การแตกตัวพอลิโพรพีลีนด้วยไฮโดรเจนโดยใช้เหล็กบนถ่านกัมมันต์จากกะลาปาล์มน้ำมัน

นางสาวพูนสุข พึ่งธรรม

HYDROCRACKING OF POLYPROPYLENE USING IRON ON ACTIVATED CARBON

FROM PALM OIL SHELL

Miss Poonsuk Phungtum

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จุดมุ่งหมายหลักของงานวิจัยนี้   มุ่งที่จะศึกษาการเปลี่ยนพอลิโพรพีลีนไปเป็นน้ำมันบนตัวเร่งปฏิกิริยาเหล็กบนถ่านกัมมันต์ในเครื่องปฏิกรณ์ขนาดเล็ก ซึ่งมีเส้นผ่านศูนย์กลางภายใน 30 มิลลิเมตร และปริมาตรภายใน 75 มิลลิตร โดยการเปลี่ยนแปลงค่าตัวแปรดังนี้ ความดันของก๊าซไฮโดรเจนระหว่าง 28-50 กก./ตร.ซม., อุณหภูมิของปฏิกิริยาระหว่าง 395-455 องศาเซลเซียสและเวลาที่ใช้ทำปฏิกิริยาระหว่าง 30-90 นาที จากผลการทดลองพบว่าอุณหภูมิที่ให้ปริมาณน้ำมันได้สูงสุดที่ 435 องศาเซลเซียส จากนั้นทดสอบผลของความดันของก๊าซไฮโดรเจน, เวลาที่ใช้ทำปฏิกิริยาและอัตราส่วนพอลิโพรพีลีนต่อตัวเร่งปฏิกิริยาเหล็กบนถ่านกัมมันต์

ผลิตภัณฑ์น้ำมันที่วิเคราะห์โดยใช้เทคนิคก๊าซโครมาโทกราฟ แบบ Simulated Distillation พบว่าเหล็กบนถ่านกัมมันต์เป็นตัวเร่งปฏิกิริยาที่เหมาะสม โดยที่อุณหภูมิ 435 องศาเซลเซียส ความดันของก๊าซไฮโดรเจน 30 กก./ตร.ซม. และเวลาในการทำปฏิกิริยา 60 นาที ผลิตภัณฑ์น้ำมันที่ได้มีปริมาณแนฟทา 40-65%, เคโรซีน, 12-14%, ก๊าซออยล์ 10-13%, และโมเลกุลไฮโดรคาร์บอนสายโซ่ยาว 4-5%

ภาควิชา……………………………………ลายมือชื่อนิสิต…………………………………

สาขาวิชา…………………………………ลายมือชื่ออาจารย์ที่ปรึกษา………………………

ปีการศึกษา………………………………ลายมือชื่ออาจารย์ที่ปรึกษาร่วม…………………

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POONSUK PHUNGTUM : HYDROCRACKING OF POLYPROPYLENE USING IRON ON ACTIVATED CARBON FROM PALM OIL SHELL. THESIS ADVISOR : ASSISTANT PROFESSOR THARAPONG VITIDSANT,Ph.D. 89 pp. ISBN 974-13-0176-6

The main objective of this research was aimed to study the conversion of polypropylene into oil product using iron on activated carbon catalyst in a microreactor, width of 30 mm inside diameter and innervolume of 75 ml, by varying operation conditions as pressure of hydrogen gas range of 28 to 50 kg/cm^2 reaction temperature between 395 and 455 $^{\circ}$C and reaction time 30 to 90 min for each catalyst. From the results, it was found that reaction temperature of 435 $^{\circ}$C was the temperature that yielded the highest quantity of oil product. This temperature was also used in studying the effect of pressure for hydrogen gas, reaction time and ratio of polypropylene to iron on activated carbon catalyst.

The analyzed oil product from gas chromatography (GC Simulated Distillation) was found that iron on activated carbon was suitable and used as catalyst at 435 $^{\circ}$C, hydrogen pressure at 30 kg/cm^2 and reaction time 60 min The product yield was in the range of 40-65% naphtha, 12-14% kerosene, 10-13% gas oil and 4-5% long residues.

Department……………………………..Student's signature………………………………

Field of study…………………………….Advisor's signature…………………………….

Academic year…………………………..Co-advisor's signature………………………….

ACKNOWLEDGEMENT

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CHAPTER I

INTRODUCTION

The problems of waste plastics together with the lack of energy from oil and hydrocarbon gas have been increasing for many years and many researches of transforming waste plastics into other useful substances have been undertaken. Especially, a transformation of waste plastics from polyolefinic plastic such as polypropylene, into hydrocarbon which is oil because polypropylene has not crosslink structure, and consists of hydrocarbon that contains high amount of hydrogen and has not contain impurity.

Currently, an effective solution of waste plastics problem should be done through 4 processes : land covering, burning and recycle energy, recycling and reduction of plastic use, however some of these processes cause the problem of air pollution and inadequate land for covering. Although, waste plastics can be recycled into plastic pellets and reused for producing new products or used with new plastics, the limitations of recycled plastics are durability and quality degradation. New products produced from recycled plastics may not be effective and durable as its original ones. This is why new researches have put emphasis on transforming plastics into other useful chemical substances by thermal cracking at high temperature together with various catalytic cracking method such as metal on zeolite support, zeolite etc. (but a disadvantange of using zeolite is that it is costly). The idea of this research is to transform polypropylene into different molecular weight hydrocarbons and use the liquid fraction as fuel or oil. This idea will lead to a reduction of plastic waste as well. The processes to serve these intended purposes have been done through catalytic cracking reaction by iron on activated carbon under hydrogen atmosphere in microreactor.

It is found that the advantage of using catalyst is that activated carbon from palm-oil shell (which is a agricultural waste product) has high carbon, low inorganic and high acidity which is suitable for cracking reaction of high molecular weight hydrocarbon. Besides, iron catalyst is cheaper than other 8 metal groups, therefore catalyst used for these processes can reduce cost of production. It is also as effective as commercial one, it can change many variables into proper conditions (such as pressure, temperature, time, catalytic amount and others). This research aims to recycle locally raw materials and waste plastics into more-valued chemical substances and more useful products. The usefulness of this research may not only serve the idea of using recycle products but also helps to reduce an environmental problem.

The objectives of this research are to :

(1) study the hydrocracking of polypropylene by using iron on activated carbon catalyst in microreactor.

(2) search for the optimum conditions of catalytic cracking reaction to yield suitable percentage of product and composition.

The scopes of this research

To investigate the performance of the prepared catalyst on the polypropylene conversion to oil under the following conditions;

- Reaction temperature range of 395-455°C
- Ratio of polypropylene per catalyst : 15 g per 0.30-0.75 g
- Pressure of hydrogen gas range of 28-50 kg/cm^{2}
- Reaction time range of 30-90 min
- %Fe on activated carbon of catalyst per polypropylene 1, 5, 10% / 15 g

The reaction products were analyzed by Distillation Gas Chromatograph.

CHAPTER II
LITERATURE REVIEW

2. Polypropylene [6]

Polypropylene is a major volume thermoplastic material ranked third in the production of plastic, after polyethylene and polyvinyl chloride. Due to its cost effectiveness, versatility, overall competitiveness and excellent environmental aspects, polypropylene is the fastest growing commodity plastic. Advance polymerization processes in conjunction with highly developed compounding techniques make it possible to target polypropylene for engineering applications. The world production volume was about 19 million tons in 1995, including 4.7 million tons in the US alone.

Polypropylene is produced by the stereospecific addition polymerization of propylene. The common name of the polymer is polypropylene, which corresponds fairly well with the name recommended by IUPAC where the repeating propylene unit is in brackets. Commercial production of polypropylene started in 1957 at Montecatini, Italy, at Hercules, USA, and at Farbewerke Hoechst AG, Germany, and was the result of the discovery of heterogeneous stereospecific catalysts by Ziegler in Germany that effected the polymerization of ethylene in 1953. Using these catalysts, Natta in Italy obtained in 1954 crystalline polymers of propylene. Earlier efforts to polymerize propylene had only resulted in amorphous polymers without any use at that time. Natta classified the three geometric forms adopted by the polymer chain of polypropylene as follows.

Isotactic; all methyl groups are situated on the same side of the chain.
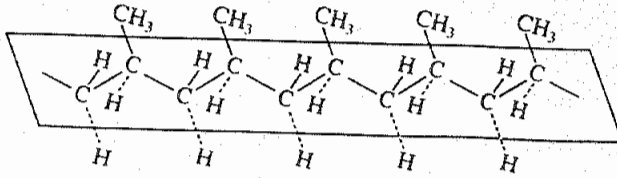
Syndiotactic; methyl groups are on alternating side.
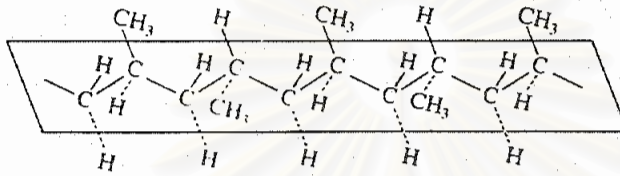
Atactic; methyl groups are situated at random.
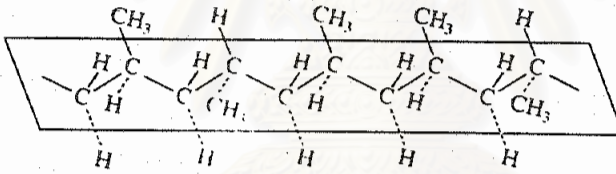
Isotactic and syndiotactic polypropylenes are crystalline, whereas atactic polymer is amorphous. As for ethylene, the raw materials for propylene are petroleum and natural gas from which the C_3 fraction is obtained after cracking and fractional distillation. Impurities such as water and methylacetylene must be carefully removed and the purity of propylene brought up to 99.7% Three different categories of polypropylene materials are produced commercially: homopolymers, copolymers and blends.

