ่งผสมกันในอัตราส่วน 1: 1: 1 นำไปวิเคราะห์สมบัติทางความร้อนแต่ละชนิดด้วย เทคนิคเทอโมกราวิเมตริก สภาวะในการทำปฏิกิริยาการแตกสลายด้วยความร้อนคือ ช่วงอุณหภูมิ 400-500 องศาเซลเซียส ที่ความดันบรรยากาศ อัตราการไหลไนโตรเจน 60 มิลลิลิตรต่อนาที และ เวลาในการทดลอง 90 นาที เพื่อให้ได้สภาวะในการทำการปฏิกิริยาที่ให้ไฮโดรคาร์บอนเหลวสูงที่สุด หลังจากนั้นทำการศึกษาอุณหภูมิบริเวณตัวเร่งปฏิกิริยาในเครื่องปฏิกรณ์แบบเบดบรรจุ ช่วงอุณหภูมิ 300-500 องศาเซลเซียส โดยมีอัตราส่วนพลาสติกผสมต่อตัวเร่งปฏิกิริยาเป็น 100:1 จากนั้นนำไฮโดรคาร์บอนเหลวจากทั้งสองระบบไปกลั่นลำดับส่วนแล้วนำเฉพาะน้ำมันเบนซินไปวิเคราะห์ต่อด้วยเทคนิคแก๊สโครมาโตกราฟเพื่อให้ทราบปริมาณเบนซีน โทลูอีน และไซลีน

จากผลการทดลองสามารถสรุปได้ว่าการแตกสลายด้วยความร้อนของพลาสติกผสมที่อุณหภูมิ 500 องศาเซลเซียส ให้สารไฮโดรคาร์บอนเหลวสูงที่สุด (65.12%) น้ำมันเบนซิน 67.24% น้ำมันก๊าด 8.78%และน้ำมันดีเซล 12.68% เมื่อใช้ตัวเร่งปฏิกิริยา HZSM-5 พบว่า ไฮโดรคาร์บอนเหลวเพิ่มขึ้นเป็น 80.43% ณ อุณหภูมิ 400 องศาเซลเซียส หลังจากนำไปกลั่นแล้วได้น้ำมันเบนซิน 63.65% น้ำมันก๊าด 6.73% และน้ำมันดีเซล 11.06% ปริมาณน้ำมันเบนซินที่ได้จากทั้ง 2 ระบบมีปริมาณ เบนซีนเกินกว่าที่กฎหมายกำหนด ดังนั้นน้ำมันเบนซินที่ได้จากการสังเคราะห์นี้ไปปรับปรุงคุณภาพก่อนนำไปใช้

67 หน้า ISBN 974-04-6333-9

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CHAPTER 1
INTRODUCTION

1.1 Background and state of the problem

In recent years the production and consumption of plastic have increased drastically. The amount of waste plastics generated from domestic and industrial usage of plastic is growing continuously. They are mostly landfilled or incinerated as conventional ways to the disposal of waste plastics. However, these methods are facing a great social resistance due to the air pollution and soil contamination [1]. In USA, more than 15 % of total municipal solid waste (MSW) was incinerated in 1990; only about 1 % of posts – consumer plastics were recycling [2-4]. In Japan, the percentage of MSW, as a fraction of MSW, that was landfilled in the early 1980s was estimated to be 45 %, incineration was 50 %, and the other 5 % was subjected to separation and recycling[5]. In Thailand, plastic wastes from household, industrial process, and market are 2.5 million ton per year. 1.3 million ton for lanfill and the other for incineration and recycling [6].

Plastics waste recycling can be categorized into four modes [7]. Primary recycling deals with conversion into products similar in nature to the original product. Secondary recycling involves conversion into products of different forms for less demanding applications. Tertiary recycling converts wastes into basic chemicals or feedstocks. Quaternary recycling retrieves energy from wastes through combustion. Nevertheless, plastics waste after numbers of primary and secondary recycling steps have to be treated in the tertiary of quaternary mode. Due to strong opposition from the public regarding the incineration of waste materials, this method can no longer be an important mode of waste recycling. In Germany, Japan, USA and elsewhere, most of these R&D programmes in the petroleum and petroleum chemical companies deal with hydrolysis, methanolysis, and ammonolysis for condensation of polymers such as polyurethane; hydrogenation, pyrolysis, gasification, hydrocracking, coking and

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visbreaking for addition of polymers such as polyolefins, polystyrene and poly(vinyl) chloride; and catalytic cracking. Thus, liquefaction have been a possible recycling method for plastic [8].

Polyethylene (PE) is the most extensively used plastic, relative low cost, its resistance to chemicals and its flexibility are also strong influences. Polypropylene (PP), with the wide range of properties, has been applied to extremely versatile materials. It can be made flexible or very stiff, tough or very strong, transparent or opaque. PP is used for a huge variety of applications: fibers, tapes, film, and sheet board. Polystyrene (PS) is characterized by great rigidity, high surface gloss and excellent transparency. In addition, it is very easy to process, because of its good flow properties. For this reason, PS has widely been used for various purposes [9].

The plastics that mostly used in Thailand are Polyethylene (PE), Polypropylene (PP), and Polystyrene (PS) [10]. Pyrolysis of mixed plastics route is favored because of the high rate of conversion into oil can be obtained [11]. This technology is one approach that macromolecular structures are broken down into smaller molecules and a wide spectrum of hydrocarbon as a liquid fuel.

For this reason, it is very interesting to investigate to see if the waste plastics are able to be produced as liquid fuel and also its chemical properties.

1.2 Objectives

The objectives of this work are:

1.2.1 To study influence of temperature in thermal and catalytic cracking process that affects on final product of mixed polymer (PE, PP, and PS)

1.2.2 To study efficiency of using catalyst (HZSM-5) incorporated in pyrolysis process.

1.3 Scope of the Study

The scopes of this work are:

1.3.1 Material used in this study is mixture of polyolefins i.e. PE ,PP, and PS with the same content. These kindly supported by Thai Petrochemical Industry Public Company Limited (TPI).

1.3.2 There are two steps involve with pyrolysis process they are

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(1) Thermal cracking process

(2) Catalytic cracking process

1.3.3 To study the performance of using HZSM-5 as a catalyst in fixed – bed reactor compare to the system without catalyst.

1.3.4 Final product will be distillated by fractional process. That obtained Gasoline will be further analyzed BTX content by Gas chromatography.

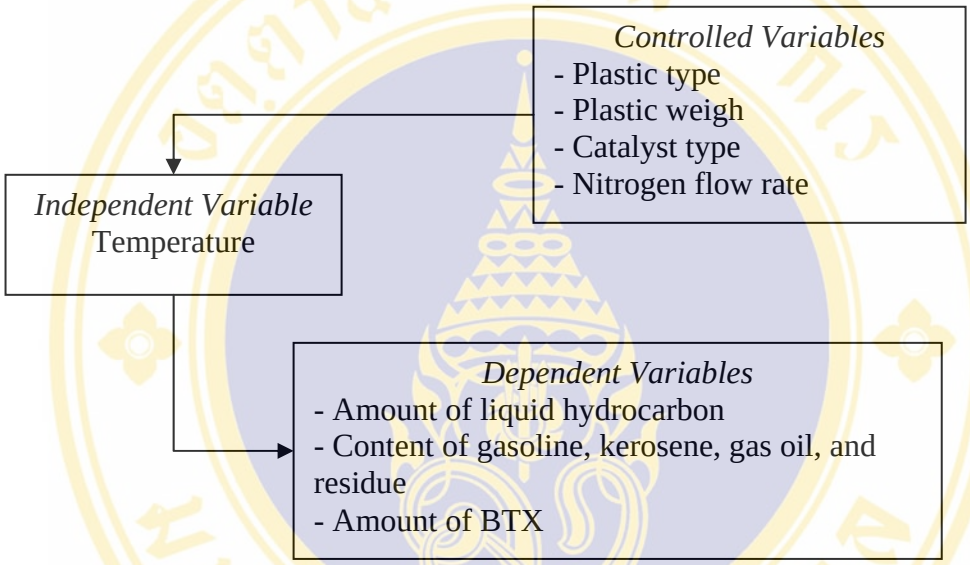

Figure 1-1 Conceptual framework

1.4 Expected Outcomes

1.4.1 To understanding relation between temperature and the final liquid product from pyrolysis process.

1.4.2 To obtain the optimal condition for pyrolysis process of mixed polymer.

1.4.3 To obtain the highest content of gasoline from final product.

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CHAPTER 2
LITERATURE REVIEWS

2.1 General description of Polyethylene (PE) [12]

Polyethylene is the most extensively used thermoplastic. The increasing demand for PE is partly due to the availability of the monomer from abundant raw materials. The ease of processing of the polymer, its relative low cost, its resistance to chemicals and its flexibility are also strong influences.

High pressure polymerization of ethylene was introduced in the 1930's. The discovery of new titanium catalyst by Karl Ziegler in 1953 revolutionized the production of linear unbranched polyethylene at lower pressures. The two most widely used grades of polyethylene are low-density polyethylene (LDPE) which has branched chains, and high-density polyethylene (HDPE), which is predominantly linear. Low-density polyethylene is produced by free radical initiated polymerization at high pressure while high – density polyethylene is produced by low - pressure process with metallic oxide catalyst of the Ziegler type. Several processes can produce polymers with a wide range of densities that cover both the low and high-density ranges as well as medium density polymers.

2.1.1 Physical and Chemical properties [13]

The mechanical properties of low-density polyethylene are between those of rigid materials like polystyrene and limp plasticized polymers like the vinyls. Polyethylene has good toughness and liability over a wide temperature range.

The electrical properties of polyethylene are outstandingly good. In thick sections polyethylene is translucent because of its crystallinity, but high transparency is obtained in thin film. Polyethylene is very inert chemically. It does not dissolve solvent at room temperature, but it slightly swelled by liquid such as benzene and carbon tetrachloride which are solvents at higher temperature It has good resistance to acids and alkalis.

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Polyethylene ages on exposure to light and oxygen. With loss of strength, elongation, and tear resistance.

--- [---CH_2----CH_2---]$_n$----

Figure 2- 1 Repeating unit of polyethylene [14]

2.2 General description of Polypropylene (PP) [15]

The production of polypropylene is made by polymerization of propylene in the presence of Ziegler catalyst. Recently, the used of metallocene catalyst in the production of polypropylene has increased due to the capability of control and design of the structure of polypropylene. There are three structural types of polypropylene (Figure 2-2) depending on the stereochemistry of the methyl groups in the macromolecule: [13]

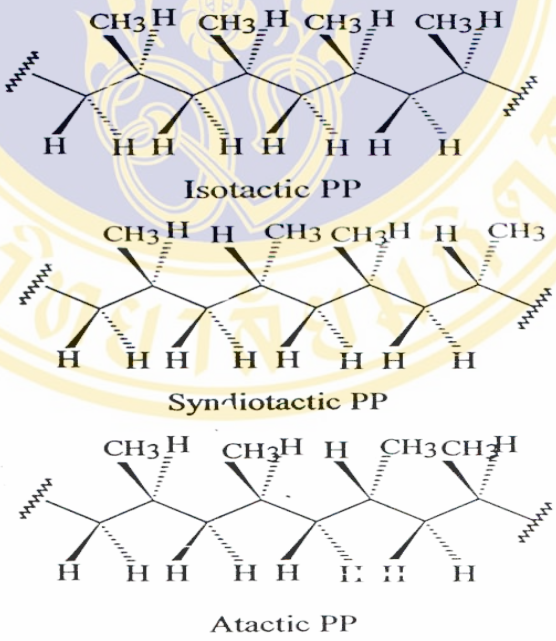

Figure 2-2 Schematic Molecular Structures of Polypropylene [15]

In isotactic polypropylene, the methyl groups are on the same side the carbon chain.

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In syndiotactic polypropylene, the methyl groups are alternated on the carbon chain.

In atactic polypropylene, the methyl groups are randomly distributed in their spatial relationship to main chain.

There are three distinct classes of polypropylene copolymer have different application areas. Random copolymer, obtained by copolymerization of mixtures of propene and the other α-olefins such as 2-6 % of ethylene, have lower melting point and improved clarity. Impact (Block) copolymer, made in two-stage polymerization process is high – impact strength grades that contain 10-40 % wt. of dispersed propene-ethylene elastomer

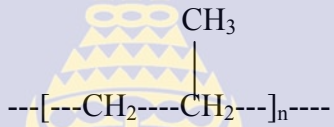

Figure 2- 3 Repeating unit of polypropylene [16]

2.2.1 Physical and Chemical properties [13]

Polypropylene is the lightest major plastic. Its high crystallinity imparts to it high tensile strength, stiffness, and hardness. The resulting high strength - to – weight ratio is and advantage in many applications. The high melting point of polypropylene allows well-molded parts to be sterilized. The other physical properties are shown in Table 2-2

Table 2-1 Properties of Polypropylene

Properties of Polypropylene	
Tensile strength	3,200 - 5,000 psi
Elongation	3 – 700%
Melting point, T_m	176 °C
Water absorption, 24 hr	0.01 %

Source: [12]

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2.3 General description of Polystyrene (PS) [17]

Polystyrene is a thermoplastic resin used in many applications Because of its low cost and easy processability. Styrene can be polymerized with other monomers. Polystyrene homopolymer produced by free radical initiators is highly amorphous.

There are three common grades of commercial polystyrene: easy-flow, intermediate-flow, and high heat. The choice of resin grade depends mostly on the fabrication method used and on the end-use application. Easy - flow resins are the lowest molecular weight resins, and usually contain 3 to 4 % added mineral oil to decrease melt viscosity and increase melt flow rate. Easy- flow resins are mostly used for injection molding. Intermediate-flow resins have melt flow and physical properties between the other grades, intermediate molecular weight, and about 1 to 2 % mineral oil added. High- heat resins have the highest molecular weight and contain the fewest additives. No mineral oil or other flow aids are added.