2.1 Polymerization

The polymerization of propylene is effected in the presence of Ziegler-type catalysts which are composed of the reaction products of titanium trichloride with aluminium compuonds such as aluminium triethyl or tributyl or aluminum diethyl monochloride. These compounds form a 10% slurry in a diluent such as naphtha. The preparation of the catalyst for propylene polymerization is the most important step in the overall process. The composition of the catalyst as well as the shape and size of its particles are determinant for the properties of the polymer. A good catalyst should produce high yield of polymer per part of catalysts, with a high content of isotactic polypropylene, and with controlled molecular weight and morphology. Molecular weight distribution are generally broader when insoluble catalysts are used and much narrower with soluble catalysts. Hydrogen is used for molecular weight control. The different technologies that are used for the polymerization of propylene using Ziegler-type catalysts are the slurry processes including the bulk process, the solution process and the gas phase process.

2.1.1 The slurry processes

The oldest and the major processes are the slurry processes. The polymerization resembles the Ziegler process described for polyethylene. It may be carried out either in stirred batch reactors in continuous loop reactors. The suspending liquid (C_4 – C_6 paraffins), the catalyst and the propylene are metered separately into the reactor and the polymerization is conducted at 50-80 $^{\circ}$C and 0.5-3.0 MPa (5-30 atmospheres).The required isotactic polymer develops around the catalyst particles and forms a slurry since it is insoluble in the diluent.

Some atactic amophous polymer that is also formed is largely soluble in the diluent. The addition of the monomer is continued until the slurry reaches 30-60% solids. At this point the reaction mixture is transferred to a flash tank for the removal and recycling of unreacted monomer. The catalyst is then solubilized and deactivated by the addition of an acidified alcohol. The slurry is centrifuged for the separation of the crystalline isotactic polymer from the diluent which contains the soluble atactic polymer and the solubilized catalyst. The polymer is washed and dried. The flow chart of the slurry process is presented in **Figure 2.1.1**

The newer, high activity and high stereospecificity magnesium-supported catalyst system provide high enough yields of polymer per unit of catalyst so that the removal of the catalyst becomes unnecessary. Thus, 40 kilograms of polypropylene are produced with today's catalyst compared to only 4 kg/g produced in the 1970s. The ratio of isotactic/atactic polypropylene is also improved and the separation of atactic polymer is no more required. With some catalysts, polypropylene may be produced as dense spherical granules so that a pelletizing operation is avoided. A variant of the slurry polymerization technology is the bulk process in which liquid monomer serves both as reactant and as suspending liquid for the resulting polypropylene.

Temperature and pressure are adjusted 45 – 80 $^{\circ}$C and 1.7-3.5 MPa , respectively, in order to maintain the propylene in the liquid phase. Polypropylene results as a slurry in liquid monomer and is continuously withdrawn from the reactor when the slurry reaches 30-50% solids. In the flash chamber the unreacted monomer is eliminated and the polymer forms a powder that is subsequently dried and pelletized with stabilizers.

2.1.2 The solution process

In solution processes that are more expensive and hence used only for specialty products, higher temperatures (160-250 $^{\circ}$C) and pressures (2.7-8.0 MPa) are employed in order to dissolve the native polymer in the liquid monomer. Polypropylene produced in this process has higher impact strength and lower brittleness temperatures than conventional polypropylene.

2.1.3 The gas phase process

The gas phase fluidized bed process introduced by Union Carbide for the production of LLDPE has been adapted for the polymerization of propylene to homopolymers or block copolymers. The plants are equipped with swing capacities for the transition from polyethylene to polypropylene and back to polyethylene. Fluidization is maintained by the high rate of gaseous monomer recycle. The reactor has two zones: the reaction zone at the bottom where the catalyst and the growing polymer particles are fluidized by the gas stream of monomer and the disengagement zone at the top where the unreacted monomer and the solid particles separate.The gas is recycled while the polymer particles fall down and are continuously withdrawn. The polymer may be obtained in granular form with spherical morphology which eliminates any pelletzing operation. The flow chart of the fluidized bed process is presented in **Figure 2.1.2** Compared to conventional polypropylene, the property spectrum of the new polypropylene types makes it possible to rate them as advanced materials designed for engineering applications. The technologies of the preparation of highly active catalysts and state-of-the art polymerization process are highly proprietary.

Totally new metallocene-based catalyst systems are entering the polypropylene manufacturing technology. Such factors as the temperature, the transition metal (Ti, Zr, Hf), the ratio alumoxane/metallocene, the substitution in the ligands (position, number and type of substituents) directly control the catalytic activity, the average molecular weight, the molecular weight distribution, the degree of tacticity, the sequence distribution and the microstructure of polypropylene. Stereoregulation in the polymerization of propylene is one of the most important capabilities of metallocenes. The possibility of steric design of the π-ligands (cyclopentadienyl, indenyl and fluorenyl) allows the synthesis of metallocenes with different symmetries, each giving rise to different stereoregulated polypropylene.

Four types of polypropylene can be produced : isotactic, syndiotactic, atactic and hemiisotactic. In hemiisotactic structure every other methyl group is in isotactic placement and the remaining methyls are placed at random. The stereoregularity of the polypropylene is controlled in two different ways: (a) by the chirality of the catalyst which governs the insertion of the monomer into the metal-carbon bond (enantiomorphic site control) and (b) in the case of achiral metallocenes, the tacticity is controlled by the configuration (chirality) of the last inserted monomer unit (chain end control) The tacticity of the polypropylene is mostly affected by the symmetry of the metallocene. Spherical megaparticles of polypropylene are formed with metallocene systems that are quite different as compared with the particles obtained with conventional Ziegler catalysts. Supported metallocenes on silica or $MgCl_2$ have also been studied. Cationic metallocenes give productivities that are six times higher than metallocene / alumoxane systems and the stereospecificity is higher at low tenperature (96.3% isotactic polypropylene at $-55\ ^\circ$C)

Propylene   Ti compound   Al compound   Diluent

```
                              ↓            ↓
                        ┌──────────────────────────┐
                        │   Catalyst preparation    │◄─────────────
                        └──────────────────────────┘
                                    ↓
                        ┌──────────────────────────┐
                        │      Polymerization       │
            ────────►   │   50-80 C; 0.5-3.0 Mpa    │◄─────────────
                        └──────────────────────────┘
                                    ↓
  ┌──────────────┐      ┌──────────────────────────┐
  │ Purification │────► │   Flashing off propylene  │
  └──────────────┘      └──────────────────────────┘
                                    ↓
                        ┌──────────────────────────┐
  Methanol + HCl ─────► │  Decomposition of catalyst │
                        └──────────────────────────┘
                                    ↓
                        ┌──────────────────────────┐      ┌──────────────────────────┐
                        │       Centrifugation       │────►│   Separation of diluent   │
                        └──────────────────────────┘      └──────────────────────────┘
                                    ↓                                    ↓
                        ┌──────────────────────────┐      ┌──────────────────────────┐
                        │    Purification  and      │      │        Atactic PP         │
                        │     drying  of  PP        │      │                           │
                        └──────────────────────────┘      └──────────────────────────┘
                                    ↓
                          Isotactic PP pellets
```
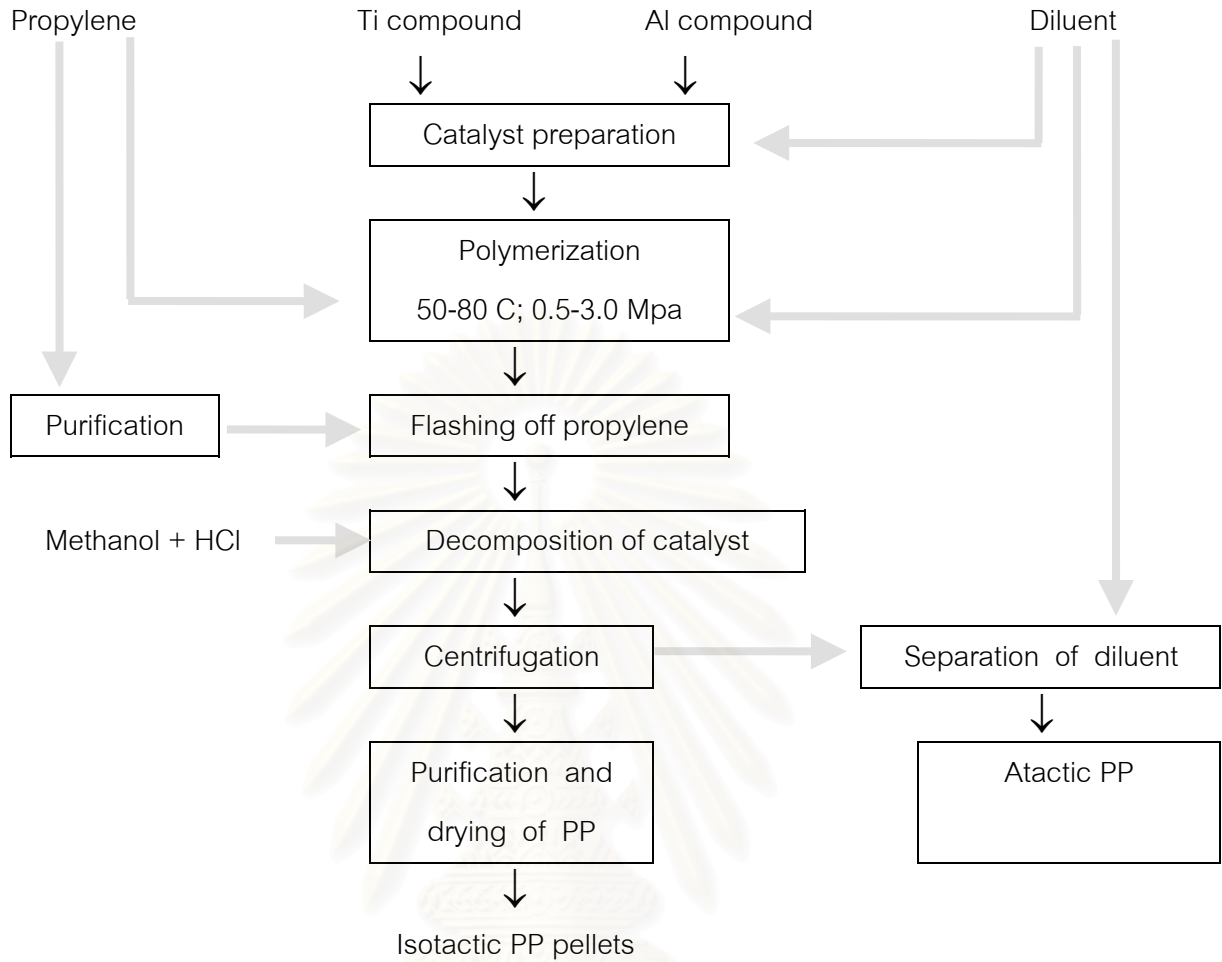
Figure 2.1.1 Polymerization of propylene by the slurry process.[6]