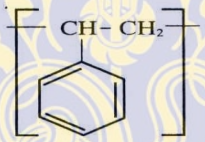

Figure 2- 4 Repeating unit of Polystyrene [12]

2.3.1 Physical and Chemical properties [17]

Polystyrene is an amorphous polymer. It is clear and colorless with excellent optical properties and high stiffness. It is brittle until biaxially oriented, at which time it becomes comparatively flexible and durable. The other physical properties are shown is Table 2-2.

Table 2-2 Typical properties of Polystyrene

Properties	
Specific gravity	1.05 g. / cu.cm.
Tensile strength	7000 p.s.i.
Flexural strength	1200 p.s.i.
Typical shrinkage	0.0045 in./in.
Elongation	2 to 3 %

Source: [17]

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Polystyrene has natural resistance to property loss from gamma sterilization. It is soluble in aromatic solvents and certain ketones and can be solvent bonded with methylethyketone (MEK)

2.4 Zeolite Catalyst [18]

Zeolites are water-containing crystalline aluminosilicates of natural or synthetic origin with highly ordered structured structures. They consist of SiO_4 and AlO_4 tetrahedra, which are inerlinked through common oxygen atoms to give a three-dimensional network through which long channels run.

In the interior of these channels, which are characteristic of Zeolites, are water molecules and mobile alkali metal ions, which can be exchanged with other cations. These compensate for the excess negative charge in the anionic framework resulting from the aluminum content. The interior of the pore system, with its atomic-scale dimensions, is the catalytically active surface of the zeolites. The inner pore structure depends on the composition, the zeolite type, and the cations. The general formula of zeolites is

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] .wH_2O$$

Zeolites are mainly distinguished according to the geometry of the cavities and channels formed by the rigid framework of SiO_4 and AlO_4^- tetrahedra. The terahedra are the smallest structural units into which zeolites can be divided. Linking these primary building units together leads to 16 possible secondary buildimg blocks (polygons), the interconnection of which produces hollow three-dimen-sional structures.

The entrances to the cavities of the zeolites are formed by 6-,8-,10-, and 12-ring apertures)small-,medium-, and widepore zeolites).

2.4.1 Production of Zeolites

Zeolite syntheses start from alkaline aqueous mixtures of aluminum and silicon compounds. The reactions are sometimes carried out at atmospheric pressure but more often in a high-pressure autoclave. The controlled crystallization of a particular zeolite requires careful control of the concentration and stoichiometry of the reaction partners, the temperature, and shearing energy of the stirrer. After mixing of the liquid

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aqueous phase occurs, whereby crystalline zeolites are formed from the amorphous particles.

2.4.2 Catalytic Properties of the Zeolites

In 1962 the zeolites were introduced by Mobil Oil Corporation as new cracking catalysts I refinery technology. They were characterized by higher activity and selectivity in cracking and hydrocracking. At the end of the 1960s, the concept of shape-selective catalysis with zeolites was introduced to petrochemistry (Selecto-forming process), and the zeolites became of increasing importance in catalysis research and applied catalysis.

No other class of catalysts offers so much potential for variation and so many advantages in application. Their advantages over conventional catalysts can be summarized as follows:

Crystalline and therefore precisely defined arrangement of SiO_4 AlO_4, te-trahedra. This results in good reproducibility in production.

Shape selectivity: only molecules that are smaller than the pore diameter of the zeolite undergo reaction.

Controlled incorporation of acid centers in the intracrystalline surface is possible during synthesis and/or by subsequent exchange.

Above 300 °C pentasils and zeolite Y have acidities comparable to those of mineral acids.

Catalytically active metal ions can be uniformly applied to the catalyst by ion exchange or impregnation. Subsequent reduction to the metal is also possible.

Zeolite catalysts are thermally stable up to 600 °C and can be regenerated by combustion of carbon deposits.

They are well suited for carrying out reactions above 150 °C, which is of particular interest for reactions whose thermodynamic equilibrium lies on the product side at high temperatures. Selhan K., [19] have studied co-processing of municipal waste plastics with HZSM-5. It showed good cracking activity at low temperature, it gave the liquid product containing highest sulfur amount.

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2.4.3 Shape Selectivity

We have seen that the inner pore system of the zeolites represents a well-defied crystalline surface. The structure of the crystalline surface is predetermined by the composition and type of the zeolite and is clearly defied. Such conditions are otherwise found only with single-crystal surfaces.

The accessibility of the pores for molecules is subject to definite geometric or steric restrictions. The shape selectivity of zeolites is based on the interaction of reactants with the well-defined pore system. A distinction is made between three variants, which can, however, overlap:

- Reactant selectivity
- Product selectivity
- Restricted transition selectivity

Reactant selectivity

Reactant selectivity means that only starting materials of a certain size and shape can penetrate into the interior of the zeolite pores and undergo reaction at the catalytically active sites. Starting material molecules that are larger than the pore apertures can not react

Especially ZSM-5 is used for shape-selective reactions. Numerous alkanes with various chain lengths and degrees of branching have been investigated.

In particular, the ability of ZSM-5 to cleave unbranched and monomethyl-branched alkanes with retention of more highly branched and cyclic isomers is exploited industrially in the dewaxing process to lower the solidification point of lubricants and in reforming processes to obtain high octane gasoline (M Forming process). ZSM-5 catalyst is able to convert polystyrene into fuel product that is mainly in the range of gasoline at high temperature of 550°C. [20]

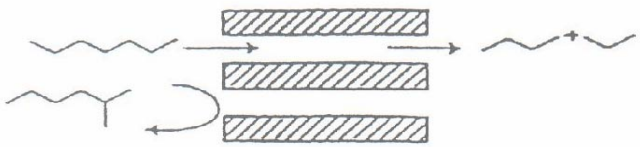

Figure 2- 5 Reactant selectivity [21]

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Product Selectivity

Product selectivity arises when, corresponding to the cavity size of a zeolite, only products of a certain size and shape that can exit from the pore system are formed. Well-known examples of product selectivity are the methylation of toluene (Fig. 2-6) and the disproportion of toluene on ZSM-5.

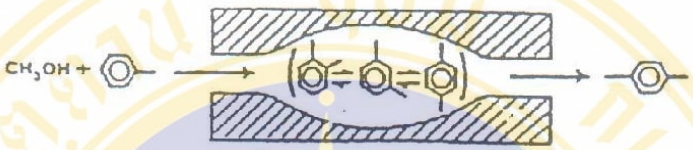

Figure 2- 6 Product selectivity [21]

Restricted Transition State Selectivity

This third form of shape selectivity depends on the fact that chemical reactions often proceed via intermediates. Owing to the pore system, only those intermediates that have a geometrical fit to the zeolite cavities can be formed during catalysis. This selectivity occurs preferentially when both monomolecular and bimolecular rearrangements are possible. In practice, it is often difficult to distinguish restricted transition state selectivity from product selectivity.

H-ZSM-5 is also used as catalyst in the large-scale MTG (methanol to gasoline) process. The products are hydrocarbons, aromatics in the benzene range, and lowed by numerous reactions that proceed via carbonium ion intermediates. The largest molecules observed, e.g., durene (1,2,4,5-tetramethylbenzen), correspond to the high-boiling components of gasoline. The favorable product distribution in this process can be attributed to restricted transition state selectivity.

Uemichi et al. [22] have studied conversion of polyethylene into gasoline – range fuel by two-stage catalytic degradation using silica – alumina and HZSM-5 zeolite. A two-stage catalytic degradation of polyethylene using amorphous silica-alumina and HZSM-5 zeolite catalysts in series has been developed for converting the polymer into high-quality gasoline-range fuels. Compared with the one-stage degradation over each catalyst, the two-stage method provides some advantages. It was an improved gasoline yield and high octane number despite low aromatic content.

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The resulting oils showed low quality, and they were transformed into high-quality gasoline on the strongly acidic sites of the HZSM-5 loaded in the lower layer at the expense of oil yield. Increase in concentration of isoparaffin and aromatics contributed to the upgrading.

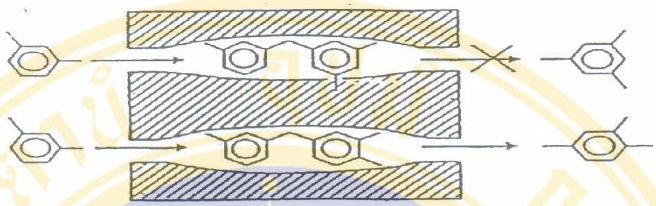

Figure 2- 7 Transient selectivity [21]

2.5 Mechanism of Cracking Processes

Cracking processes were assigned to two fundamental classes:

2.5.1 Thermal Cracking [23]

Thermal cracking, where free radicals (lacking one hydrogen atom on carbon atom in the hydrocarbon molecule) are intermediate species which cracked by a β - scission mechanism.

The most successful present explanation of thermal cracking of hydrocarbon is Rice free radical theory as modified by Kossiakoff and Rick. This will be called the "RK-theory" as follows to explain the cracking of normal paraffin:

The normal paraffin molecule loses a hydrogen atom by collision and reaction with a small free hydrocarbon radical or a free hydrogen atom, thereby becoming a free radical itself. This radical may immediately crack or may undergo radical isomerization prior to cracking. Radical isomerization presumably occurs through a coiled configuration of a single radical, in which the hydrogen donor and acceptor carbon atom much closely approach each other. Radical isomerization is a change of the position of hydrogen atom, usually to yield a more stable radical in order of tertiary > secondary > primary free radical.

Cracking of either the original or isomerized radical the takes place at a carbon-carbon bond located in the β position to the carbon atom lacking one hydrogen

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atom. Cracking at the β position gives directly an olefin and a primary radical (lacking one hydrogen atom on primary carbon atom); in this step no change of position of any hydrogen atom with respect the carbon skeleton.

The primary radical derived form this step may immediately recrack at the β bone to give ethylene and another primary radical, or it may first isomerizes. In the absence of radical isomerization, only primary radicals form cracking reaction of normal paraffin: primary radicals are deriving form cracking reaction of normal paraffin; primary radicals thus give only ethylene as the olefin product. Radical isomerization reduces the amount of ethylene, but it still remains the major product. By successive recracking, the radicals ultimately are reduced to methyl or ethyl fragments. These radicals then react with feedstock molecules to produce new free radicals and are themselves converted to methane or ethane. Thus, cracking is propagated as chain reaction

A schematic representation of polyethylene cracking is as follows;

1. Initiation Step

$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R_2 \xrightarrow{\text{heat, hv}} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} + R_2^{\bullet}$

2. Propagation Step

2.1 β-fission

$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} + CH_2{=}CH_2$

$R_1\text{-}CH_2\text{-}\overset{\overset{H}{|}}{C}H\text{-}\ CH_2^{\bullet} \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH{=}CH_2 + H^{\bullet}$

2.2 Chain transfer

$R_1\text{-}CH_2\text{-}CH_2\text{-}(CH_2)_4\text{-}CH_3 + H^{\bullet} \longrightarrow R_1\text{-}C^{\bullet}H\text{-}(CH_2)_4\text{-}CH_3$

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3. Termination Step

The high – temperature liquefaction of commingled post – consumer plastics, the reaction was carried out in a tubing bomb micro reactor with operating temperature of ~ 500 °C, hydrogen pressures of ~ 790 kPa cold reaction time of 0 - 30 min without catalysts, The commingled post – consumer plastics were converted to asphaltenes, oil , gas and coke. Maximum yield of liquid product was obtained at ~ 500 ° [5].

2.5.2 Catalytic Cracking [24]

Catalytic cracking is the most important and widely used refinery process for converting heavy oil into more valuable gasoline and lighter product. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced thermal cracking because of more gasoline having a higher octane and less heavy oil and unsaturated gases are produced

Commercial cracking catalysts can be divided into three classes:[25]

1. Acid-treated natural aluminosilicates
2. Amorphous synthetic silica-alumina
3. Crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves.

Most catalysts used in commercial units today are either class (3) or mixtures of classes (2) and (3) catalysts. The advantages of the zeolite catalyst over the natural and synthetic amorphous catalysts are:

1. Higher activity
2. Higher gasoline yields at a given conversion
3. Product of gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons

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4. Lower coke yield

5. Increased isobutane production

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 that free radicals. Acid catalysts such as amorphous silica alumina and crystalline zeolites promote the formation of carbonium ions.

Depolymerization of HDPE and commingled post-consumer plastic waste in autoclave reactor at 400-435 °C, 60 min, under H_2 or , N_2 with or without $TiCl_3$ or HZSM-5 as catalyst. The optimum oil yields were obtained over $TiCl_3$ catalyst, while the maximum gas yields were produced over HZSM-5 catalyst [26].

2.6 History Plastics Recycling [27]

Four events focused attention of plastics recycling prior to 1990. First was the oil crisis of the early 1970s. The synthetic rubber and plastics industries largely depend on petroleum and natural gas for both their energy needs and feedstock requirements. When the price of a barrel of oil began to skyrocket in the early 1970s, efforts turned to reusing the energy content or material content of plastics as an alternative to purchasing oil from oversees market. This stimulated a number of industries and government-led and government-led R&D initiatives from about 1975 until 1985 to explore technology for the recovery and recycling of scrap plastics. As one might expect, given the strong and lightweight properties of plastics, the automotive industry was the focus of much of this early R&D. It was broadly recognized that the expanded use of lightweight plastics would save gasoline though improved automotive fuel economy as well as provide additional energy and material conservation benefits if recovered and recycled.

Because of the concerns about an adequate and reliable supply of petroleum due to the pricing action of the Organization of the Petroleum Exporting Countries (OPEC), the 1970s also saw an interest in the development of bio-based feedstocks for the production of plastics and elastomers. In recent year this area has seen renewed attention as companies pursue their sustainability objectives and look to replace

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nonrenewable feedstock with renewable feedstock where economically and environmentally sustainable.

The second event that increased attention on plastics recycling was the establishment of a deposit fee on bottles for carbonated beverages. Although at the time the fee was imposed by several glass bottles predominated, as product manufacturers and bottle fillers increasingly turned to plastic bottles, a recycling infrastructure for the plastic was established. This infrastructure grew significantly during the 1980s. The plastic that predominated in the carbonated beverage market, and still does, was polyethylene tereophtalate (PET).