Propylene   Catalyst

```
┌──────────┐        ┌─────────────────────┐
│ Cyclone  │ ◄───── │ Disengagement  zone │
└──────────┘        ├─────────────────────┤ ◄─────
          ──────►   │ Polymerization  zone │
                    └─────────────────────┘
                              │
                              ▼
                    Isotactic  PP  granules
```

Figure 2.1.2 Gas phase fluidized bed polymerization of propylene[6]

2.2 Properties

The tacticity of polypropylene plays a major role in determining its properties. The isotactic polypropylene has the most regular structure with the carbon chains arranged into right-hand and left-hand helices. Each turn of the helix is formed by three monomer units. The methyl groups are on the outside of the helix. These regular helices can pack closely together to form crystalline regions. Commercial polymers are 75-98% isotactic and may contain some atactic and syndiotadtic forms as separate macromolecules or as block. Stereoblock chain may also be present in which right-hand and left-hand blocks alternate. When the inversion of these blocks is not frequent the polymers behave like isotactic structures. The greater the amount of isotactic structure, the higher the degree of crystallinity.

Polypropylene is a crystalline polymer and the rate and manner in which the crystals have been formed from the melt influence the crystalline structure. This in turn largely determines both physical properties and processing characteristics of the polymer. Nucleation agents (crystalline organic acids or metal salts) are added in amounts below 0.1% to provide additional crystallization sites and the formation of smaller and more numerous polymer crystals. This controlled morphology of the polymer, referred to as high crystallinity polypropylene, results in higher bulk properties of the material, namely the softening point, the stiffness, the tensile strength, the modulus and the hardness. The melting temperature, T_m, of isotactic polypropylene is 176 $^\circ$C, some 40 $^\circ$C higher than that of HDPE and this fact makes possible steam sterilization of many polypropylene articles. Strain-free articles retain their shape even at 135-140 $^\circ$C.

The glass transition temperature, T_g, of polypropylene is situated at about 0 $^\circ$C and below this temperature the impact strength drops down and the polymer becomes brittle. A way to improve this behavior is by block copolymerization with ethylene. Some properties of polypropylene are: density (g/cm^3)=0.903; tensile strength (MPa)=35.5; tensile modulus(MPa)=1380; flexural modulus(MPa)=1690.The non-polar nature of polypropylene provides the material with excellent electrical properties similar to those of HDPE. Chemical resistance to most chemicals and solvents is exceptionally high. The polymer is insoluble at room temperature and dissolves in hydrocarbon and chlorinated hydrocarbons only above 80°C. Unlike polyethylene, polypropylene does not suffer environmental stress cracking. Polypropylene differs from polypropylene by the presence of methyl side branches and of relatively labile tertiary hydrogen atoms at every second carbon atom on the backbone.

This makes the polymer more susceptible to oxidation by oxidizing agents and by air at elevated temperatures. Antioxidants must be used in all commercial compounds. The general practice is to incorporate small quantities of stabilizers even before the drying operation or before a long-term storage. Additional stabilizers are blended with the polymer during pelletizing. The general antioxidants are hindered phenols, hydroperoxide decomposers or various phosphites and they are synergistic. For special applications more specific stabilizers are added.

Unlike polyethylene which may be crosslinked by high radiation, by heating which peroxides or by chlorosulfonation, polypropylene is degraded to lower molecular weight products by similar treatments. Polypropylene is produced in a large variety of melt flow index (MFI) from 0.3 to 800 g/10min. Weight-average MW of commercial polymers is in the range 220,000-700,000 and MWD is 5.6-11.9. Both MW and MWD are dependent on many factors such as the polymerization process, the temperature, the pressure, the concentration of the monomer , the composition of the catalyst system, and the addition of hydrogen as chain transfer agent. A common practice to narrow the MWD is a post-reaction treatment usually with peroxides that also produces some chain scission.

The products are known as controlled rheology grades (CR) and they manifest a better balance of physical properties and processing characteristics. The specific heat of polypropylene is lower than that of polyethylene allowing an increase in the plasticizing capacity of the injection molding machines compared to polyethylene. The higher the degree of induced crystallinity by the processing conditions, the higher will be the molding shrinkage of the material. The reduction of the shrinkage can be realized by coupling a higher temperature of the melt with a lower temperature of the mold.

Besides antioxidants, other additives have been used with polypropylene. Different mineral fillers such as talc, calcium carbonate or glass fibers confer an improved range tensile of properties, For example 25% by weight of glass fiber leads to a fourfold increase of the strength and to an eightfold increase of the rigidity of polypropylene at 100 $^\circ$ C. Rubbers, especially ethylene-propylene rubbers taken in amounts of up to 50% by weight, have been used as fillers in order to improve the impact strength of polypropylene. Pigments, flame retarders, carbon black and ultraviolet absorbers have been used for specific applications. Foaming agents contribute to improve the stiffness/weight ratio and to eliminate the shrinkage. Processing methods such as injection molding, blow molding, fiber extrusion and film manufacture (tubular bubble process or flat process) are the general processing techniques used with polypropylene. The bulk of the film is used in biaxially oriented form which provides higher strength and better barrier properties.

2.3 Applications of polypropylene

Around 30% of polypropylene and its related copolymers is used as fibers and filaments produced by extrusion. Excellent wear and resistance to staining associated with low cost have led to uses in woven and non-woven forms for carpeting in indoor and outdoor construction, for clothing, inner liners, drapes, tea bags, wall coverings, furniture and automotive upholstery, and for ropes and netting. Coaltings for wire, piping or ducts, sheeting and film are produced by extrusion. Another large market for polypropylene and for its copolymers is as film (both oriented and cast) for packaging of food and tobacco products and for textile goods. Injection molded objects represent about 30% of polypropylene applications. These are toys, laboratory and medical supplies, housewares, closures, appliances, luggage, automotive and truck battery cases, washing machines, agitators, pump housings, different parts in dishwashers, refrigerators, and freezers.

In addition to its light weight, polypropylene provides outstanding resistance to creep, high temperature rigidity, impact strength and resistance to corrosion. Disposible syringes and other medical applications are based on the possibility of applying sterilization either by autoclaving or by radiation. Atactic polypropylene, which was an unwanted by-product for many years, is now specially produced for some applications. The material, which is intermediate between wax and a rubber, is compatible with mineral fillers and bitumens. It has found use for roofing materials, as asphalt additive, for the formulation of sealing and adhesive compounds and for paper laminating. Syndiotactic polypropylene, which is not yet commercially available, has lower T_m, better impact resistance and more clarity than isotactic polypropylene. An obvious advantage of polypropylene is its ease of recycling , this is especially important in many of the packaging and automotive applications.

2.4 Literature reviews

Huffman et al.,[10] investigated the direct liquefaction of medium and high density polyethylene(PE), polypropylene(PPE), poly(ethylene terephthalate) (PET), and a mixed plastic waste, and the coliquefaction of these plastics with coals of three different ranks. The results established that a solid acid catalyst(HZSM-5 zeolite) was highly active for the liquefaction of the plastics alone, typically giving oil yields of 80-95% and total conversions of 90-100% at temperatures of 430-450 $^{\circ}$ C. In the coliquefaction experiments, 50:50 mixtures of plastic and coal were used with a tetralin solvent(tetralin : solvent = 3 : 2). Using~1% of the HZSM-5 catalyst and a nanoscale iron catalyst, oil yields of 50-70% and total conversions of 80-90% were typical.

Anderson et al.,[2] studied coliquefaction of coal and waste polymers. Coal can be converted into distillable liquid fuels with the addition of hydrogen. Waste polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene teraphthalate(PET) contain hydrogen at levels of approximately fourteen percent , since such a small fraction of the plastic and other polymer materials are currently recycled these materials could, in principle, provide the hydrogen to aid in the liquefaction of coal. Coal alone and pure waste polymers, as well as a commmingled waste polymer mixture, have been liquefied separately and mixtures of coal and various polymers have been coprocessed. Thermal and catalytic processing shows that such coprocessing can be a viable method to produce high quality liquid fuels and to mitigate the disposal problem of waste polymers.

Hyun et al.,[11] investigated coprocessing of waste plastics with petroleum resid to determine the effect of resid on reactivity and conversion. The coal used in this study was Blind Canyon bituminous coal, the resids were Maya and Maniji, and the model plastics tested were polystyrene, poly(ethylene terephalate) (PET), and low-density polyethylene(LDPE). Three systems , the individual species, binary combinations, and ternary combinations, were reacted at conditions of 430 $^{\circ}$C and 8.7 Mpa of H_2 introduced at ambient temperature for 60 min of reaction time. Presulfided $NiMo/Ai_2O_3$ was used as the catalyst, typically at 1 wt% loading, although other catalyst loading levels of 3 and 10 wt% were tested. Under these conditions polystyrene and PET reacted readily, while LDPE was difficult to convert. Binary reaction with resids resulted in high conversions of ~94% from polystyrene and PET, while the reactions with LDPE somewhat less conversion of ~72%. By contrast, reactions of plastics with coal converted substantially less, ranging from 70.2% for polystyrene and coal to 39.9% for LDPE and coal.