2.6.1 Basic plastics recycling definitions and nomenclature

As in any technical field, when communicating about the technology of plastics recycling, it is important to use common terminology and definitions. Early (pre-1970) terminology for commercial, industrial, and post consumer recycling of materials developed around the needs of the paper and textile recycling industries and the metal and glass recycling industries. After the first oil price shock of the 1970s, plastic recycling gained attention, and it soon became apparent that the recycling definitions and nomenclature for the other commodities did not apply adequately to the collection and recycling of plastics. The problem reflected both the unique properties of plastics along with their versatility and limitations in terms of some processing technologies.

Primary metals for the most part can be recycled into secondary metals that either have the purity to compete directly with primary metals in high-performance applications or have somewhat diminished properties and restricted applications. In all cases, the practical form of recycling is metal back to metal. The same is essentially true for glass-to-glass and fiber-to-fiber recycling. Plastics on the other hand have high energy content and can also be burned as fuel to recover their feedstock energy. The heat content of most commodity plastics is significantly greater than that of wood or coal. Many plastics can also be thermally or chemically depolymerized into monomers, petrochemical feedstocks, and fuels. The end result is that several forms of plastics recycling can be defined. D5033-00 describes the follow:

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Primary recycling is the processing of scrap plastic product into a product with characteristics similar to those of the original product.

Secondary recycling is the scrap plastic into a product that has characteristics different from those of the original product.

Tertiary recycling is the production of basic chemicals or fuels from segregated plastic scrap or plastic material that is part of municipal waste stream or other source.

Quaternary recycling is the useful retrieval of the energy content of scrap plastic by its use as a fuel to products such as steam, electricity, and so forth.

Primary and secondary recycling are often referred to as mechanical recycling since the principal recycling processes involve cleaning and separation of plastic by mechanical rather than chemical or chemical thermal means. Quaternary plastic recycling is not universally recognized by government agencies in the United States or Europe as a form of plastics recycling. Energy recover in the form of steam, hot water, or electricity by direct, controlled combustion of plastics as well as via the intermediate production of liquid, gaseous, or solid fuels from scrap plastic by thermal or chemical methods are often referred to as resource recovery process rather than recycling. In Japan, quaternary recycling is often referred to as thermal recycling and is include in the broad definition of plastics recycling.

There is also uncertainty in the regulatory status of tertiary recycling when it does not result in the direct production of monomers suitable for polymerization into new plastic. The European Commission has at times supported the chemical recycling (depolymerization) of condensation polymers such as polyethylene telephthalate back to monomer (e.g., dimethyl terephtalate) as recycling for the purpose of government-mandated plastics recycling rate calculations, but not the liquefaction of polyolefin plastics back to petrochemical feedstocks for reprocessing in a refinery. Discussion around these types of definitional issue, and environmental and economic implications, are likely to continue for many tears to come.

Lastly is the subject of postconsumer and preconsumer plastics, In the United States for the purpose of making recyclability recycling content claims for products, it is important to differentiate postconsumer from preconsumer plastics (16 CFR Part 260 Guides for the Use of Environmental Marketing Claims, available from U.S. Federal Trade Commission, www.ftc.gov). The paper industry now widely

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differentiates between postconsumer fiber and preconsumer fiber. The following definitions of postconsumer plastics are contained in ASTM D5033-00:

Postconsumer plastic: “Plastic material or finished product that has served its intended use and has been diverted or recovered from waste destined for disposal, having complete its life as a consumer item.”

Preconsumer plastic: “Plastic materials diverted from the waste steam following an industrial process, but excluding reutilization of material such as rework, regrind, or scrap generated in a process and capable of being reclaimed within the same process.”

The term posture plastic is sometimes used to cover both post consumer and preconsumer plastics. The above definitions are in line with the recycling industry’s position that scrap destined for recycling is not waste.

2.7 Polymer Recycling Technologies [28]

2.7.1 Melt Reprocessing

Reprocessing of generic thermoplastics recovered by sortation/ reclamation from post-consumer discard streams and industrial scrap regrind is done in conventional polymer processing equipment. The reclaimed resins are formulated in limited quantities with virgin resins and additives to obtain the desired properties in the plastic object being produce. These practical are different from those used in processing commingled polymer waste into plastic lumber applications. The present recycling rates for generic thermoplastics are quite low

Estimates of market penetration will depend on many factors in addition to cost; the nature of the market, desired properties for the plastic objects and the characteristics of the reclaimed resin will determine the permissible ratio of virgin/reclaimed resins, i.e. the recycle ratio. Of critical importance in determine the characteristics of the reclaimed resin is the extent to which degradation of the plastics has occurred during cycles of use and reclamation. However, studies by Throne suggest that products incorporation reclaimed polymers that have undergone significant reduction of physical properties in each recycle, may still retain an acceptable fraction of the virgin resin property level. The retention is a result of the

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incorporation of virgin resin un each recycle and the loss of old polymer into fraction that are not reclaimed. However, the extent to which reclaimed polymers can be reprocessed is an open issue requiring extensive further research.

The reprocessing of thermosets is not well advanced compare to thermoplastics. Reprocessing has been limited to the incorporation of reclaimed/reground resins into new polymer formulations with a minimum of flow or additional deformation occurring during processing. While few products are produced from reclaimed thermosets from waste stream, several commercial plants in Europe and Japan have been using SMC plant scrap as filler; similarly, plant scrap has been blended into PUR foams.

Development studies are focusing on maximizing the quantity of thermosets regrind that can be incorporated in phenolics, epoxies, PUR, BMC, SMC, and thermoplastics with acceptable properties and surface appearance. In principle, thermosets after being cured can be usable repeatedly since the degradation upon repeated recycles should be minimal. Synthesis of new thermally processable resins combining the flow characteristic of thermoplastics with the physical properties of thermosets would open up new recycling approaches.

Processing of mixed thermoplastics to produce marketable products is essential for the expansion of plastics recycling. Separation of many commingled polymers into generic resins cannot be done in a cost effective manner at this time. The processes currently available for fabrication of products from commingled plastics are limited to bulky products that can displace wood in some application areas. Compatibilization technologies will expand significantly the range of application areas.

2.7.2 Chemical Conversion

Step growth polymers such as polyester, polyamides and polyurethanes can be converted to their monomers or to oligomers/chemicals by solvolytic processes. Utilizing modification of current technologies it should be possible to recover in relatively high purity monomers from the PET, PUR, nylon 6 and nylon 6,6 polymers contained in the waste streams.

The commercial success of methanolysis and glycolysis processes for source separated PET beverage bottles reflects the importance and technical feasibility of

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these processes for step-growth polymers. This implies that waste feedstocks can meet certain specifications with respect to contamination levels. The technical feasibility of applying solvolytic processes such as hydrolysis and glycolysis has already been demonstrated in scale experiments for such complex mixtures as PUR foam/nylon fibers and PET/nylon 6.In addition to processing PET, PUR and nylons, solvolytic processes could be extended to feedstocks containing other step-growth polymers such as polycarbonates (PC) and polyureas and cured unsaturated polyesters.

Pyrolytic processes involve the heating of plastics to produce gases, liquid and solid residues, chars and inorganic fillers. However, in pyrolytic processes the decomposition of the plastic occurs at elevated temperatures during which oxygen is largely exclude. Consequently, it is not combustion that occurs, but rather a complex set of reactions that depends both on the plastics involved and the precise nature of the pyrolytic processes used. Among the possible reaction pathways are:

• Decomposition into monomers, e.g. PMMA [29]

• Fragmentation of the principal chains into organic moieties of variable size, e.g. PE and PP [30].

• Simultaneous decompositions and fragmentation, e.g. PS

• Elimination of the simple inorganic moieties leaving charred residues, e.g. PVC

• Elimination of side chains, followed by crosslinking

In addition, the course of the pathways can be modified by addition of controlled quantities of hydrogen or oxygen or the presence of contaminants (catalyst).

Pyrolysis, therefore, can be utilized to recover materials (monomers and other organic chemicals), fuel (liquid and gases) or both materials and fuels. Many pyrolytic processes to convert wastes to monomers, chemicals and liquid and gaseous fuel products have been studies and practiced on a limited commercial scale over the past 50 years. There are paper reviews recent development in plastics cracking, a process developed to recycle plastic waste into useful petrochemical materials. Under thermal cracking condition, plastic waste can be decomposed into three fractions: gas, liquid and solid residue. The liquid products are usually composed of higher boiling point hydrocarbon. Plastic cracking is only an elementary conversion technology; its application has to be combined with other technologies such as municipal solid waste

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collection, classification and pretreatment at the front end, as well as hydrocarbon distillation and purification at the back end [32].

K. Lee. et. al . [1] have reported the catalytic degradation of waste plastics such as polyethylene, polypropylene and polystyrene over spent fluid catalytic cracking (FCC) catalyst was carried out at atmospheric pressure , 400 °C. The catalytic degradation of waste polyethylene and polypropylene gave the liquid yield of 80-85 % and the solid yield of below 1% , waste of polystyrene produced much more liquid, solid product and much less gas products, Accumulative liquid product weight by catalytic degradation strongly depended on the degradation temperature of plastics.

In pyrolytic processes plastics waste are only feedstocks (for a given process technology) will depend on both the relative selectivity to the desire products and the cost structure. The embodied energy content of the plastic waste is not relevant, only the heat of combustion is. In most cases the recovery of embodied energy in pyrolytic process will not be significantly higher than combustion, i.e. waste-to-energy. The only exceptions are pyrolytic processes involving polymers to caprolactam that cannot be produced in one-step petrochemical processes.

All published studies and approximate calculations indicated that the maximum value of plastic wastes in most fuel and petrochemical processes will be in the range of 5-10 c/ib; this is equivalent to a crude oil price range of $ 15-30/ barrel. Moreover, it is reasonable to believe that value of plastics wastes (purity acceptable as a feedstock for pyrolytic processes) will fluctuate with price of crude corrected for any difference in the heat of combustion. Therefore, it is highly unlikely that plastic wastes will be economical for many pyrolytic processes unless their use is subsidized or legislatively mandated.

Polymers may be chemically modified in order to meet specific cost/performance/processability characteristics. Due to the limitation of unmodified resins, chemically modified products have found commercial applications in end-uses which could have been otherwise unattainable. Modification may involve single polymers or mixtures of two or more polymers. Reactive modification of single polymers may be accomplished with a variety of reagents or through radiation. Modification of polymer blends is usually accomplished through agents commonly

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known as compatibilizers that may be added separately, or formed in situ during mixing/compounding. In general, reactions are carried out in polymer solutions, in bulk, e.g. in the melt, or on the surface of the plastic part or pallets; the reactions may be promoted or retarded by a variety of foreign substances.

Recent advances in the technology and economics of modification for single polymers and polymer blends (particularly in the absence of solvents, as in reactive extrusion) suggest that this route of chemical conversion should be applicable to polymer wastes. However, all polymer wastes contain polymeric and other contaminants; the specific modification reactions may be affected to different degrees by these contaminants.

Selhan K. [13] have studied co-processing of municipal waste plastics with vacuum gas oil over HZSM-5 , DHC-8 (commercial silica – alumina catalyst) and cobalt loaded active carbon catalyst Co – processing experiments were carried out under hydrogen atmosphere at temperature between 425 and 450 °C . The product distribution and the composition of liquid were changed depending upon the temperature and the catalyst type. Cobalt loaded active carbon was neutral catalyst; it showed the cracking activity as well as HZSM-5 and more than DHC-8. HZSM-5 showed good cracking activity at low temperature, it gave the liquid product containing highest sulfur amount.

Fawzi A., Al-A. [32] studied liquefaction of polypropylene, polyethylene and polystyrene by oxidation with gas oil as a carrier and phenol as a catalyst was performed in an autoclave. Air pressure, temperature and reaction time were varied. The optimum cracking conditions were 0.7 MPa air pressure, 400 °C and 30 min reaction, yielding 32 wt % gasoline, 15 wt % kerosene and 27 wt % gas oil. The oils obtained can be used as chemical feedstocks.

E.-Y. Hwang. [33] have studied the degradation of polypropylene was carried out with mixture of polypropylene and catalyst at 400 °C. The liquid products from the catalytic degradation of polypropylene are distributed in narrower range of carbon numbers compared with those obtained by thermal degradation. The increase of temperature accelerated the cracking of intermediate degraded fragments to lower hydrocarbon.

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CHAPTER 3
RESEARCH METHODOLOGY

This study has been carried out in the Department of Chemical Engineering, Faculty of Engineering, Kasetsart University. The major studies in this work are spent on the influences of temperature on the final liquid product in a pyrolysis process of the plastic mixtures, and to determine the optimal condition for the highest yielding.. Only liquid in the gasoline fraction is further investigated to see, if it contains the amount of BTX exceeding the standard regulation established by law.

The following section describes the materials and equipments used in this study. Pyrolysis process and characterization techniques as well as methodology are also explained in this chapter. The overview of the experiment is illustrated in the Figure 3-1.