Ternary reactions with coal, plastic, plastic, and resid resulted in high conversions for all systems(~89-95) except those with LDPE (~77-81). The effect of coprocessing binary and ternary systems compared to individual systems on the basis of conversion, hexane solubles, and gas productions was determined. The effect of adding a third species into the binary systems was also evaluated. The hexane-soluble products from the three reaction sets were analyzed by simulated distillation to determine the amount of the reaction product boiling at less than 500 $^{\circ}$C. Reactions containing LDPE produced substantially less material that boiled 500 $^{\circ}$C than did the other reactions.

Kaoru et al.,[7] studied an iron supported coal-derived active carbon catalyst showed excellent activity for liquefaction of polypropylene(PP) at low temperature (380 $^{\circ}$C) to give colorless distillates selectivity (92 wt%). Free radical on active carbon should initiate cracking reaction by hydrogen abstraction from polypropylene to form hydrocarbon radical. However, the consecutive cracking of the hydrocarbon radical is suppressed by hydrogenation on the iron particle to give colorless distillates selectively.

Paul et al., [14] studied interaction of plastics in mixed-plastics pyrolysis. The pyrolysis of mixed-plastic waste has been proposed as a means of recycling to produce petrochemical feedstock. The interaction of the main plastic types in plastic mixtures is significant in predicting the likely yield and composition of products from different plastic mixtures. The six main plastics in municipal solid waste are high-density polyethylene(HDPE), low-density polyethylene(LDPE), polypropylene(PP), polystyrene(PS), poly(vinyl chloride)(PVC), and poly(ethylene terephthalate)(PET).

Each of the plastics was pyrolyzed individually in a fixed-bed reactor heated at 25 $^\circ$C/min to a final temperature of 700 $^\circ$C. Polystyrene was then mixed with each of the other five plastics in a ratio of 1:1 and pyrolyzed in the fixed-bed reactor under the same pyrolysis conditions. The yield and composition of the derived oil/wax and gases was determined. The main gases produced from the individual plastics were hydrogen, methane, ethane, propane, propene, butane, and butene and for the PET plastic carbon dioxide and carbon monoxide. Hydrogen chloride was also produced with PVC. Analysis of the oil/wax showed that the polyalkene plastics, HDPE, LDPE, and PP, gave a mainly aliphatic composition consisting of a series of alkanes, alkenes, and alkadienes. PVC gave a mainly aromatic oil, and PS and PET, which have aromatic groups in their structures, also showed a more aromatic composition. There was a higher gas yield from the mixtures of the plastics with PS than would be expected from the pyrolysis of the individual plastics, coupled with a reduction in the oil/wax phase. The average molecular weight of the oil/wax from the mixed plastics was less than expected from the individual molecular weights. Compositional analysis of the oil/wax showed that changes in the concentration of aromatic hydrocarbons and polycyclic aromatic hydrocarbon were produced with the mixture compared to that expected from the individual plastics.

CHAPTER III

THEORY

3.1 Metal Catalyst[12]

For metals and metal alloys in particular, relationships have been sought between collective properties and catalytic behavior. The metallic state was generally described by the simple band model or the Pauling valence structure theory.
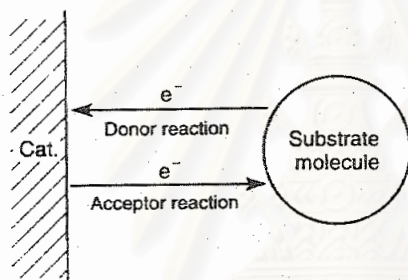
Figure 3.1 Electron transfer between catalyst and substrate[12]

In metal the valence shell is formed by the s or d band. The main-group elements with their s bands are typical electron donors and form strong bongs with electron acceptors such as sulfur or oxygen; stable sulfides and oxides are formed. These metals are therefore not suitable as catalysts. In contrast the transition metals with their d bands are excellent catalysts. It is noteworthy that both hydrogenations and oxidations can be carried out with d-block elements.

Let us now describe the electronic structure of the transition metals with the aid of the band model. According to this model the metal is a collective source of electrons and electron holes (**Fig 3.2**). In a row of the periodic table, the metals on the left have fewer d electrons to fill the bands. There are two regions of energetic states, namely, the valence band and the conduction band with mobile electrons or positive holes. The potential energy of the electrons is characterized by the Fermi level, which corresponds to the electrochemical potential of the electrons and electron holes.
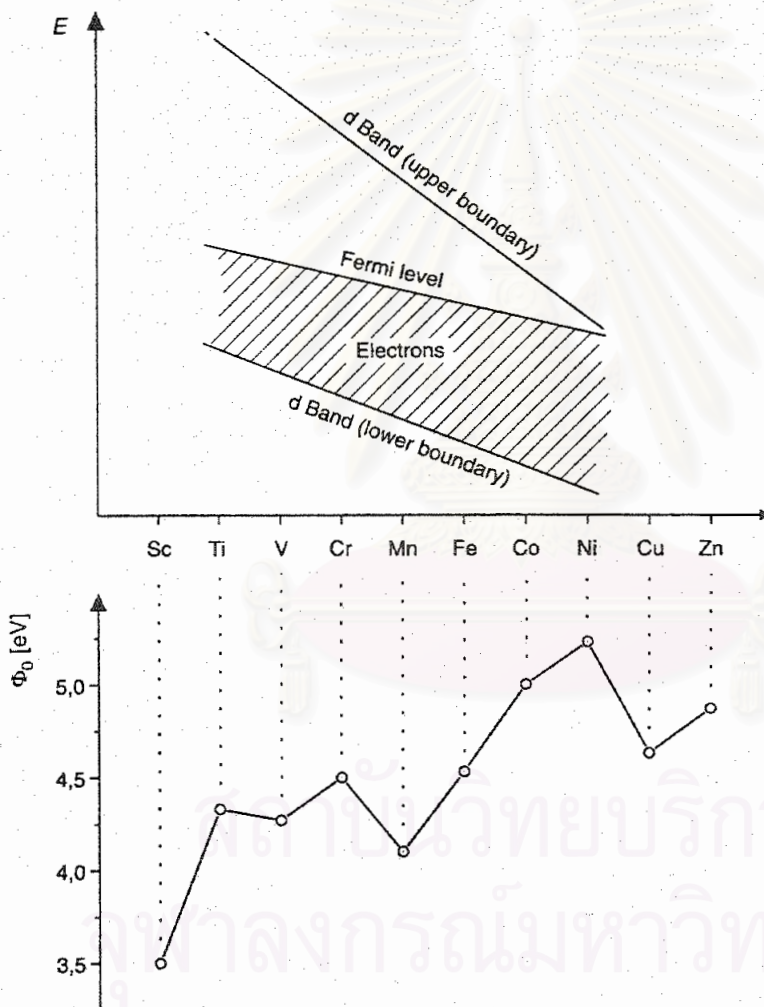
Figure 3.2 Electron density of the 3d band and work function ϕ_0 of the transition metals of the fourth period[12]

The position of the Fermi level also indicates the number density of electrons in the band model. The energy required to transport an electron from the edge of the Fermi level into vacuum corresponds to the work function ϕ_0 (Fig 3.3.a). For the d-block metals, the work function is around 4 eV and therefore in the UV range. A certain number of free levels or d-holes are available for bonding with adsorbates. The lower the Fermi level, the stronger the adsorption. How do donors and acceptors function in the band model. In the surface layer, the free electrons or holes allow molecules to be bound to the surface, whereby the strength of binding depends on the position of Fermi level. An acceptor removes electron density from the conduction band of the metal as a result of which the Fermi level drops to E_F and the work function $\phi_A > \phi_0$ (Fig 3.3b). A donor donates electrons to the conduction band of the metal, and the work function becomes corresponding lower: $\phi_A < \phi_0$ (Fig 3.3c).
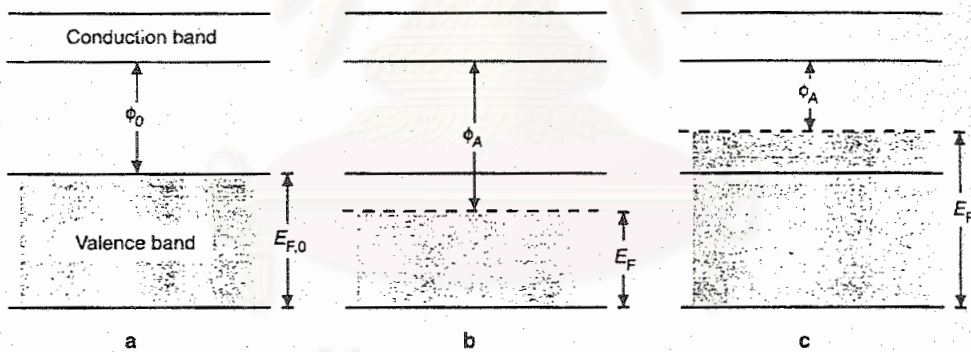
Figure 3.3 Acceptor and donor function according to the band model

a) No adsorption ; b) Acceptor ; c) Donor

$E_{f,0}$ =Fermi level ; E_f = Fermi energy[12]

Metals normally have a narrow d band. The catalytic properties are strongly in-fluenced by the occupational density of the electrons in this band. In many cases a direct relationship has been found between the catalytic activity of transition metals and the electronic properties of the unfilled d bands. This is shown by the general trend of the rate of adsorption along the transition metal rows. For atomic species strong binding is observed on the left-hand side of a row. For molecular species it was found that the rate of dissociative adsorption on the noble metals increases from right to left as a function of the d-band occupation. Besides the electron occupation of the d bands, another description can be used for obtaining correlations, namely, the valence bond theory of metals. The bonding in transition metal is partially due to unpaired electrons in bonging d orbitals. The contribution of these d electrons to the valence bonding was termed "percentage d character" of the metallic bonding by Pauling, who made a distinction between three types of d orbitals in transition metals:

Bonding d orbitals involved in covalent dsp hybrid bonds

Metallic (free) d orbitals

Atomic d orbitals

3.2 Catalyst preparation and manufacture[5]

Most catalysts are either a finely divided metal supported on a carrier such as alumina or silica, or a compound, more or less complex, either on a carrier or unsupported. Metal-sulfide catalysts are prepared first as the oxide and then treated with hydrogen sulfide or another sulfur compound in the presence of hydrogen to convert it to the sulfide. Either of two types of processes, generally termed the precipitation method and the impregnation method, is commonly used for making catalysts. The first involves in its initial stages the mixing of two or more solutions or suspensions of material, causing precipitation; this is followed by filtration, washing, drying, forming, and heating.

Simple wet mixing without precipitation is occasionally used, but it may not provide the degree of intimate contact between species that is usually desired. High temperatures can subsequently be applied to provide homogeneity and compound formation by thermal diffusion and solid-state reaction, but this usually causes an undesired degree of sintering and consequent loss of surface area. Sometimes the desired degree of mixing can be achieved by kneading.

If a carrier is to be incorporated in the final catalyst, the original precipitation is usually carried out in the presence of a suspension of the finely divided support, or a compound or suspension that will eventually be converted to the support may be initially present in solution. The final size and shape of the catalyst particles are determined by the forming process, which may also affect pore size and pore-size distribution. Larger pores can be introduced into a catalyst by incorporating into the mixture 5 to 15 percent of wood flour, cellulose, starch or other material that can subsequently be burned out. Final catalyst material rejected for chemical or physical reasons may in some cases by recycled without harm to product specifications by powdering it and incorporating it into the catalyst mixture. Such incorporation, however, may change the pore size distribution of the final catalyst with a gelatinous precipitate, mechanical manipulation may have a significant effect on the ultimate pore size distribution. After it is dried and formed, the precursor catalyst is activated; that is, it is converted into its active form through physical and chemical changes. This typically involves heating to cause calcination or decomposition, followed by reduction if a metallic catalyst is desired. In some cases a supported metal catalyst is pyrophoric, and reduction is carried out in the plant reactor rather than by the catalyst manufacturer to avoid hazards upon shipping and reactor loading. Some advantages of the precipitation method are that it generally provides more uniform mixing on a molecular scale of the various catalyst ingredients, the distribution of active species through the final catalyst particle is uniform, and the ultimate sizes and shapes are not limited to the forms in which desired carriers are available.

Also, more control may be available over pore size and pore size distribution. If two or more metal compounds are present, in a batch-type operation they may precipitate at different rates or in sequence rather than simultaneously, thus affecting the final structure of the solid. Both the ultimate physical and chemical structure of the catalyst are frequently very sensitive to the pH of the precipitation, in which case precipitation is carried out continuously in a well-mixed vessel with careful control of pH. Impregnation is the easiest method of making a catalyst. A carrier, usually porous, is contacted with a solution, usually aqueous, of one or more suitable metallic compounds. The carrier is then dried, and the catalyst is activated as in the case of precipitated catalysts.The size and shape of the catalyst particles are that of the carrier. The impregnation technique requires less equipment since the filtering and forming steps are eliminated and washing may not be needed. It is the preferred process in preparing supported noble metal catalysts, for which it is usually economically desirable to spread out the metal in as finely divided a form as possible. The noble metal is usually present in the order of 1 wt % or less of the total. This makes maximum use of a very expensive ingredient; in a precipitated catalyst some of the active ingredient may be enclosed by other material present and thus unavailable for reaction.

3.2.1 Precipitation Method of Catalysts

3.2.1.1 Precipitation

In a common procedure an aqueous metal salt solution is contacted with an aqueous alkali, ammonium hydroxide or ammonium carbonate, to cause the precipitation of an insoluble metal hydroxide or carbonate. These can be readily converted to oxides by heating. The starting compounds are generally chosen because of their availability and high water solubility, and in some cases to avoid introducing elements that may be deleterious in the final catalyst or that may cause difficulties in subsequent processing.

Control of air and water pollution is also an important factor. NO_x from nitrates must be removed , e.g., by scrubbing with aqueous alkali; many heavy metals are more or less toxic and cannot be simply discharged. If the final catalyst is to be a supported metal, sulfate may be undesirable, since it can be reduced to a sulfide, which is a common poison for metal catalysts, the metal nitrate salt is often preferred because it usually is highly water-soluble, generally available, and cheap, but NO_x control is required. An organic compound such as a formate or oxalate may be used, although these are more expensive and organic fragments from their decomposition on heating may adsorb on the catalyst to cause partial inactivation. Also, the average ultimate metal particle size may be considerably different if it is formed by decomposition of a compound rather than by reduction of an oxide. Sulfates and chlorides are generally water-soluble, but the anions must usually be removed by washing, and disposal of waste water may be problem. A preferred base is usually ammonium hydroxide since it leaves no cation residue, but it may complex with some metals and keep them in solution.

If a relatively crystalline precipitate is formed, the size of the crystals may affect the ultimate particle size of a supported metal catalyst. Thus, fine crystals may be desired to produce high surface area of a supported metal catalyst, but crystals that are too fine may be difficult to filter. The size of such crystals may be controlled by a variety of techniques. In a multi component catalyst, crystals may be smaller if the metals are truly coprecipitated rather than precipitated in sequence. Crystal size may also be affected by temperature and by stirring, since this affects nucleation and the degree of super saturation. Ripening, in which a precipitated is allowed to stand for a period, can allow for re-crystallization in which small and/or amorphous particles dissolve and crystalline particles grow. This may convert a gelatinous precipitate to a more crystalline and filterable solid.

Silicic acid and a number of metal hydroxides, e.g., those of aluminum, iron, and titanium, form gelatinous colloids, this can make them extremely difficult to filter or to purify by washing. Such gels may be coagulated by electrolytes, but the process of washing to remove electrolyte impurities may cause them to redisperse into colloidal solution, termed peptization. Hence, a silicic acid gel may be washed with dilute hydrochloric acid, or an aluminum hydroxide gel with aqueous ammonium nitrate, to maintain an ionic environment and hence the coagulated form. The additives can be subsequently removed by heating, gels readily occlude ionic impurities, which may be difficult to remove by washing. The possibility of reaction between carrier and reagents should also be considered in this step. Thus, acidic solutions of reagents may react with basic carriers, and vice versa.

3.2.1.2 Forming operations

The nature of the forming operations is determined by a balance among several factors, including rheological properties of the mixture, and the necessity to achieve satisfactory strength, an open-pore structure, and high activity in the ultimate catalyst, in addition to economics. Relatively hard materials, which typically have high melting points, cannot be made into pellets without suitable additives. Operations causing an increase in crushing strength usually also decrease pore volume and average pore size, and hence may cause diffusion limitations. Typically, commercial catalysts have a void fraction of about 0.5 cm^3 of voids per cubic centimeter of porous pellet.

3.2.1.3 Calcination

This may have several purposes. One is to eliminate extraneous material such as binders and die lubricants, as well as volatile and unstable anions and cations that have been previously introduced, but are not desired in the final catalyst. Second, a substantially elevated temperature is usually needed to increase the strength of the final pellet or extrudate by causing incipient sintering. Excessive sintering will reduce the catalyst activity by reducing surface area, and it may also cause diffusion limitations by reduction of pore size, so an optimum is desired. If a metallic catalyst is the ultimate goal, conversion to the oxide form is frequently sought prior to reduction. If a complex catalyst is the goal, a substantially elevated firing temperature may be required to cause mixing by diffusion of individual species to form a desired compound or crystal phase. In any event, the catalyst should be heated under controlled conditions to a temperature at least as high as will be encountered in the plant reactor to remove bound water, carbon dioxide, etc. If these decompositions occur to a significant extent in the plant, they may cause structural weakness in pellets, leading to breakup, dusting, and so on, that may cause excessive pressure drop and premature reactor shutdown.

For small production runs, conventional batch-type multi tray driers and calciners are common, but labor costs are high. For larger production runs, a continuous rotary kiln may be used. More precise temperature control is achievable with a continuous tunnel kiln. This may be heated electrically with numerous zones so that temperature rise can be programmed. Trays may be fastened onto a stainless steel mesh belt and automatically loaded and dumped, or trays may be placed and removed manually. Upon heating pellets in a tray calciner, an exothernic reaction may develop that can lead to excessively high temperature locally, affecting the catalyst adversely.

The effect can stem from an exothermic decomposition reaction, as in the thermal decomposition of an ammonium copper chromate to form a "copper chromite" catalyst or by reactions among pellet ingredients, such as that between a metal nitrate and organic admixtures such as cellulose, graphite, or stearates. Combustion in air of these organic substances or of remaining organic solvents may also occur. The effect is most pronounced with thick layers of pellets from which heat generated internally cannot easily escape. It may be controlled by using a slower rate of heatup or using thinner layers of pellets, although it may necessary to use layers as thin as inch or so.

3.2.1.4 Reduction to the metal

Most commonly, a metal is formed by reduction of the oxide at an elevated temperature by contact with flowing hydrogen or hydrogen diluted with nitrogen, the latter for safety reasons. A considerable excess of hydrogen may be required to sweep away the product water. If present in too high a concentration, water vapor may accelerate the sintering of and oxide, and it can also retard the rate of the reduction reaction by forming a hydroxylated surface.

Some metal compounds can be reduced by chemical reagents, such as formaldehyde, formic acid, or hydrazine, but these methods are usually more expensive. Alternately, the metal may be formed by decomposition of an organic compound, as by decomposition of nickel formate to yield deposited nickel. In this case, however, organic fragments may become adsorbed onto the metallic catalyst, possibly giving rise to considerably different properties than that of a catalyst reduced in hydrogen. Moreover, the ultimate metal particle size is determined by the sintering characteristics of the metal produced, whereas in oxide reduction, particle size may be determined in part, in a rather complicated way, by the formation of metal nuclei and their growth from the oxide particles.

3.2.2 Impregnation

Two methods of contacting may be distinguished. The support is sometimes dipped into an excess quantity of solution, whereupon the uptake is the sum of solution occluded in the pore plus material adsorbed onto the pore surfaces. If two or more compounds are present, they are frequently adsorbed on the support surface in a ratio different from that in the solution, and solution concentrations also change with continued contacting. Additions to the solution must take these effects into account. Moreover, material may be dissolved from the support into the treating solution. More precise control is achieved by a technique termed dry impregnation, or impregnation to incipient wetness, which is commonly used industrially. A batch of the support is tumbled and sprayed with a solution of appropriate concentration, corresponding in quantity to the total known pore volume of the support, or slightly less. This allows accurate control of the amount of the active ingredient that will be incorporated into the catalyst, but the maximum loading obtainable in a single impregnation is limited by the solubility of the reagent. The resulting catalyst is then usually dried and calcined.