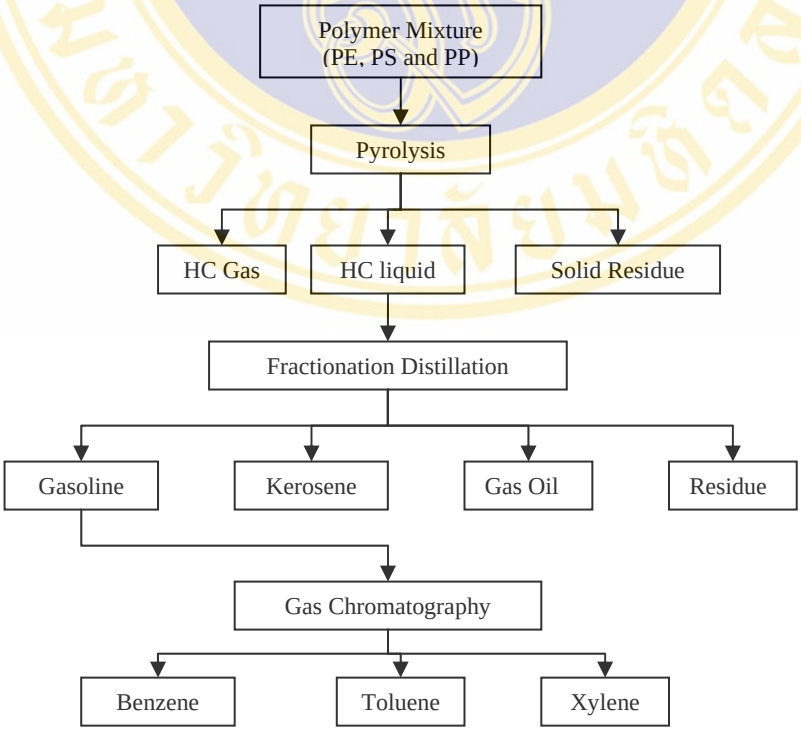

Figure 3-1 The Overview of the Experiment

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3.1 Materials and Equipments

3.1.1 Materials and Chemical reagents

1) Polyethylene (high density); PE
2) Polypropylene; PP
3) Polystyrene; PS
4) HZSM- 5 catalyst
5) Silica sand

All types of plastic used in this experiment are kindly supported by Thai Petrochemical Industry Public Company Limited (TPI). Each of plastic is characterized its thermal property by TGA as will be described in the next section. For this work, mixture of the 3 plastics is pyrolyzed. The mixture composes from the same amount of PE, PP and, PS by using the dry-blend technique.

During the study of temperature influence, silica sand is placed in the catalytic reactor as a fixed bed in thermal system. After the temperature study, effects of using catalyst are focused. Zeolite, named HZSM-5, is used as a catalyst in the pyrolysis process. It replaced the silica sand in the catalytic reactor. HZSM-5 is prepared from ZSM-5 by ion-exchange technique in the laboratory. The received HZSM-5 is primary analyzed its physical properties as will be explained in the following section.

3.1.2 Tools and Equipments

1) Packed – bed reactor
2) Thermogravimetric and Differential Thermal Analyzer TA Instrument (SDT 2960 Simultaneous DTA -TGA)
3) Gas chromatography; GC (Shimadzu GC-8APF)
4) Absorb -1 apparatus
5) Electric furnace
6) Distillation Apparatus
7) Digital balance
8) Gas syringes
9) Liquid syringes
10) Gas sampling bottom

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Packed bed reactor used in this study is illustrated in Figure 3-2. There is a reactor as called pyrolyzer attached to the pipe containing fixed bed identified as catalytic reactor. The pyrolyzer and catalytic reactor are temperature controllable chambers. During the pyrolysis reaction is taking place; the polymers are broken down into small hydrocarbon (HC) molecules. Nitrogen as a carrier gas is flowed into the pyrolyzer with a constant flow rate and carries the vaporized gases through the catalytic reactor and condenser. The final products, gas and liquid HC, will be collected in the suction flask connected to the condenser. The residue solid in the pyrolyzer, an unbreakable HC, is collected as well.

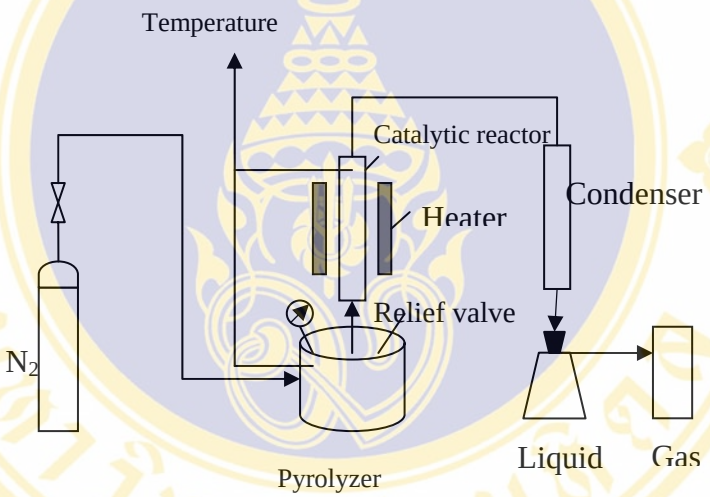

Figure 3-2 Diagram of experimental apparatus

3.2 Methodology

It is divided into 3 parts as follows: Catalyst preparation, Material characterization and Reaction study.

3.2.1 Catalyst preparation

ZSM-5 is ion-exchanged with 1 M ammonium nitrate ($NH_4NO_{3)}$ solution for 72 hr. The zeolite exchanged with NH_4^+ and then calcined at 400°C to obtain the proton (H^+) – exchange zeolites like HZSM-5.

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3.2.2 Material characterization

1) N_2 physisorption (Autosorb-1): The physical properties of HZSM-5 catalyst were determined using Autosorb-1 apparatus. The result of surface area, pore volume, and pore size are measured and reported in the next chapter.

2) TGA/DTA: Thermal properties of polymers, i.e. PE, PP, and PS, were analyzed by Thermogravimetric and Differential Thermal Analyzer for investigating the thermal characteristic of each plastic. The degradation temperature range of each polymers are verified and the result will be used for design temperature range in the experiment.

3.2.3 Reaction study

In the study of pyrolysis system, the experiment is divided into two parts as followed:

1) Study of the influences of temperature in the thermal pyrolysis

There are many parameters involved with pyrolysis process. This study focuses on the influences of the system temperature. The other parameters are kept constant as shown in the table 3-1.

Table 3-1 Conditions for studying the influence of temperature in pyrolysis reaction

Condition	Temperature (°C)		Material in Packed bed	N_2 flow rate (ml/min)	Reaction time (min)
	Pyrolysis Chamber	Catalytic reactor			
1	400	400	silica sand	60	90
2	450	450	silica sand	60	90
3	500	500	silica sand	60	90

For the thermal pyrolysis system, the study focuses on the temperature of the system that affects on the reaction and final product. The temperatures in both of pyrolyzer chamber and catalytic reactor are similar and varied from 400, 450, and 500 °C. Other parameters such as weight of plastic mixture, N_2 flow rate, and reaction time are kept constant at 60.0 g, 60 ml/min, and 90 min, respectively. All reactions in this work have been done under atmosphere pressure. The final product from the reactor are in liquid, solid (as residue), and gas form. After reaction time has reached, liquid and solid product will be weighted. The amount of gas product is calculated by balancing from the weight of initial raw materials and final liquid and solid product.

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From the pyrolysis reaction, the interesting product is in liquid form. The weight of liquid product will be used for calculating the yielding of reaction. The liquid product is then processed by fractionation distillation according to ASTM D68 for examine its composition.

Products from fractionation distillation are gasoline, kerosene, gas oil, and residue. Each of them is weighed and determined its ratio. The major product, gasoline, is further analyzed its component by gas chromatography. Benzene, Toluene and Xylene or BTX are obtained. The amount of benzene in gasoline is necessary to know in the case that gasoline will be used as a fuel of an engine.

2) The study of the influences of temperature in the catalytic reaction.

In the pyrolysis reaction, catalyst is often used to increase the efficiency of the system. This study also determines the efficiency of using HZSM-5 as a catalyst in the pyrolysis process. The temperature of the catalytic reactor is varied as well. The temperatures and other parameters are listed in the Table 3-2. The product analysis has been carried out as described above similar to the previous section (the study of the influences of temperature in the thermal pyrolysis)

Table 3-2 Conditions for studying the influence using catalyst and temperature in catalytic reaction

Condition	Temperature (°C)		Material in Packed bed	N_2 flow rate (ml/min)	Reaction time (min)
	Pyrolysis chamber	Catalytic reactor			
1	500	300	HZSM-5	60	90
2	500	350	HZSM-5	60	90
3	500	400	HZSM-5	60	90
4	500	450	HZSM-5	60	90
5	500	500	HZSM-5	60	90

3.2.4 Liquid analysis

The liquid hydrocarbons from both pyrolysis system are fractional distillated. Fractional distillation is the method for refining mixed-liquid hydrocarbon which possess different boiling point. Fractional distillation can be done following the standard method ASTM D 68 by using petroleum distillation apparatus. Distillation occurs in this method by difference of boiling points. That is, when temperature in the

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distillation system increase, a lowest boiling point hydrocarbon will reach its boiling temperature and evaporated to be a gas. The gas then will be condensed in condenser. Other liquid hydrocarbon in a mixture will also be evaporated at their boiling point therefore the separation can be occurred.

Methodology of fractional distillation

1) Place some ice and water into condenser behind the distillation apparatus

2) Fill a mixture of liquid hydrocarbon into distillation flask with 5 glass balls.

3) Insert the thermometer which is able to measure the temperature up to 400°C into rubber lid. Attach them to the distillation flask then place on heating mantle.

4) Turn on distillation system to heat up liquid hydrocarbon to initial boiling point (IBP) then the first fraction of liquid hydrocarbon (gasoline) start to be collected until the temperature is raised up to 200°C, the following fractions of kerosene and gas oil are collected at the temperature ranging of 201 -250°C and 251 - 370°C. The remaining at the bottom of the flask is residue. The flask with residue is allowed to be cool down to room temperature then weight

5) Only obtained fraction of gasoline is subjected to be analysis for Benzene, Toluene and Xylene (BTX) by using Gas chromatography

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CHAPTER 4
RESULT AND DISCUSSION

The study of pyrolysis reaction for polymer mixture is the major concern in this work. The optimal condition giving the highest yield is focused.

In this chapter the results is reported. The study can be classified into two major parts. First part, the materials analysis will be reported and discussed. Polymers i.e. PE, PP, and PS were analyzed by thermogravimetric technique. The catalyst, HZSM-5, was analyzed in term of surface area, pore volume, and pore size. In the second part, the thermal pyrolysis was determined. The optimal condition of reaction, which obtained highest liquid yield, was study. The catalytic pyrolysis reaction was study as well. The comparison of the efficiency by pyrolysis with and without catalyst is in the interest and will be discussed in the last section of this chapter.

4.1 Materials characterization

4.1.1 Catalyst characterization

Catalyst used in this work is a porous Zeolite named HZSM-5, prepared in the laboratory. Surface area, pore size, and pore volume were analysis by Autosorb-1. The results are presented in the Table 4-1 as follows:

Table 4-1 Properties of HZSM-5 catalyst

HZSM-5 catalyst	
surface area (m^2/g)	251.5
pore volume (cc/g)	0.1066
pore size (A^o)	13.4

From the result, pore size of HZSM-5 catalyst is 13.4 A^o. This result indicate that this catalyst have a microspores structure which is an effective character for being used as a catalyst in pyrolysis reaction. This structure allows small molecules of

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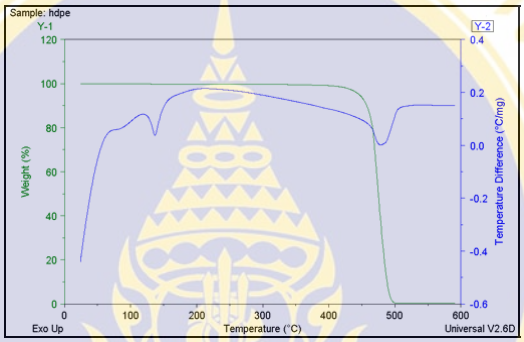
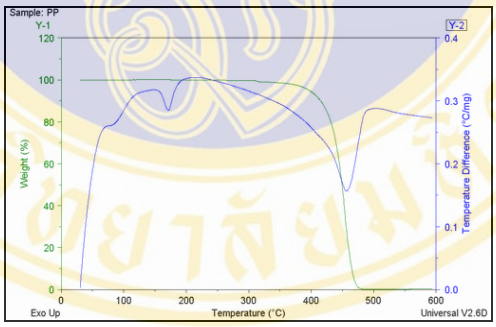
hydrocarbon such as methane pass through and reformation of a small molecule can be happened as well.

4.1.2 Thermal pyrolysis process

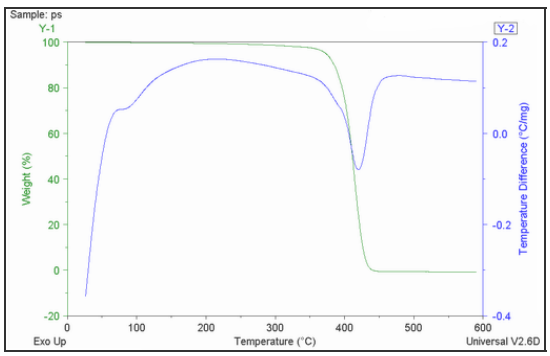
PE, PP, and PS were materials used for pyrolysis in this work. In order to understand the thermal characteristic of these materials (PE, PP, and PS), investigation of the initial and final degradation temperature were determined. Thermogravimetric analysis was performed and the results of each polymer were illustrated in Fig.4-1.



(a) Polyethylene (PE)



(b) Polypropylene (PP)



(c) Polystyrene (PS)

Figure 4-1 Thermogravimetric curve of PE, PP, and PS

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The initial degradation temperature is the temperature that a polymer weight started to decrease. From the thermogravimetric curves in Figure 4-1 (a)-(c) show the initial degradation temperature of PE, PP, and PS at 415, 315, and 350°C, respectively. The final temperature is the temperature that degradation of PE, PP, and PS is completed. They are correspondingly shown at the temperatures of 500, 450, and 444 °C. The difference in thermal behavior could obviously be attributed to the molecular structure and degradation mechanism. PE and PP thermal degradation consist of free radical formation and hydrogen abstraction steps whereas PS thermal degradation is radical chain process including initiation, transfer, and termination steps [N.Kiran]. The degradation temperature of PE in this work is higher than PP and PS because of its structure is branch. The degradation temperature ranges of the three polymers were concluded again in Table 4-2.

Table 4-2 Temperature of polymer .

Polymer type	Initial temperature (°C)	Final temperature (°C)
Polyethylene (PE)	415	500,
Polypropelene (PP)	400	450
Polystylene (PS)	378	444

4.2 The study of pyrolysis reaction

4.2.1 Effect of thermal pyrolysis temperature on liquid product.

At present, the thermal pyrolysis process is more interesting. Many attention were paid on possibility to use this process for plastic recycling to obtain liquid hydrocarbon as final product. Most of the studies were focused on pyrolysis reaction of a single polymer. This work studies about thermal pyrolysis process of plastic mixture which is more rarely studied and was considerate to be useful in the case of the materials are a mixed plastic waste.

From the previous section, the degradation temperature ranges of PE, PP, and PS indicate that the temperature used in pyrolysis process for the polymer mixture should be in the range of 400-500 °C. In order to obtain optimal temperature, the

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temperatures of pyrolyzer and catalytic reactor were similarly set and varied from 400, 450 to 500 °C. The reaction time is 90 min for all condition, nitrogen flow rate was kept constant at 60 ml/min and all reactions were done under atmospheric pressure. All condition is prior concluded in the previous chapter (see Table 3-1). Silica sand was packed in catalytic reactor for controlling the retention time of the reaction. The products of pyrolysis reaction were concentrated and consequently characterized.

Products from thermal pyrolysis were classified into three forms i.e. liquid, gas, and solid. Hydrocarbon liquid is focused as main product, which can be further distilled to yield gasoline, kerosene, gas oil, and residue. The gasoline, kerosene and gas oil are hydrocarbon substance that compraise of $C_6 - C_8$, $C_1 - C_4$, and $C_1 - C_4$, respectively. In case of gas product is also hydrocarbon substances which contain carbon in the range of $C_1 - C_4$, i.e. methane, ethane, ethylene, and propane. The solid content which is unbreakable macromolecule and remains in the pyrolyzer is residue. The result of temperature study for thermal pyrolysis at different temperature is shown in Figure 4-2

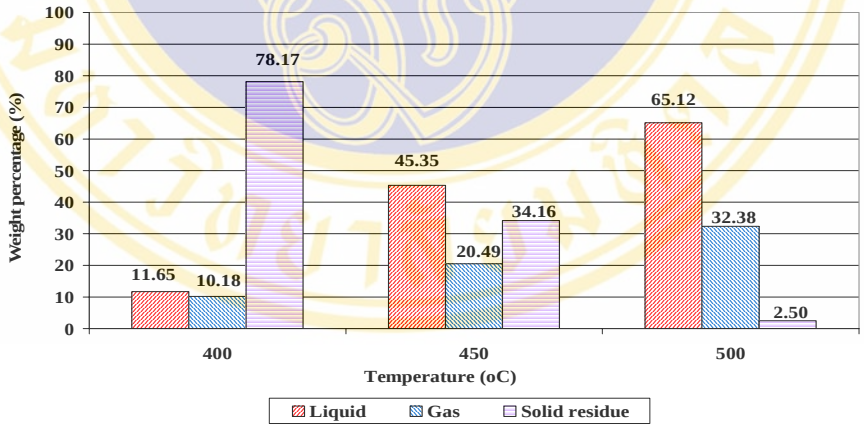

Figure 4-2 Product from thermal pyrolysis.

From the Figure 4-2, the temperatures can differently affect the final product of the pyrolysis reaction. When temperature is raised up from 400 to 450 and 500 °C, the liquid hydrocarbon product is increased from around 12% to 45% and 65%, respectively. In contrast, the solid content (as residue) is decreased from approximately 78% to 34% and 3% when the temperature is increased. It must be note that when the reaction has been done at 500 °C, the reaction time needs only 40 min to

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be completed. These results can be explained by referring to the degradation temperature from the previous section. At reaction temperature of 400 °C, all polymers are initially degraded then only little cracking took place, but at 500 °C the degradation of all polymers can be completed more perfectly, so cracking at this temperature yields the higher amount of the liquid and gas product. These results are consistant with work done by A.Demirbas [34] who found that the yield of liquid product increase with increasing pyrolysis temperature. In case of amount of liquid obtained, it is appeared that close to the results obtained by Chompunut, 58.40% liquid yield and 41.60% gas yield, who work on thermal cracking of PE with nitrogen flow rate at 60 ml/min, under atmospheric pressure at reaction temperature of 500°C[35]. While Monnut have reported the amount of liquid hydrocarbon yield and gas yield of 57.57% and 42.43% at 500°C, using PP without catalyst at the same reaction condition [36].

Regarding, the results of liquid hydrocarbon yield obtained from thermal coprocessing of mixed polymers (65.12%), it is found to be similar to the degradation of single polymer (58.40% and 57.57%) while the obtained gas yield is lower However, the differences have occurred in the solid residue from the mixture pyrolysis. In comparison with work done on thermal cracking of single polymer; waste PE using fluidized–bed at 400°C, the results is quite highly differences when the product of liquid, gas product, and residue found only 3.1%, 2.4% and 93.5% respectively [37]. In addition, the thermal cracking at 380 °C of PP done by Yusaku et.al. [38] have reported highly amount of liquid product, gas product and residue at 64.9%, 24.7 % 10.4 %, which is contrast to results from this work at 400°C (11.65%, 10.18% and 78.17%). The superiority of product yield of 81.0% of liquid yield, 8.5% of gas, and 9.8% of residue by the reaction at 400°C of PS without catalys in semi-batch reactor with N_2 flow rate of 60 $mlmin^{-1}$ [39]. Accordingly, Kim, J.R. [40]have presented the product yields of 75.1% of liquid product, 10.3% of gas and 14.6% of residue for the thermal degradation of mixed plastics (PP+PS) at 400°C for 120 min.

As earlier mentioned, the liquid hydrocarbon product is a major concern. The reaction temperature at 500 °C will be used for further studies of catalytic pyrolysis, due to this condition yields the highest content of liquid hydrocarbon. In addition, this

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temperature also yields the lowest undegradable solid in pyrolyzer and need the shorter reaction time to complete the reaction as well.

The liquid hydrocarbon product from each condition is further distilled and analyzed. The technique used in this study is fractional distillation which can separate the liquid mixture by the different boiling point of each liquid in the mixture. The product after fractional distillation is gasoline, kerosene, gas oil, and residue. The reaction of pyrolysis at different temperatures yield the different amount of liquid product which imply from their compositions as can be seen in Figure 4-3.

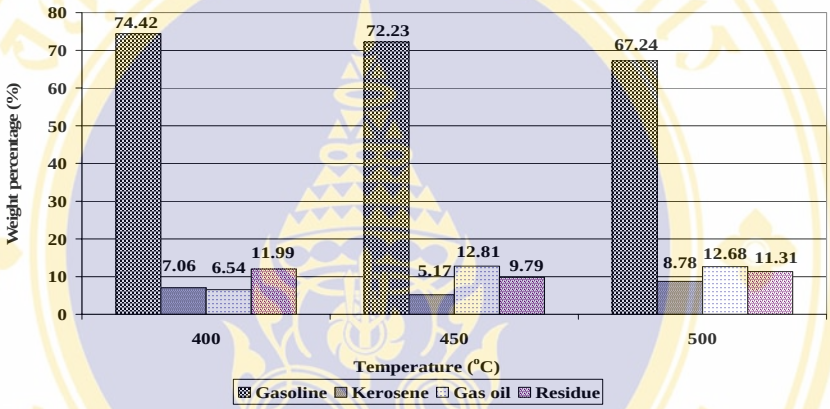

Figure 4-3 Liquid hydrocarbon from fractional distillation of thermal cracking processes

In Figure 4-3, it can be seen that the main component of liquid product is gasoline. The liquid product of gasoline obtained from condition of 400, 450 and 500 °C is slightly decreased from approximately 74% to 72% and 67 wt%, respectively. The other components, kerosene gas oil, and residue are also slightly varied with different reaction temperatures. As we can see variation of kerosene is slightly (7.06, 5.2 and 8.8) while little changing (6.5, 12.8 and 12.7) in gas oil and rather stable (12.0, 9.8 and 11.3) in residue are appeared.

Gasoline, the major component, obtained from the fractional distillation is additional analyzed by Gas Chromatography (GC). The results of Benzene, Toluene, and Xylene concentration, the principal aromatic from PE and PP degradation [41], are illustrated in Fig.4-4. It can be seen that at 400 °C the concentration of benzene is 3.57 mol/l but it is decreasing to 0.187 and 0.535 mol/l when the temperatures are rising up

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to 450 and 500 °C. At low temperature the benzene concentration is highest because small molecules are cracking down to benzene radical, stable structure,. At high temperature polymers are able to break down better low temperature, the free radical can be formed new structure like toluene and xylene more than benzene.

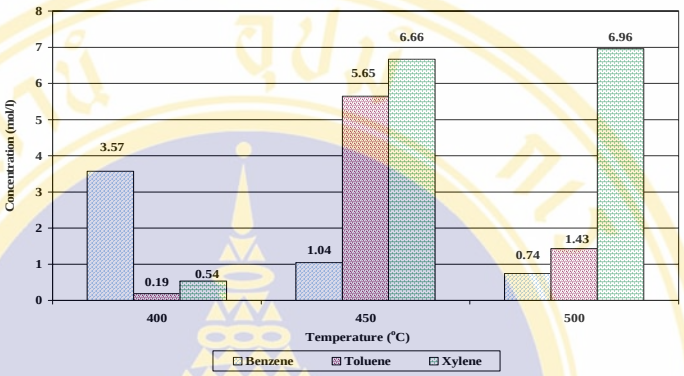

Figure 4-4 Benzene, Toluene, and Xylene from thermal cracking processes

4.4 Effect of catalytic pyrolysis temperature on liquid product

Catalytic pyrolysis is pyrolysis system, which use HZSM-5 catalyst placed in catalytic reactor, in order to improve thermal pyrolysis. The experimental condition of this catalytic reaction is temperature which is varied i.e. 300, 400, 450, and 500 °C. Other parameters such as weight of plastic mixture, N_2 flow rate, reaction time, and pyrolyzer temperature are kept constant at 60.0 g, 60 ml/min, 90 min, and 500 °C

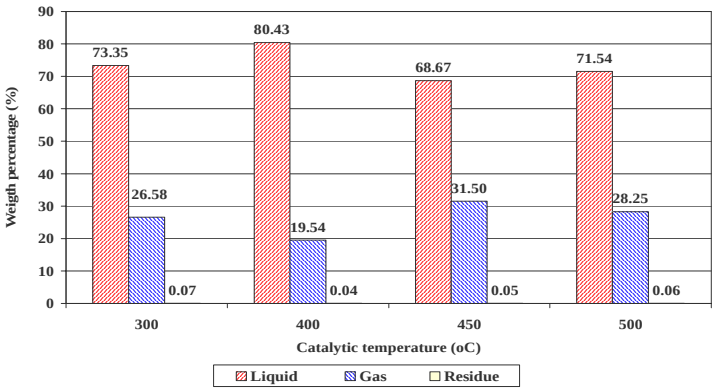

Figure 4-5 Products from catalytic cracking processes

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The products from catalytic pyrolysis are liquid, gas, and solid similar to thermal pyrolysis system. The weight percentage of each product are illustrated in Figure 4-5. It can be seen that the highest amount of liquid product (80.43%) with the lowest amount of gas (19.54%) and residue is appeared at 400°C, meaning the suitable reaction temperature for this catalytic pyrolysis is 400°C. However, the liquid hydrocarbons of 73.35%, 68.67%, and 71.54% at 300°C, 450°C, and 500°C are more or less the same. The trend of gas product of 26.58, 31.49, and 28.25% at 300°C, 450°C, and 500°C is reversely higher than that of 400°C, showing liquid products are cracking down to smaller molecule of gas at the temperature above 400°C.

N.Miskolczi have reported the yield of HDPE waste cracking with HZSM-5 at 400°C and 450°C, it is appeared that the products yield of liquid, gas and residue at 400°C and 450°C are 14.3%, 12.0%, 73.7% and 81%, 15.1%, 3.9% [37]. While work done by Y.-H. Lin [42] yield of liquid from catalytic pyrolysis of HDPE at 360°C over HZSM-5 is only 1.26% and the main product is gas (94.21%).

However, S.Y. Lee have reported the degradation of PS for 2 hr at 400°C that the liquid oil is main product (75.1%) [43]. While the liquid yield obtain in catalytic cracking of PS at 375°C done by Serrano et.al [44], using reaction time 30 min for plastic/catalyst mass ratio 18 is in range 60-70%.

Work done by Lin and Yen [45] found that the main products of PP degradation at reaction temperature of 360 °C over HZSM-5 catalyst are 2.31% of liquid, 94.77% of gas and 3.92% of residue. While the product yields for catalytic degradation of PP by Sakata et.al at 380°C are 47% liquid, 50% gas, and 3.0% residue

The products from degradation of the mixture of PP and PS, at 400°C for 120 min, with HZSM-5 catalyst are 61.4% of liquid, 28.3 of gas and 10.3% of residue [40].

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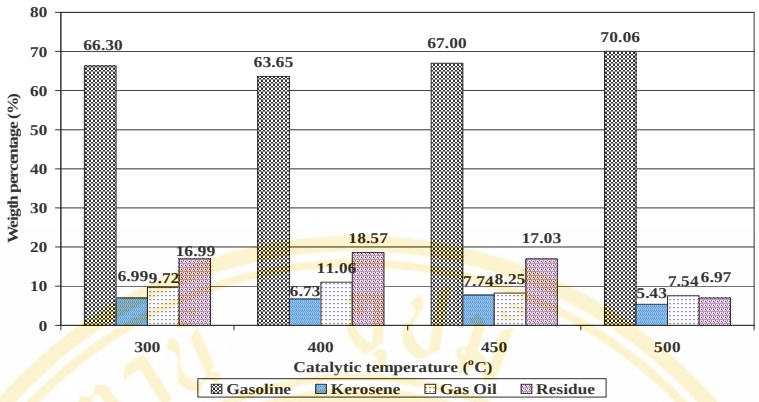

Figure 4-6 Products from fractionation distillation of catalytic cracking system

From Figure 4-6, the gasoline products of 66.30%, 63.65%, 67.00%, and 70.06 % by weigh are of the catalytic reaction at temperatures of 300°C, 400°C, 450°C, and 500°C respectively.