In a few cases, the active ingredient may be fixed inside the catalyst by immersing the impregnated catalyst in a reagent to cause precipitation to occur.Oxide supports such as alumina and silica are readily wet by aqueous solutions, as are most activated carbons, which have a layer of chemisorbed oxygen on them. Capillary forces then ensure that liquid is sucked into the entire porous structure. Because of capillary pressure, even pores closed at one end are nearly filled, and the solution of gas in the liquid assists the process. If the support is not readily wetted, e.g., a carbon that is highly graphitized or without chemisorbed oxygen, an organic solvent may be used or the support may be impregnated under vacuum. These procedures are somewhat more costly to use in the plant than incipient impregnation.

3.2.2.1 Distribution through pellet

Most metal reagents are adsorbed to varying degrees on most supports, but the characteristics of the process are complicated since various types of adsorption are possible. Silica and zeolites are acidic and adsorb cations. Alumina is amphoteric. Titania is also amphoteric, but more acidic than alumina. For these adsorbents the relative adsorption of cations and anions can be controlled by adjusting pH. Metal ions may be cation-exchanged with a surface containing hydroxyl groups or containing alkali or alkaline earth-metal ion, or they may be held by coordination. The surface structure of the carrier may also be altered by the impregnation procedure, thus changing its adsorption characteristics. The ultimate degree of dispersion of metal through the catalyst pellet is also determined by the interplay of a large number of factors whose relative importance varies with circumstances. These include the method of impregnation, the strength of adsorption, the extent to which the metal compound is present as occluded solute (that in the bulk liquid in the pores) in contrast to adsorbed species on pore walls, and the chemical reactions that occur upon heating and drying.

The situation may be further complicated by attack on the support. Silica gel is attacked at high pH, and alumina, which is amphoteric, is attacked at a pH that is either too high or too low. Indeed, during the impregnation of an alumina support with an acidic liquid, some solution of alumina may first occur, followed by precipitation as the pH increases. It may be desirable to control this effect by using a buffer.It is also possible to control the deposition by competitive adsorption, e.g., by adding a citrate to the impregnating solution. This procedure has been used to embed a catalytically active layer slightly inside a catalyst particle. Such a structure may be desired for prolongation of catalyst life in an application in which poisons are deposited on the outside surface of a porous catalyst support. An example is supported platinum catalysts for oxidation of pollutants in automobile engine exhaust.

In general, use of the dipping method with a great excess of solution should lead to an essentially uniform deposit of adsorbed material if sufficient time is allowed for diffusion of reagent species to the interior and if side reactions are unimportant. If adsorption is initially non uniform and not too strong, redistribution continues even after the pallet is removed from solution, leading to a more uniform distribution. The dry process can also affect the distribution of an active ingredient. The crystallite size of a resulting supported metal catalyst may also be alerted if a considerable portion of the soluble metal is occluded rather than adsorbed. Again, the effects are complex, and little can be said of general guidance. Initially, evaporation occurs at the outer surface of the particle, but liquid evaporated from small pores will be replaced by liquid drawn from large pore by capillarity. The places where crystallization begins and the ultimate distribution of metal depend on such factors as the initial degree of saturation of the liquid, the rate of nucleation, the rate of heating, connectivity (the degree of connection of liquid paths between pores) at the time of crystallization, and the possibility of surface migration. Commercially available impregnated catalysts are usually found to have a higher concentration of metal at the outside than at the center, even when a more or less uniformly deposited catalyst is desired.

3.3 Catalyst support

The early concept of a support or a carrier was of an inert substance that provided a means of spreading out an expensive catalyst ingredient such as platinum for its most effective use, or a means of improving the mechanical strength of an inherently weak catalyst. However, the carrier may actually contribute catalytic activity, depending on the reaction and reaction conditions, and it may react to some extent with other catalyst ingredients during the manufacturing process. It can also help stabilize the catalytically active structure. The carrier may be used as pellets or powders to be impregnated, a powdered carrier may be incorporated into a mixture to be precipitated, or the carrier may itself be precipitated from solution in the manufacturing process.

Some substances such as colloidal alumina or colloidal silica may play a double role, acting as a binding agent in catalyst manufacture and as a carrier in the ultimate product. Alumina in the γ form is intrinsically weakly acidic, but such a substance may be a truly inert carrier for many reactions. In other cases it can be used by itself as a catalyst, as in dehydration of an alcohol. High-area carriers are sometimes loosely referred to as active carriers in contrast to low-area inert carriers, but this usage may be misleading.

The selection of a carrier is based on its having certain desirable characteristics. In addition to possible chemical effects certain physical properties are importance:

1.Inertness to undesired reaction

2.Desirable mechanical properties, including attrition resistance, hardness, and compressive strength

3.Stability under reaction and regeneration conditions

4.Surface area (high surface area is usually, but not always, desirable)

5.Porosity, including average pore size and pore-size distribution (High area implies fine pores, but relatively small pores, such as<2 nm, may become plugged in catalyst preparation, especially if high loadings are sought.)

6.Low cost

3.3.1 Activated carbon[19]

Activated carbon is a processed carbon material with a highly developed porous structure and a large internal specific surface area. If you take a look at a cross section of an activated carbon particle, it looks like a beehive. It consists, principally of carbon (87 to 97%), but also contains such element as hydrogen, oxygen, sulfur and nitrogen, as well as various compounds either originating from the raw material used in its production or generated during its manufacture.Activated carbon has the ability to absorb various substances both from the gas and liquid phases.

It is widely used for adsorption of pollutants from gaseous and liquid steams, for recovery of solvent and as a catalyst or catalyst support. In the nuclear industry, activated carbon is used for adsorption of iodine and noble gases form gaseous effluents. One of the most important fields in terms of consumption is in water and wastewater treatment. To obtain these activated carbons from cheap and readily available precursors. Raw materials for the production of activated carbon such as wood, peat, coconut, shell, coal.

3.3.1.1 Production of activated carbon

Activated carbon is usually production by the carbonization and activation of carbonaceous materials.

- Carbonization (or pyrolysis)

The carbonaceous material that constitutes the basis for the production of activated carbon by the steam-gas method must meet certain requirements among which the most important are: (i) low content of volatile matter, (ii) high content of elemental carbon, (iii) definite porosity and (iv) sufficient strength of attrition. Of course, raw materials do not meet all these requirments simultaneously and therefore they require carbonization. This is one of the most important steps in the production process of activated carbons since it is in the course of carbonization that the initial porous structure is formed. During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material, and the freed atoms of elementary carbon are grouped into organized crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular, so that free interstices remain between them and apparently as the result of deposition and decomposition of tarry substances, these becomes filled or at least blocked by disorganized ("amorphous") carbon.

These are three clear stages in the carbonization process: (a) loss of water in the27-197 $^{\circ}$C range: (b) primary pyrolysis in the 197-497 $^{\circ}$C range with evolution of most gases and tars with formation of the basic structure of the char: (c) consolidation of char structure at 497-847 $^{\circ}$C with a very small weight loss. The resulting carbonized product has only a very small adsorption capacity. Presumably, at least for carbonization at lower temperatures (400-600 $^{\circ}$C), part of the tar remains in the pores between the crystallites and on their surface. A carbon with a large adsorption capacity, however, can be produced only by activating the carbonized material under such conditions that the activation agent (steam, carbon dioxide, etc.) reacts with the carbon

- Activation

Generally, there are two main types of production of activated carbon:

a) By carbonizing material with the addition of activating agents ($ZnCl_2$, $CaCl_2$,H_3PO_4). This method is generally known as "chemical activation".

b) By allowing the inactive carbonized product (prepared by the usual methods of carbonization) to react with oxidizing gases (steam, carbon dioxide, oxygen). This method is generally known as "physical activation".

a) Chemical activation

For chemical activation, the common chemicals used are dehydrating agent such as $ZnCl_2$, $CaCl_2$, $MgCl_2$ and some acid such as H_3PO_4 and H_2SO_4. The activated agent influences the pyrolytic processes so that the formation of tar is restricted to minimum and the amount of the aqueous phase in the distillate is also less than that in the normal carbonization. The activation agent also changes the chemicals nature of the cellulose substrate by dehydration, which decomposes the organic substances by the action of the action of heat and prevents the formation of tar.

Chemical activated is usually carried out at temperatures from 400-600 $^{\circ}$C. These temperature are lower than those needed for activation with gaseous agent (physical activation). An important factor in chemical activation is the degree (coefficent) of impregnation ; this is the weight ratio of the anhydrous activation salt to the dry starting material. The effect of the degree of impregnation on the resulting product is apparent from the fact that the volume of salt in the carbonized material equals the volume of pores which are freed by its extraction. For small degree of impregnation the increase in the total pore volume of the product with increase in the degree of impregnation is due to the increase in the number of small pores. When the degree of impregnation is further raised, the number of large-diameter pores increases and the volume of the smallest decreases.

b) Physical activation

The basic method of activating coal-based granules consists of their treatment with oxidizing gases (steam, carbon dioxide, oxygen) at elevated temperatures. In the activation process, carbon reacts with the oxidizing agent and the resulting carbon oxides diffuse from the carbon surface. Owning to the partial gasification of the granules or grains, a porous structure builds up inside them. The structure of the carbonization product consists of a system of crystallites similar to those of graphite bonded by aliphatic type bonds to yield a spatial polymer. The spaces between the neighboring crystallites constitute the primary porous structure of the carbon. The pores of the carbonized granules are often filled with tar decomposition products and are blocked with amorphous carbon. This amorphous carbon reacts in the initial oxidation step, and as a result the closed pores open and new ones are formed. In the process of further oxidation, the carbon of the elementary crystallites enters into reaction due to which the existing pores widen. Deep oxidation leads to a reduction in the total volume of micropores due to the burning off of the walls between the neighbouring pores, and in consequence the adsorptive properties and mechanical strength of material decrease.

In the first stage of activation, when burn-off is of not higher than 10% (which occurs at low reaction times), this disorganized carbon is burnt out preferentially and the closed and clogged pores between the sheets are freed. In the course of further activation at the second stage, carbon of the aromatic sheet is burnt. When the burn-off is less than 50%, a microporous activated carbon is obtained, when it is large than 75% (which occurs at high reaction times) a macroporous product is obtained ; and when the burn-off is between 50 and 75%, the product is of mixed structure and contains both micro-and macropores, Development of macropores due to coalescence or widening of micropores under fast reaction conditions. Carbon oxidation is a complex heterogeneous process encompassing the transport of reagents to the surface of the particles, their diffusion into the pores, chemisorption on the pore surface, reaction with carbon, desorption of the reaction products, and diffusion of these porducts to the particle surface. The concentration profile of the oxidizing agent of the granule volume, and hence the formation of the carbon porous structure, depends of the rate of the particular steps of the process.

At low temperatures the rate of the chemical reaction of carbon with the oxidizing agent is small, so it is this reaction that limits the overall rate of the process. This results in a dynamic equilibrium becoming established between the concentration of the oxidizing agent in the pores and that in the interparticle spaces. In such a case the activation process yields a homogeneous product with a uniform distribution of the pores throughout the whole volume of the granule, with increase of the oxidation temperature. The rate of the chemical reaction increases much faster than that of diffusion, and then the overall rate of the process becomes limited by the rate of transport of the oxidizing agent into the granule. At very high temperatures the oxidation reaction rate becomes so high that the whole oxidizing agent reacts with carbon on the external surface of the granule.

In such a case significant losses of the material occur due to superficial burn-off, and a porous structure is not formed. The rate of the oxidation process is limited by the reactivity of the initial carbonaceous material towards the oxidizing agent. The greater is the reactivity of the substrates, the lower the optimal temperature of the process at which uniform formation of pores in the granule.

- Pyrolysis and steam activation

Usually the production of activated carbons involves two stages: the carbonization of the raw materials followed by a high temperature activation, at 800-1000 $^{\circ}$C, of the resulting chars. The method used in this study combines the two stage into a single one, while the treatment temperature is considerably lower, 600-800 $^{\circ}$C. This method is preferable to the two-stage treatment from an economic point of view. During the pyrolysis and steam activation of carbon-containing materials the following main processes take place:

1. Oxidation-thermolytic conversion of the carbon material leading to the accumulation of oxygen-containning groups.

2. A thermal destruction process including the decomposition of the oxygen-containing groups accompanied by the formation of carbon oxides and water.

3. Condensation process.

4. Deeper penetration of the water molecules and opening up of the initially closed pores into the structure of the carbon materials.

3.3.1.2 Molecular, crystalline and porous structure of activated carbon

The graphite-like microcrystalline structure is the basic structural unit of activated carbon, as in the case of carbon black. The ordering of carbon atoms in an elementary microcrystallite indicates considerable similarity to the structure of pure graphite, the crystals of which consist of parallel layers of condensed regular hexagonal ring space 0.335 nm. apart. Such interlayer spacing is diagnostic of interaction by means of Van Der Waals forces, The length of the carbon-carbon bond in individual layers is 0.142 nm. Each carbon atom bonds with the three adjoining ones by means of covalent bonds, and the fourth delocalized π-electron may move freely in a system of conjugated double bonds of condensed aromatic ring. The formation of the crystalline structure of activated carbon begins early during the carbonization process of the starting material. Thus sets of condensed aromatic ring of various numbers, which are the nascent center of graphite-like microcrystallites, are formed. Although their structure resembles that of a crystal of graphite there exist some deviations from that structure. Thus, among other things, the interlayer distances are unequal in crystals of activated carbon and range from 0.34 to 0.35 nm. Again, the orientations of the respective layers generally display deviations, such deviations from the ordering characteristic of graphite, called a turbostratic structure. Disordering of the crystal lattice may be caused to a considerable degree both by its defects (vacant lattice sites) and by the presence of built-in heteroatoms. It is resulted from the kind of the raw material used, the nature and quantity of its impurities as well as the methods and conditions of the production processes of the active carbon. The average activated carbons have a strongly developed internal structure (the specific surface often exceeds 1000 and sometimes even 1500 m^2/g), and they are usually characterized by a polydisperse capillary structure, featuring pores of different shapes and sizes. Bearing in mind the values of the effective radii and the mechanism of adsorption of gases, Dubinin proposed three main types of pore, namely macropores, mesopores and micropores.

Macropores are those having effective radii $\geq$ 100-200 nm and their volume is not entirely filled with adsorbate via the mechanism of capillary condensation (it may occur only for a relative pressure of adsorbate of nearly one). The volumes of macropores are usually in the range 0.2-0.8 cm^3/g and the maximum of volume distribution curves according to the radii are usually in the range 500-2000 nm. The values of their specific surface area not exceeding 0.5 m^2/g are negligibly small when compared with the surface of the remaining type of pore, Consequently macropores are mot of great importance in the process of adsorption as they merely act as transport arteries rendering the internal parts of the carbon grains accessible to the particles of adsorbate.

Mesopores, also known as transitional pores, have effective radii falling in the range of 1.5-1.6 nm to 100-200 nm The process of filling their volume with adsorbate takes place via the mechanism of capillary condensation. For average activated carbons, the volumes of mesopores lie between the limits 0.1-0.5 cm^3/g and their specific surface area in the range of 20-100 m^2/g. The maximum of the distribution curve of their volume versus their radii is mostly in the range of 4-20 nm. Mesopores, besides their significant contribution to adsorption, also perform as the main transport arteries for the adsorbate.

Micropores have sizes comparable with those of adsorbed molecules. Their effective radii are usually smaller than 1.5-1.6 nm and for average activated carbons their volumes usually lie between 0.2-0.6 cm^3/g. The energy of adsorption in micropores is substantially greater than that for adsorption in mesopores or at the non porous surface, which causes a particularly large increase of adsorption capacity for small equilibrium pressure of adsorbate. In micropores, adsorption proceeds via the mechanism of volume filling. For some activated carbon, the microporous structure may have a complex nature, e.g. two overlapping microporous structure: firstly one for effective pore radii smaller than 0.6-0.7 nm and termed specfic micropores, and the secondly one exhibiting pore radii from 0.6-0.7 to 1.5-1.6 nm termed supermicropores.

3.3.1.3 Chemical nature of the surface of activated carbon

The chemical nature of activated carbons significantly influences their adsorptive, electrochemical, catalytic, acid-base, redox, hydrophilic-hydrophobic, and other properties. It is determined decisively by type, quantity and bonding of various heteroatoms, especially oxygen. Heteroatoms may be combined both with peripheral carbon atoms at the corners and edges of crystallites and in intercrystalline spaces and even in defect zones of particular planes constituting the crystallites. Most heteroatoms are grouped at the surface of activated . Apart from their different locations, the heteroatoms are strongly differentiated in terms of their chemical reactivity. Surface-bound heteroatoms are believed to adopt the character of the functional groups typical for aromatic compounds. The surface functional groups often consist of more than one type of heteroatom, e.g. oxygen and hydrogen together as –OH or –COOH.Surface functional groups can originate from the starting material from which a particular activated carbon is produced. Substantial quantities of oxygen can be introduced during the production process itself, e.g. during activated carbonaceous materials by oxidizing gases, such as water vapor and air. Activated carbon used predominantly for practical purposes generally includes some percentage by weight of chemically-bond oxygen and usually much smaller quantity of hydrogen combines with surface carbon atoms either directly or through oxygen.

3.3.1.4 Estimation of the properties of activated carbon

The commercial use of activated carbons, their transport, storage and sales require knowledge of the properties of these materials. The methods for estimating these properties are approved by the members of the activated carbons sector group of the European Council of Chemical Manufactures' Federations (CEFIC). The tests require highly professional laboratories and advanced equipment.

Most of the testing methods have been developed and by approved such organizations as the American Society for Testing Material (ASTM), the American Water Works Association (AWWA), the Deutsches Institute fur Normung e.V. (DIN), or the International Organization for Standardization (ISO).

- B.E.T. Surface area

To measure total surface area, nonspecific physical adsorption is required, but even with physical adsorption the isotherm varies somewhat with the nature of the adsorbent (the solid). Most physical adsorption isotherms may be grouped into five types, as originally proposed by Frunauer, Deming, Deming and Teller (BDDT). More recently, the grouping has generally been termed the *Bruneuer, Emmett, and Teller* (BET) *classification*. In all cases the amount of vapor adsorbed increase as its partial pressure is increased, becoming at some point equivalent to a monolayer, but then increasing to a multilayer, which eventually merges into a condensed phase as the relative pressure, P/Po approaches unity.

- Physical test

- *Bulk density*. The bulk density is defined as the mass per unit volume of the activated carbon sample in air including both the pore system and the void between the particles. The bulk density of activated carbon, depending on the shapes, sizes and densities of the individual particles is indispensable for determining the size of unit packages.

- Adsorption tests

The adsorption properties of activated carbons are generally estimated by determining the isotherms of adsorption from the liquid phase. The determination of the adsorption of one test substance from an aqueous solution is often insufficient for characterizing the adsorption properties of a carbon.

Thus the properties of activated carbons are estimated by comparing the result of measurements for different adsorbates, e.g. by comparing the adsorptions of fairly large molecules of methylene blue or iodine.

- *Iodine adsorption*. The study of the process of iodine adsorption and also the determination of the iodine number is a simple and quick test for estimating the specific surface area of activated carbon. The iodine number is defined as the number of milligrams of iodine adsorbed by 1 g of activated carbon from an aqueous solution when the iodine concentration of the residual filtrate is 0.02 N. If the final values obtained are different from 0.02 N but lie in the range of 0.007-0.03N, appropriate corrections are necessary. In this method it is assumed that iodine at the equilibrium concentration of 0.02 N is adsorbed on the carbon in the form of a monolayer, and this is the reason why there is a relationship between the iodine number of activated carbon and its specific surface area which may by determined, for example , by the BET method. The specific surface areas of activated carbons with highly developed microporous structures as determined by the iodine number method are too low. This is because iodine is adsorbed chiefly on the surface of pores much larger than 1 nm, while in activated carbons with large specific surface areas the proportion of vary fine pores inaccessible to iodine molecules is significant.