The obtained kerosene at different reaction temperature (6.98, 6.73, 7.74, and 5.43) is nearly constant at the weight approximately of 7 %. In case of gas oil contents in liquid hydrocarbon of 9.72%wt, 11.06%wt, 8.25%wt, and 7.54%wt at 300 to 500 °C appear to be slightly different. However, the appearance of residue after distillation is highest at catalytic temperature of 400°C, in which it is the suitable condition that the highest liquid hydrocarbon yield is obtained. It can be seen that, although amount of liquid hydrocarbon is hightly raised up but amount of gasoline become unchange, while the addition has gone to gas oil and residue. These results are quite different to work done by Garforth, A.A which gasoline from HZSM-5 catalyzed degradation of HDPE at different reaction temperature (from 290 to 430°C), fluidizing with N_2 rate of 70 $mlmin^{-1}$ and using 40%wt/wt of polymer-to-catalyst, total reaction time of collection 30 min, are decreased with increasing reaction temperature (31.42%, 30.29%, 27.09%, 26.04%, and 24.80%) [46]. Similar yield of gasoline (28.06%) from pyrolyzed HDPE over HZSM-5 catalyst at 360°C is demonstrated by Y.H.Lin [42]

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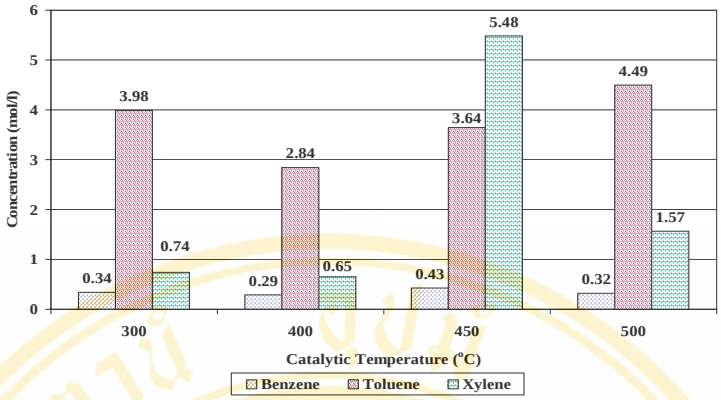

Figure 4-7 Benzene, Toluene, and Xylene from catalytic cracking processes

After liquid hydrocarbon is fractional distilled, the products of gasoline are directly subjected to analysis by using Gas chromatography into benzene, toluene, and xylene (BTX). The BTX of catalytic pyrolysis system present in term of concentration. Benzene concentration is clearly smaller than toluene and xylene. The most product of BTX is toluene in every experiment (3.98, 2.83, 3.64 and 4.49), except for at reaction temperature of 450°C, xylene concentration is of 5.48 mol/l in gasoline. This result seem to be clear in the effect of temperature to xylene conversion. This aromatic formation is evidence and consistent with work done D.W. Park [47] who found the amount of xylene higher than toluene and benzene (45.7% of xylene, 15.4% of toluene, and 0.7% of benzene) in the catalytic degradation of PE at 450°C for 1 hr. This might be due to close retention time of derivative compounds to peak of xylene are occurred and overay with xylene peak area causing unrealistic result. From the obtained results, the most selective product is, therefore, toluene in most catalytic temperature experiments and xylene is most selective product at 450°C. S.Y. Lee et.al [43] have reported a similar result to selectivity of aromatic formed is toluene as main product (toluene>xylene>benzene) in catalytic degradation of PS at 400°C.

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CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The conclusion can be drawn from this work are as follows:

From the reported result it is demonstrated that the degradation temperature ranges polymers i.e. PE, PP, and PS are similar. They are able to co processing.

5.1.1 The polymers have degradation temperature range between 380 – 500 °C. they are able to co-process.

5.1.2 The thermal pyrolysis system at 500 °C, Nitrogen flow rate 60 ml/min, atmosphere pressure, and reaction time 40 min. are the best condition that obtained highest liquid hydrocarbon yield.

5.1.3 The thermal pyrolysis system at 500 °C is obtained liquid hydrocarbon yield higher the condition at 400 and 450 °C. the percentage of liquid hydrocarbon is 65.12. Although high temperature is obtained highest liquid hydrocarbon yield but the gasoline occur at 500 °C is the less, 67.24% by weigh.

5.1.4 The optimal condition for using HZSM-5 catalyst in catalytic reactor is 400 °C, which obtained highest liquid hydrocarbon, 80.43 % by weigh.

5.1.5 The catalytic pyrolysis system is improved with HZSM-5 catalyst in catalytic reactor that can be obtaining liquid hydrocarbon more thermal pyrolysis system.

5.1.6 Amount of BTX is not to trend.

5.2 Recommendation

5.2.1 The catalyst should be varied in order to investigate efficiency of each catalyst types.

5.2.2 The nitrogen flow rate should be varied to investigate quantity of yield.

5.2.3 The fractionation distillation should be use GC Simulated Distillation for investigate the boiling point ranges of liquid hydrocarbon products.

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5.2.4 The gas product from pyrolysis step should be analyzed by Gas chromatograph coupled with Mass spectrometer to precision result.

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APPENDIX

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Appendix A

Catalyst analyzed result from Autosorb-1 Apparatus

Quantachrome Corporation

Quantachrome Autosorb Automated Gas Sorption System Report

Autosorb for Windows Version 1.24

Sample ID HZSM-5

Comments

Sample Weight 0.1190 g

Adsorbate Nitrogen Outgas Temp 300.0°C Operator monnut

Cross-Sec Area 16.2 $^{o}A^{2}$/molecule Outgas Time 1.0 hrs Analysis Time 239.3 min

NonIdeality 6.580E-05 P/Po Toler 0

Molecular Wt 28.0134 g/mol Equil Time 3 Bath Temp. 77.40

AREA-VOLUME-PORE SIZE SUMMARY

SURFACE AREA DATA

Multipoint BET	2.515E+02	m^2/g
Single Point BET	2.653E+02	m^2/g
Langmuir Surface Area	3.923E+02	m^2/g
t-Method External Surface Area	5.758E+01	m^2/g
t-Method Micro Pore Surface Area	1.939E+02	m^2/g
DR Method Micro Pore Area	3.881E+02	m^2/g

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PORE VOLUME DATA

t-Method Micro Pore Volume	1.066E-01	cc/g
DR Method Micro Pore Volume	1.379E-01	cc/g
HK Method Cumulative Pore Volume	1.304E-01	cc/g
SF Method Cumulative Pore Volume	1.311E-01	cc/g

PORE SIZE DATA

DR Method Micro Pore Width	6.259E+01	A^o
DA Method Pore Diameter (Mode)	1.340E+01	A^o
HK Method Pore Width (Mode)	1.677E+01	A^o
SF Method Pore Diameter (Mode)	3.183E+01	A^o

DATA REDUCTION PARAMETERS

Thermal Transpiration: ON

Effective Molecule Diameter (D) 3.5400 A^o

Effective Cell Stem Inner Diameter (d) 4.0000 nm

Last Po Acquired 775.30 mmHg

MaxiDose: ON

Initial Fill: OFF

DoseWizard: OFF

BJH/DH Moving Average Size: 1

Interaction Constant (K) 2.9600 nm^3 x kJ/mol

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ADSORBATE MODEL PARAMETERS

Adsorbate Type	=	Nitrogen
Adsorbate Temp.	=	77.3500 K
Molecular Weight	=	28.0134 g/mol
Cross-Sect. Area	=	16.2000 A^2/Molecule
Liquid Density	=	0.8080 g/cc
Critical Temp.	=	126.2000 K
Critical Pressure	=	33.5000 atm
Average Diameter	=	0.3000 nm
Polarizability	=	1.4600 (cc/molec) x 1e-24
Magnetic Suscept.	=	2.0000 (CC/molec) x 1e-29
Adsorbent Type	=	Carbon
Atom Diameter	=	0.3400 nm
Polarizability	=	1.0200 (cc/molecule) x 1e-24
Magnetic Suscept.	=	13.5000 (cc/molecule) x 1e-24
Surface Atom Density	=	38.4500 (molec/cm^2) x 1e14
Adsorbent Density	=	2.2460 g/cc
DR exponent (n)	=	2.0000

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Appendix B

Analysis of Benzene, Toluene, and Xylene (BTX)

In order to study the composition of benzene, toluene, and xylene of liquid hydrocarbon product received from pyrolysis system, the liquid hydrocarbon products will be analyzed by using gas chromatography technique. By this technique, standard curve has to be firstly created as described follow;

(1) Prepare standard solution by mixing 2 ml of ethanol to 6 μl of benzene, 6 μl of toluene, and 6 μl of xylene.

(2) Inject the standard solution with various amount i.e., 1, 2, 3, to 5 μl from (1) into Gas chromatography that giving peak area chromatogram, as illustrated in Figure A-1

(3) Calculated the under curve area of each chromatogram and determine the relation of peak area and concentration of each of peak area and concentration of chemical substances. The relation that will be used to determine the concentration of unknown sample.

Figure A-1 Standard solution chromatogram

Example

Determining the quantity of benzene in standard solution

The compositions of standard solution are 2000 μl of ethanol and benzene, toluene, and xylene which content is 6 ml so,

2018 μl of standard solution contains 6 μl of benzene

Then 1 μl of standard solution contains 2.97×10^{-3} μl

The number of benzene can be calculated by equation

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$N_B = \rho_B V_B / M_B$

Where N_B is number of mole benzene

ρ_B is density of benzene (g / l)

V_B is volume of benzene (ml)

M_B is molecular weight of benzene

The density and molecular weight of benzene, toluene, and xylene are listed in Table A-1

Table A-1 Density and molecular weight of BTX

Type	Density (g/ml)	Molecular weight (g/mol)
Benzene	0.879	78.11
Toluene	0.866	92.13
Xylene	0.881	106.16

Now the number of mole of benzene can be calculated as follow;

$N_B = (0.879 \times 2.97 \times 10^{-6}) / 78.11$ mole

$N_B = 3.34 \times 10^{-8}$ mole

Therefore

1 μl of standard solution contains 3.34×10^{-8} mole of benzene

And 1000000 μl standard solution contains 3.34×10^{-2} mole of benzene

Now, compare the mole number of benzene to peak area and repeat the calculation to toluene and xylene. The peak area and concentration of benzene , toluene, and xylene are presented in Table A-2

Table A-2 Average peak area and concentration of standard solution

(μl)	Benzene		Toluene		Xylene	
	Average peak area	Concentration (mol/l)	Average peak area	Concentration (mol/l)	Average peak area	Concentration (mol/l)
1.0	6214	0.0334	5715	0.0028	4972	0.0243
2.0	9417	0.0669	8746	0.0559	7888	0.0487
3.0	15094	0.1003	13940	0.0839	12332	0.0730
4.0	18816	0.1338	17295	0.1118	15437	0.0973
5.0	24352	0.1672	22162	0.1397	19708	0.1217

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Relation of peak area and concentration of standard solution can be determined from the plot of peak area and concentration as shown in Figure A-1 (benzene), A-2 (toluene), and A-3 (xylene).

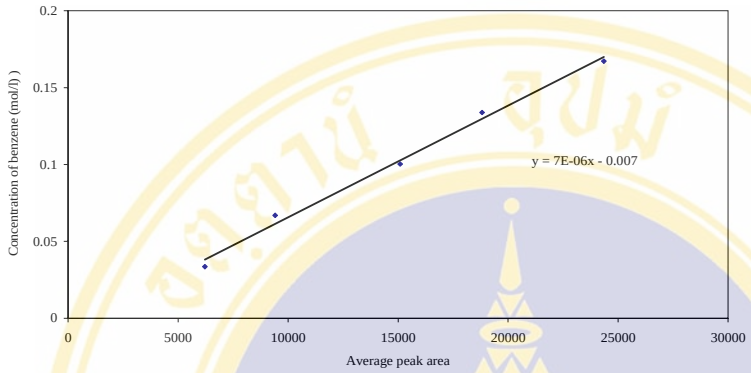

Figure A-1 Standard curve performed relation between concentration of benzene in standard solution and peak area

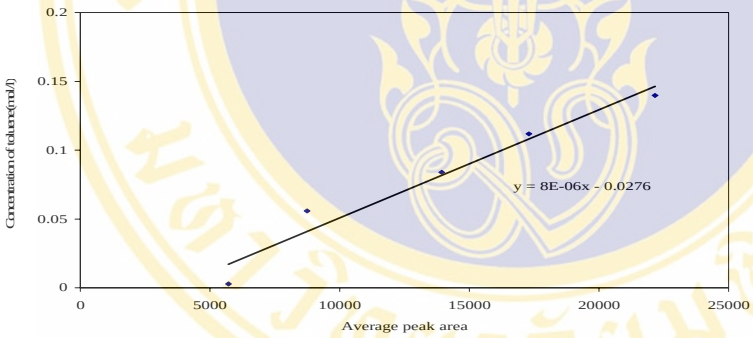

Figure A-2 Standard curve performed relation between concentration of toluene in standard solution and peak area

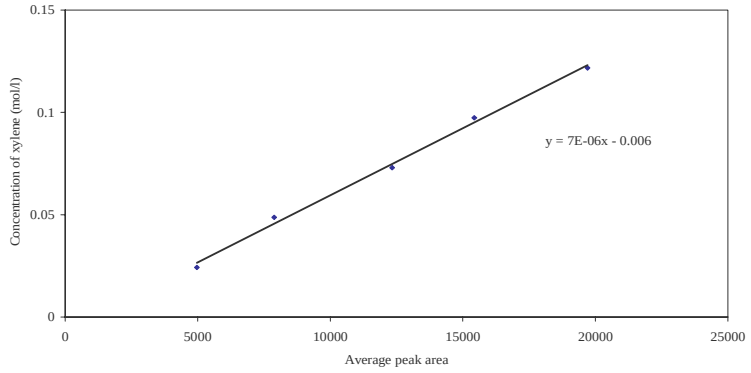

Figure A-3 Standard curve performed relation between concentration of xylene in standard solution and peak area

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The relation between peak area and concentration of each substance are listed in Table A-3 and they can be used for predicting the concentration of each substance that exist in a liquid hydrocarbon product

Table A-3 The equation for product of BTX

Retention time	Type	Equation
4.6	Benzene	y = 7E-06x-0.007
5.8	Toluene	y = 8E-06x-0.0276
7.1	Xylene	y = 7E-06x-0.006

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Appendix C

Experiment Instrument

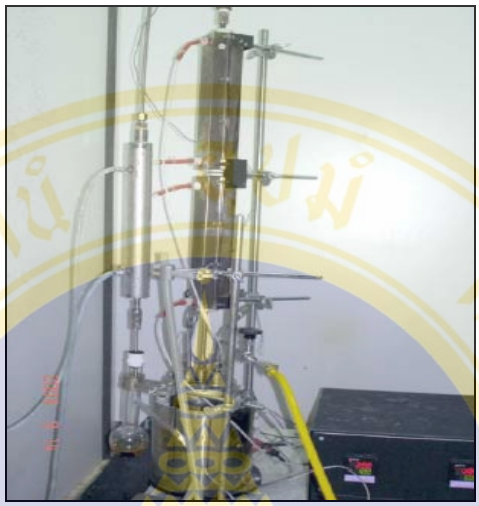

Figure C-1 Pyrolysis system

Figure C-2 Pyrolyzer

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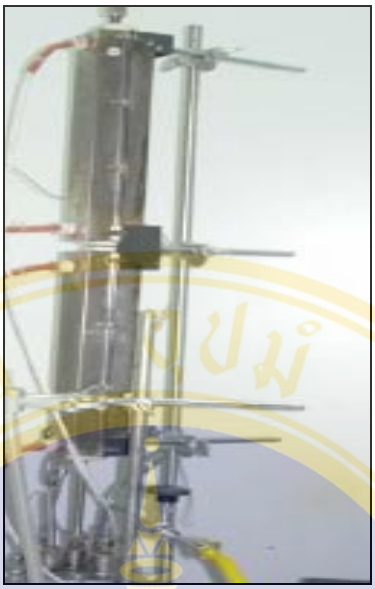

Figure C-3 Catalytic reactor

Figure C-4 Sampling bottom

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Figure C- 5 Condenser

Figure C-6 Temperature control

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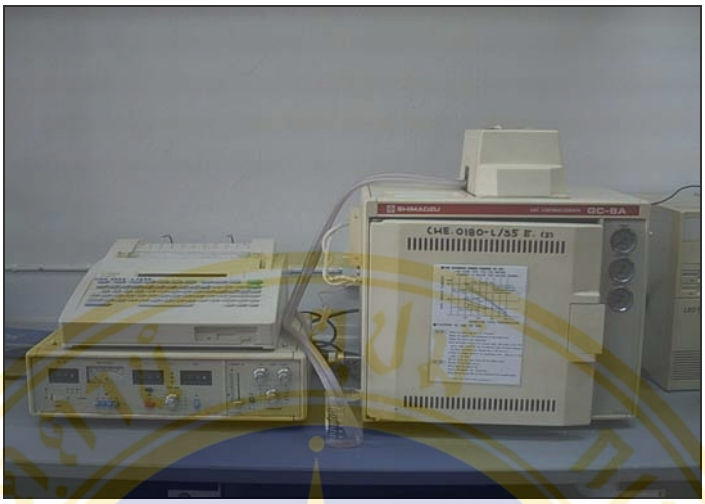

Figure C- 7 Gas chromatography

Figure C- 8 Liquid hydrocarbon

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Figure C- 9 Distillation apparatus

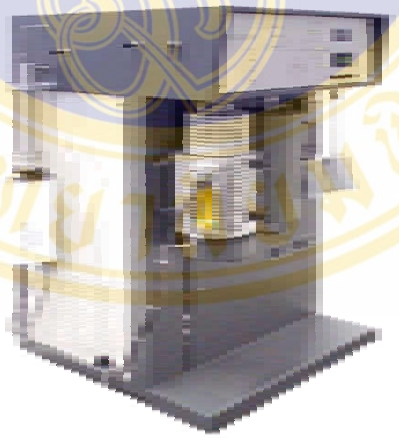

Figure C-10 Absorb -1 apparatus

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Appendix D

Quality of Gasoline

ประกาศในราชกิจจานุเบกษา ฉบับประกาศทั่วไป เล่ม 121 ตอนพิเศษ 8 ง ลงวันที่ 22 มกราคม พุทธศักราช 2547)

ประกาศกรมธุรกิจพลังงาน
เรื่อง กำหนดลักษณะและคุณภาพของน้ำมันเบนซิน
พ.ศ. 2547

.....

โดยที่เป็นการสมควรแก้ไขปรับปรุงข้อกำหนดลักษณะและคุณภาพของน้ำมันเบนซิน ให้เหมาะสมยิ่งขึ้น อาศัยอำนาจตามความในมาตรา 25 วรรคหนึ่ง แห่งพระราชบัญญัติการค้าน้ำมัน เชื้อเพลิง พ.ศ. 2543 อธิบดีกรมธุรกิจพลังงานออกประกาศไว้ ดังต่อไปนี้

ข้อ 1 ประกาศนี้เรียกว่า " ประกาศกรมธุรกิจพลังงาน เรื่อง กำหนดลักษณะและคุณภาพของน้ำมันเบนซิน พ.ศ. 2547 "

ข้อ 2 ประกาศนี้ให้ใช้บังคับตั้งแต่วันที่ 26 มกราคม พ.ศ. 2547 เป็นต้นไป

ข้อ 3 ให้ยกเลิกประกาศกรมทะเบียนการค้า เรื่อง กำหนดลักษณะและคุณภาพ ของน้ำมันเบนซิน พ.ศ. 2545 ลงวันที่ 13 กันยายน พ.ศ. 2545

ข้อ 4 ให้กำหนดชนิดของน้ำมันเบนซินเป็น 2 ชนิด คือ

(1) น้ำมันเบนซินออกเทน 91

(2) น้ำมันเบนซินออกเทน 95

ข้อ 5 ภายใต้บังคับของข้อ 6 ลักษณะและคุณภาพของน้ำมันเบนซิน ให้เป็นไปตามรายละเอียดแนบท้ายประกาศนี้

การเติมสารเติมแต่งในน้ำมันเบนซิน ให้ผู้ค้าน้ำมันแจ้งขอความเห็นชอบและต้องได้ รับความเห็นชอบจากอธิบดีกรมธุรกิจพลังงาน แล้วจึงจะดำเนินการได้

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ข้อ 6 ลักษณะและคุณภาพของน้ำมันเบนซินที่ผู้ค้าน้ำมันจำหน่ายหรือมีไว้เพื่อจำหน่ายดังต่อไปนี้ จะไม่เป็นไปตามที่กำหนดในรายละเอียดแนบท้ายประกาศนี้ก็ได้

(1) น้ำมันเบนซินสำหรับการส่งออกไปนอกราชอาณาจักร

(ก) โดยการขนส่งทางเรือ

(ข) โดยการขนส่งทางรถยนต์

(2) น้ำมันเบนซินสำหรับการนำไปใช้กับยานพาหนะที่ออกไปนอกราชอาณาจักร

(3) น้ำมันเบนซินสำหรับการนำไปใช้ในการอื่นนอกเหนือจากการใช้กับเครื่องยนต์เบนซิน

(4) น้ำมันเบนซินสำหรับการนำไปใช้ตามโครงการหรือนโยบายของรัฐบาล หรือ งานวิจัย

(5) น้ำมันเบนซินสำหรับเตรียมไว้เพื่อจำหน่ายให้กับผู้ค้าน้ำมัน หรือประชาชนเฉพาะในข้อกำหนด เรื่อง สารเติมแต่ง

(6) น้ำมันเบนซินสำหรับการจำหน่ายให้ผู้ค้าน้ำมันตามมาตรา 7 เพื่อนำไปผสม เอทานอลในการผลิตเป็นน้ำมันแก๊สโซฮอล์

(7) น้ำมันเบนซินที่ผู้ค้าน้ำมันตามมาตรา 7 นำเข้ามาในราชอาณาจักร สำหรับใช้เป็นวัตถุดิบในการผลิตน้ำมันเชื้อเพลิง

(8) น้ำมันเบนซินสำหรับการจำหน่ายให้ผู้ค้าน้ำมันตามมาตรา 7 เพื่อนำไปใช้เป็น วัตถุดิบผลิตน้ำมันเชื้อเพลิง

(9) น้ำมันเบนซินสำหรับการจำหน่ายให้แก่ผู้ค้าน้ำมันตามมาตรา 7 ด้วยกัน เพื่อวัตถุประสงค์ตาม (1) (2) (3) (4) และ (5)

ข้อ 7 ผู้ค้าน้ำมันที่ประสงค์จะจำหน่ายหรือมีไว้เพื่อจำหน่ายน้ำมันเบนซินตามข้อ 6(1)(ก) ต้องจัดให้มีผู้ตรวจสอบปิโตรเลียม (surveyor) ซึ่งได้รับความเห็นชอบจากกรมธุรกิจพลังงาน เป็น ผู้ดำเนินการตรวจสอบ ชนิด ปริมาณ ลักษณะและคุณภาพของน้ำมันเบนซินก่อนการจำหน่ายทุกครั้ง และผู้ตรวจสอบปิโตรเลียมต้องรายงานผลการตรวจสอบให้กรมธุรกิจพลังงานทราบ ภายใน 7 วัน ทำการ นับแต่วันที่มีการขนส่งน้ำมันเบนซินออกจากท่าเทียบเรือ

การขอและการให้ความเห็นชอบเป็นผู้ตรวจสอบปิโตรเลียมตามวรรคหนึ่ง ให้เป็นไปตามระเบียบที่กรมธุรกิจพลังงานกำหนด

กรณีที่จะไม่ดำเนินการตรวจสอบตามวรรคหนึ่ง ผู้ค้าน้ำมันจะต้องแจ้งลักษณะและคุณภาพของน้ำมันเบนซินเฉพาะในส่วนที่ไม่เป็นไปตามที่กำหนดในรายละเอียดแนบท้ายประกาศนี้ เพื่อขอรับความเห็นชอบตามแบบ นพ. 416 ท้ายประกาศนี้ทุกครั้งก่อนที่จะมีการจำหน่ายน้ำมันเบนซินไปนอกราชอาณาจักร และต้องได้รับความเห็นชอบจากกรมธุรกิจพลังงานก่อนการจำหน่าย

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ข้อ 8 ผู้ค้าน้ำมันที่ประสงค์จะจำหน่ายหรือมีไว้เพื่อจำหน่ายน้ำมันเบนซินตามข้อ 6(1)(ข) ถึง 6 (9) ต้องแจ้งลักษณะและคุณภาพของน้ำมันดังกล่าวเฉพาะในส่วนที่ไม่เป็นไปตามที่กำหนดในรายละเอียดแนบท้ายประกาศนี้ เพื่อขอรับความเห็นชอบโดยยื่นแบบแจ้งตามแบบ นพ. 416 ท้ายประกาศนี้

การขอรับความเห็นชอบน้ำมันเบนซินเพื่อการผสมเป็นน้ำมันแก๊สโซฮอล์ ตามข้อ 6(6) จะต้องจัดทำรายละเอียดขั้นตอนการขนส่ง การรับวัตถุดิบ การผลิต การควบคุมคุณภาพ รวมทั้งการตรวจติดตามการควบคุมคุณภาพน้ำมันแก๊สโซฮอล์ที่จำหน่าย แนบมาพร้อมแบบ นพ. 416

ข้อ 9 เมื่ออธิบดีให้ความเห็นชอบลักษณะและคุณภาพของน้ำมันเบนซิน ที่ผู้ค้าน้ำมันแจ้งตามข้อ 8 แล้ว กรมธุรกิจพลังงานจะออกหนังสือรับรองการให้ความเห็นชอบตามแบบ นพ. 417 ท้ายประกาศนี้

หนังสือรับรองการให้ความเห็นชอบตามวรรคหนึ่ง ให้มีกำหนดระยะเวลา 1 ปี นับแต่ วันที่ออก

ข้อ 10 ผู้ค้าน้ำมันที่ได้รับหนังสือรับรองการให้ความเห็นชอบข้อ 9 ต้องปฏิบัติตามเงื่อนไขดังนี้

(1) การเก็บ และการขนส่งน้ำมันเบนซินตามข้อ 6(1)(ข) ถึง 6(9) ต้องเป็นไปตามรายละเอียดที่ผู้ค้าน้ำมันได้ระบุไว้ในแบบแจ้งเพื่อขอความเห็นชอบ

(2) รายงานข้อมูลการจัดหา การจำหน่าย และยอดคงเหลือของน้ำมันเบนซินตาม ข้อ 6(1)(ข) ถึง 6(9) ตามแบบ นพ. 418 ต่อกรมธุรกิจพลังงาน ภายในวันที่ 15 ของเดือนถัดไป

ข้อ 11 ให้ผู้ค้าน้ำมันที่จะเติมสารเติมแต่งในน้ำมันเบนซิน ยื่นแบบแจ้งเพื่อขอรับความเห็นชอบการเติมสารเติมแต่งในน้ำมันเบนซินตามแบบ นพ.419 ท้ายประกาศนี้ พร้อมตัวอย่างสารเติมแต่งจำนวน 0.5 ลิตร ตัวอย่างน้ำมันเบนซินที่ไม่เติมสารเติมแต่ง จำนวน 3 ลิตร และตัวอย่างน้ำมันเบนซิน ที่เติมสารเติมแต่งแล้ว จำนวน 1 ลิตร

ข้อ 12 เมื่ออธิบดีให้ความเห็นชอบการเติมสารเติมแต่งในน้ำมันเบนซินที่ผู้ค้าน้ำมันแจ้งแล้ว กรมธุรกิจพลังงานจะออกหนังสือรับรองการให้ความเห็นชอบตามแบบ นพ. 420 ท้ายประกาศนี้

ข้อ 13 ให้ผู้ค้าน้ำมันที่ได้รับหนังสือรับรองการให้ความเห็นชอบตามข้อ 12 เตรียมเอกสารบันทึกเกี่ยวกับการเติมสารเติมแต่งในน้ำมันเบนซินไว้ที่สำนักงานใหญ่หรือคลังน้ำมันที่เติมสารเติมแต่ง เพื่อให้พนักงานเจ้าหน้าที่ตรวจสอบได้ตลอดเวลา

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ข้อ 14 การยื่นแบบแจ้งเพื่อขอรับความเห็นชอบตามข้อ 7 วรรคสาม ข้อ 8 หรือข้อ 11 ให้ยื่นต่อสำนักคุณภาพน้ำมันเชื้อเพลิง กรมธุรกิจพลังงาน

ข้อ 15 เมื่ออธิบดีได้ให้ความเห็นชอบลักษณะและคุณภาพของน้ำมันเบนซินตามข้อ 9 หรือให้ความเห็นชอบการเติมสารเติมแต่งในน้ำมันเบนซินตามข้อ 12 แล้ว หากปรากฏหลักฐานภายหลังว่าเอกสารที่ใช้ในการขอรับความเห็นชอบดังกล่าวมีความคลาดเคลื่อน หรือผิดพลาดไปจากความ เป็นจริง อธิบดีอาจมีคำสั่งให้ผู้ค้าน้ำมันจัดส่งเอกสารเพิ่มเติมเพื่อขจัดความคลาดเคลื่อน หรือแก้ไข ข้อผิดพลาดนั้น ภายใน 30 วัน นับแต่วันที่ผู้ค้าน้ำมันได้รับคำสั่งดังกล่าว

หากผู้ค้าน้ำมันไม่จัดส่งเอกสาร หรือแก้ไขข้อผิดพลาดภายในระยะเวลาที่กำหนดใน วรรคแรก อธิบดีอาจมีคำสั่งยกเลิกหนังสือรับรองที่ออกตามข้อ 9 หรือข้อ 12 ได้

ข้อ 16 ผู้ค้าน้ำมันที่ประสงค์จะทำการเพิ่มเติมหรือเปลี่ยนแปลงรายละเอียดใดๆ ที่ได้แจ้งหรือระบุไว้ในแบบแจ้งตามข้อ 8 และข้อ 11 ซึ่งได้รับความเห็นชอบแล้ว ให้ผู้ค้าน้ำมันทำหนังสือแจ้ง ต่อกรมธุรกิจพลังงาน ล่วงหน้าไม่น้อยกว่า 15 วัน ก่อนวันที่ประสงค์จะเพิ่มเติมหรือเปลี่ยนแปลง

ข้อ 17 ประกาศฉบับนี้ไม่กระทบกระเทือนการให้ความเห็นชอบลักษณะ และคุณภาพ หรือการให้ความเห็นชอบการเติมสารเติมแต่ง ซึ่งผู้ค้าน้ำมันได้รับหนังสือรับรองการให้เห็นชอบไปแล้วตามประกาศกรมทะเบียนการค้า เรื่อง กำหนดลักษณะและคุณภาพของน้ำมันเบนซิน พ.ศ. 2545 ลงวันที่ 13 กันยายน พ.ศ. 2545 ที่ใช้บังคับอยู่ก่อนวันที่ประกาศฉบับนี้มีผลใช้บังคับ

ประกาศ ณ วันที่ 13 มกราคม พ.ศ. 2547

(ลงชื่อ) วิโรจน์ คลังบุญครอง
(นายวิโรจน์ คลังบุญครอง)
อธิบดีกรมธุรกิจพลังงาน

รับรองสำเนาถูกต้อง

(นางสาวพีรพัฒน์ อินทรชุบ)
นักวิทยาศาสตร์ 8ว

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รายละเอียดแนบท้ายประกาศกรมธุรกิจพลังงาน
เรื่อง กำหนดลักษณะและคุณภาพของน้ำมันเบนซิน
พ.ศ. 2547

รายการ	ข้อกำหนด	อัตราสูงต่ำ	ออกเทน 91	ออกเทน 95	วิธีทดสอบ
1	ค่าออกเทน (Octane Number)				
	1.1 โดยวิธีวิจัย (Research Octane Number ; RON)				ASTM D 2699
	(1) ผู้ผลิตจำหน่าย ณ จุดส่งมอบ	ไม่ต่ำกว่า	91.0	95.0	
	(2) ผู้จำหน่าย	ไม่ต่ำกว่า	90.6	94.6	
	1.2 โดยวิธีมอเตอร์ (Motor Octane Number ; MON)				ASTM D 2700
	(1) ผู้ผลิตจำหน่าย ณ จุดส่งมอบ	ไม่ต่ำกว่า	80.0	84.0	
	(2) ผู้จำหน่าย	ไม่ต่ำกว่า	79.6	83.6	
2	ปริมาณตะกั่ว *กรัม/ลิตร* (Lead Content, *g/l*)	ไม่สูงกว่า	0.013	0.013	ASTM D 5059
3	ปริมาณกำมะถัน *ร้อยละโดยน้ำหนัก* (Sulphur Content, *%wt.*)	ไม่สูงกว่า	0.05	0.05	ASTM D 4294
4	ปริมาณฟอสฟอรัส *กรัม/ลิตร* (Phosphorus Content, *g/l*)	ไม่สูงกว่า	0.0013[1/]	0.0013[1/]	ASTM D 3231[1/]
5	การกัดกร่อน (Corrosion)	ไม่สูงกว่า	หมายเลข 1	หมายเลข 1	ASTM D 130
6	เสถียรภาพต่อการเกิดปฏิกริยาออกซิเดชั่น *นาที* (Oxidation Stability, *minutes*)	ไม่ต่ำกว่า	360	360	ASTM D 525
7	ปริมาณยางเหนียว *กรัม/100 มิลลิลิตร* (Existent Gum, *g/100 ml*)	ไม่สูงกว่า	0.004	0.004	ASTM D 381
8	การกลั่น *°ซ.* (Distillation, *°C*)				ASTM D 86
	8.1 อุณหภูมิ				
	(1) การระเหยในอัตราร้อยละ 10 โดยปริมาตร (10% Evaporated)	ไม่สูงกว่า	70	70	
	(2) การระเหยในอัตราร้อยละ 50 โดยปริมาตร (50% Evaporated)	ไม่ต่ำกว่า และ	70	70	
		ไม่สูงกว่า	110	110	
	(3) การระเหยในอัตราร้อยละ 90 โดยปริมาตร (90% Evaporated)	ไม่สูงกว่า	170	170	
	(4) จุดเดือดสุดท้าย (End Point)	ไม่สูงกว่า	200	200	
	8.2 กากน้ำมัน *ร้อยละโดยปริมาตร* (Residue, *% vol.*)	ไม่สูงกว่า	2.0	2.0	
9	ความดันไอ ณ อุณหภูมิ 37.8 °ซ. *กิโลปาสคาล* (Vapour Pressure @ 37.8 °C , *kPa*)	ไม่สูงกว่า	62	62	ASTM D 4953

(ต่อ - 2 -)

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รายการ	ข้อกำหนด	อัตราสูงต่ำ	ออกเทน 91	ออกเทน 95	วิธีทดสอบ
10	ปริมาณเบนซีน *ร้อยละโดยปริมาตร* (Benzene Content, *% vol.*)	ไม่สูงกว่า	3.5	3.5	ASTM D 5580
11	ปริมาณสารอะโรมาติก *ร้อยละโดยปริมาตร* (Aromatic Content, *% vol.*)	ไม่สูงกว่า	35	35	ASTM D 5580
12	สี (Colour)				(1) เปรียบเทียบสีและปริมาณเนื้อสีกับน้ำมันมาตรฐานที่เตรียมขึ้นใหม่ โดยใช้สีละลายในน้ำมันก่อนการย้อมสีให้มีปริมาณเท่ากับที่กำหนด แล้วนำมาบรรจุแยกกันในภาชนะที่ใช้ในการวัดสีตามวิธีทดสอบ ASTM D 1500 แล้วตรวจพินิจด้วยสายตา หรือ (2) ASTM D 2392 หรือ (3) ASTM D 1500
	12.1 ชนิดของสี (Hue)		แดง[2/]	เหลืองอ่อน[3/]	
	12.2 ปริมาณเนื้อสี *มิลลิกรัม/ลิตร* (Dye Content, *mg/l*)	ไม่ต่ำกว่า	7.0	-	
	12.3 ความเข้มของสี (Intensity)	ไม่ต่ำกว่า และ ไม่สูงกว่า	- -	0.5 1.5	
13	ปริมาณน้ำ *ร้อยละโดยน้ำหนัก* (Water Content, *% wt.*)				
	13.1 กรณีที่ไม่มีสารออกซิเจนเนตเป็นส่วนผสม (Non – Oxygenate Blends)	-	ไม่มี	-	ตรวจพินิจด้วยสายตา
	13.2 กรณีที่มีสารออกซิเจนเนตเป็นส่วนผสม (Oxygenate Blends)	ไม่สูงกว่า	0.7	0.7	ASTM E 203
14	ปริมาณสารออกซิเจนเนต *ร้อยละโดยปริมาตร* (Oxygenated compounds, *% vol.*)	ไม่ต่ำกว่า และ ไม่สูงกว่า	- 11.0[4/]	5.5[4/] 11.0[4/]	ASTM D 4815
15	ลักษณะทั่วไปที่ปรากฏ (Appearance)		เป็นของเหลวใส ไม่ขุ่น ไม่แยกชั้น และไม่มีสารแขวนลอย		ตรวจพินิจด้วยสายตา
16	มีสารเติมแต่ง ที่มีคุณสมบัติชะล้างทำความสะอาด (Detergent Additive)				
	16.1 หัวฉีด (Port Fuel Injector)	-	X[5/]	X[5/]	
	16.2 ลิ้นไอดี (Intake Valve)	-	X[5/]	X[5/]	
17	สารเติมแต่งอื่น (ถ้ามี)	ให้เป็นไปตามที่ได้รับความเห็นชอบจากอธิบดีกรมธุรกิจพลังงาน			

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หมายเหตุ วิธีทดสอบอาจใช้วิธีอื่นที่เทียบเท่าก็ได้ แต่ในกรณีที่มีข้อโต้แย้งให้ใช้วิธีที่กำหนดในรายละเอียดแนบท้ายนี้

1/ ทดสอบเฉพาะกรณีที่เติมสารเติมแต่ง (Additive) ที่มีธาตุฟอสฟอรัสเป็นองค์ประกอบ

2/ ใช้สารประกอบประเภท 2- naphthalenol [(phenylazo) phenyl] azo alkyl derivatives และ 1,3-benzenediol ,2,4-bis [(alkylphenyl) azo-] ในอัตราส่วน 57 : 8 โดยน้ำหนัก หรือใช้อัตราส่วนแตกต่างจากสีที่กำหนดก็ได้ แต่ต้องมีความเข้มของสีเทียบเท่าสีแดงมาตรฐานที่กำหนดไว้ข้างต้น และใช้วิธีทดสอบตาม (1) หรือ (2)

3/ ใช้วิธีทดสอบตาม (3)

4/ ถ้าผสมด้วยเมทานอล (Methanol Blends) ต้องมีปริมาณไม่สูงกว่าร้อยละ 3.0 โดยปริมาตร

5/ ให้เป็นไปตามที่ได้รับความเห็นชอบจากอธิบดีกรมธุรกิจพลังงาน

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Appendix E

Experimental data

Table E-1 Products from Thermal cracking processes

Pyrolyzer Temperature (°C)	Catalytic Temperature (°C)	Nitrogen flow rate (mi min^{-1})	Reaction time (min)	Weight of mixed plastic (g)	Gas (g)	Liquid (g)	Solid Residue (g)
500	400	60	90	60.073	3.113	7.00	46.960
500	450	60	90	60.47	12.389	27.424	20.357
500	500	60	90	60.47	19.582	39.375	1.513

Gas = Weight of mixed plastic – Liquid- Solid Residue

Table E-2 Liquid hydrocarbon products from thermal cracking processes

Pyrolyzer Temperature (°C)	Catalytic Temperature (°C)	Nitrogen flow rate (mi min^{-1})	Gasoline (g)	Kerosene (g)	Gas oil (g)	Residue (g)
400	400	60	14.712	1.395	1.292	2.371
450	450	60	16.054	1.149	2.847	2.176
500	500	60	18.03	2.681	3.869	3.451

Table E-3 Concentration of Benzene Toluene and Xylene (BTX) from thermal cracking processes

Pyrolyzer Temperature (°C)	Catalytic Temperature (°C)	Nitrogen flow rate (mi min^{-1})	Benzene (mol/l)	Toluene (mol/l)	Xylene (mol/l)
400	400	60	3.571	1.042	0.742
450	450	60	0.187	5.648	1.433
500	500	60	0.535	6.665	6.961

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Table E-4 Products from catalytic cracking processes

Pyrolyzer Temperature (°C)	Catalytic Temperature (°C)	Nitrogen flow rate (mi min^{-1})	Reaction time (min)	Weight of mixed plastic (g)	Gas (g)	Liquid (g)	Solid Residue (g)
500	300	60	90	60.286	16.023	44.222	0.041
500	400	60	90	60.919	11.901	48.995	0.023
500	450	60	90	60.221	18.902	41.270	0.032
500	500	60	90	60.103	17.012	43.083	0.036

Table E-5 Liquid hydrocarbon products from catalytic cracking processes

Pyrolyzer Temperature (°C)	Catalytic Temperature (°C)	Nitrogen flow rate (mi min^{-1})	Gasoline (g)	Kerosene (g)	Gas oil (g)	Residue (g)
500	300	60	29.321	3.089	4.299	7.513
500	400	60	31.183	3.295	5.418	9.099
500	450	60	27.650	3.196	3.404	7.026
500	500	60	30.184	2.339	3.248	7.311

Table E-3 Concentration of Benzene Toluene and Xylene (BTX) from catalytic cracking processes

Pyrolyzer Temperature (°C)	Catalytic Temperature (°C)	Nitrogen flow rate (mi min^{-1})	Benzene (mol/l)	Toluene (mol/l)	Xylene (mol/l)
500	300	60	0.341	3.985	0.739
500	400	60	0.288	2.839	0.652
500	450	60	0.427	3.644	5.480
500	500	60	0.320	4.495	1.566

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