- *Methylene blue adsorption*. The methylene blue value gives an indication of the adsorption capacity of an activated carbon for molecules having similar dimensions to methylene blue , it also gives an indication of the specific surface area of the carbon which results from the existence of mesopores of dimensions greater than 1.5 nm.

- Physico-chemical Test

- *Volatile matter content*. The international standard used for determination of volatile matter in hard coal and coke is also applicable to activated carbon. A sample of powdered (<0.1 nm) activated carbon is heated at $950 \pm 25\,^{\circ}C$ for 7 min $\pm$ 10 s.

Volatile matter content is determined by establishing the loss in mass resulting from heating an activated carbon sample under rigidly controlled conditions

- *Moisture content*. A simple method of determining the water content is drying activated carbon in a dryer. The sample of powdered (1-2 g) or granular (5-10 g) carbon is dried at 150 $^\circ$C to constant weight (usually about 3 hr.). The weight loss is expressed as a percentage of the weight of the original sample.

- *Ash content*. The ash content in various types of activated carbon varies over a wide range, depending primarily on the type of raw material. The relative ash content also increases with increase in the degree burning of the coal during activation. Ash consists mainly of oxides and in smaller amounts, of sulfates, carbonates, and other compounds of iron, aluminium calcium, sodium, potassium. Magnesium and many other metals. Depending upon the type of raw material, it may comprise different and often fairly large quantities of silicon. The commonly used method of removing ash is to leach activated carbon with acids. Due to the complex composition of ash, mixture of acids, e.g. hydrochloric or hydrofluoric acid, are often used if ash contains substantial quantities of silicon. The ash content of activated carbon can be determined by ignition of the crucible in an electric muffle furnace. Ignition is conducted at 650 $\pm$ 25 $^\circ$C for 3 to 16 hr, depending on the type activated carbon and dimensions of its particles, to constant mass. The weight of the ashed carbon is expressed as a percentage of the weight of the original carbon sample.

3.3.1.5 Uses of activated carbon

The advantage of using activated carbon is that in certain circumstances a single stage of adsorption may replace several and physical separations or it may permit separation of compounds of the same boiling point. As states earlier, activated carbon are used mainly in the purification and decolorization of liquids and as such are used mostly in powder form and derived from cellulose raw materials (about 85% of total use). Some the advantages of using activated carbon are listed below:

Dry cleaning solvent. With the increase in dry cleaning in recent years, particularly in coin-operated machines, the need has arisen for convenient on the spot method of purifying the solvent which with the passage of time because of contaminated with oils and grease. These become rancid as well as dark colored and impart obnoxious odors to the cleaning liquid. The odors are reduced but not eliminates by distillation of the solvents. Activated carbon has proved to be effective in decolorizing and deodorizing.

Sugar. The main action of the carbon is in decolorization but it also removes nitrogenous substance and lyophilic colloids. By doing so it improves filtration, reduces foaming during evapration and increase the speed of crystallization. When saturated the carbon is removed and regenerated by heating in steam and air at a red heat.

Water. Water is usually treated with chlorine to destroy bacteria but this can at times impart an unpleasant taste, which is especially marked when the chlorine has reacted with micro-organisms and with phenol. The bad taste becomes very noticeable when the supplying river is at a low level but it can be removed by treating the water with activated carbon. This should be an increasing market, particularly if the cost of activated carbon can be reduced.

Tyres. It has been found that white wall tyres retain their whiteness better if activated carbon is incorporated in the reinforcing carbon black.

Pharmaceuticals. Activated carbon has the property of concentrating the active component from a broth. The desires component can be recovered from the carbon by solvents. Penicillin was the first to be treated on a large scale by this method. With the increasing emphasis being placed on pollution by effluents it would seem that activated carbon may play an important part in reducing this problem.

Foodstuffs. Here activated carbons are used to remove soaps and peroxides from edible fats to prevent poisoning of hydrogenation catalysts. They also improve color and flavour, e.g. in soup stocks and vinegar, and improve the storage properties of freshly distilled whisky.

3.4 Mechanism of cracking processes

Cracking processes were assigned to two fundamental classes;

3.4.1 Thermal cracking[18]

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 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 then takes place at a carbon-carbon bond located in the β position to the carbon atom lacking one hydrogen atom. Cracking at the β position gives directly an alpha 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 to the carbon skeleton.

The primary radical derived from this step may immediately recrack at the β bone to give ethylene and another primary radical, or it may first isomerize. In the absence of radical isomerization, only primary radicals are derived from 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 polypropylene cracking is as follows;

1. Initiation Step

R_1-CH_2-CH_2-CH_2-CH_2-CH_2-R_2 ———— heat, hν ———— R_1-CH_2-CH_2-CH_2-CH_2-CH_2● + R_2●

2. Propagation Step

   2.1 β-fission

R_1-CH_2-CH_2-CH_2-CH_2-CH_2● ——β-fission——→ R_1-CH_2-CH_2-CH_2● + CH_2=CH_2

$\overset{\displaystyle H}{R_1\text{-}CH_2\text{-}CH\text{-}CH_2}$● ——$\beta$-fission——→ R_1-CH_2-CH_2=CH_2 + H●

   2.2 Chain Transfer

R_1-CH_2-$(CH_2)_4$-CH_3 + H● ————————→ R_1-$\overset{\displaystyle ●}{CH}$-$(CH_2)_4$-$CH_3$

3. Termination Step

R_1● + R_2● ————————→ R_1-R_2

R_3-CH_2-CH_2● + ●CH_2-CH-R_4 ————————→ R_3-CH_2-CH_3 + CH_2=CH-R_4
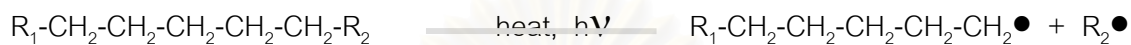
3.4.2 Catalytic cracking[8]

Catalytic cracking is the most important and widely used refinery process for converting heavy oil 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.

There are two possibilities for the initial step in the catalytic cracking of polypropylene. The first involves the simultaneous loss of a hydride ion from the polypropylene molecule and of a proton from the acidic catalyst surface. This produces a carbonium ion in combination with acid anion and molecular hydrogen:

$$R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 \ + \ H^+A^- \longrightarrow R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 \ + \ H_2 \ + \ A^-$$

Alternatively a small amount of olefin, created by thermal cracking could initiate the reaction:

$$R_1\text{-}CH\text{=}CH\text{-}R_2 \ + \ H^+A^- \longrightarrow R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 \ + \ A^-$$
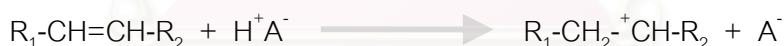
Chain propagation involves an exchange reaction in which a carbonium ion reacts with a polypropylene to give a new hydrocarbon and a carbonium ion of the polypropylene to be cracked (hydride transfer).

$$R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 \ + \ R_3\text{-}\overset{\displaystyle CH_3}{CH}\text{-}CH_2\text{-}CH_2\text{-}R_4 \longrightarrow R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 \ + \ R_3\text{-}{}_+\overset{\displaystyle CH_3}{C}\text{-}CH_2\text{-}CH_2\text{-}R_4$$
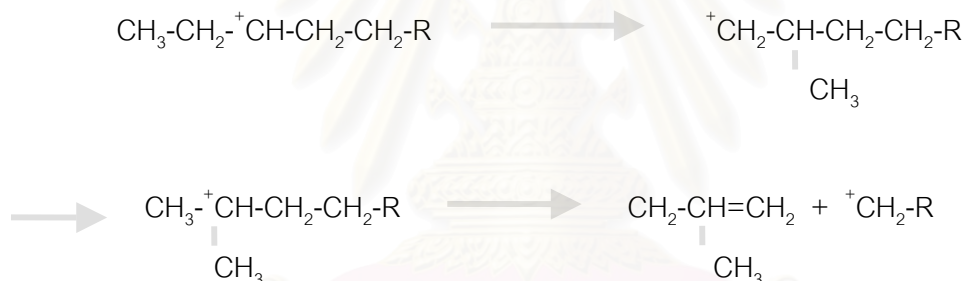
The next step is the decomposition of the activated molecule. The primary rule involved is that the carbon-carbon cleavage occurs at the position one carbon atom away from the carbonium ion, i.e. β-scission:

$$\begin{array}{ccc}
\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}} & & \overset{\displaystyle CH_3}{\underset{\displaystyle |}{}} \\
R_3\text{-}{}_{+}C\text{-}CH_2\text{-}CH_2\text{-}R_4 & \longrightarrow & R_3\text{-}C{=}CH_2 \;+\; {}^{+}CH_2\text{-}R_4
\end{array}$$

A hydride shift then converts the primary carbonium ion formed into a secondary carbonium ion:

$$ {}^{+}CH_2\text{-}R_4 \longrightarrow CH_3\text{-}{}^{+}CH\text{-}R_4 $$

Subsequent step involve further β-scission and hydride transfer and proceed unit the chain becomes so short that cracking at the β position is no longer a rapid reaction. Large amounts of iso-compounds are formed in catalytic cracking. This is readily explained by the rearrangement of the secondary carbonium ion:

$$ CH_3\text{-}CH_2\text{-}{}^{+}CH\text{-}CH_2\text{-}CH_2\text{-}R \longrightarrow \overset{\displaystyle {}^{+}CH_2\text{-}CH\text{-}CH_2\text{-}CH_2\text{-}R}{\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}} $$

$$ \longrightarrow \overset{\displaystyle CH_3\text{-}{}^{+}CH\text{-}CH_2\text{-}CH_2\text{-}R}{\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}} \longrightarrow \overset{\displaystyle CH_2\text{-}CH{=}CH_2 \;+\; {}^{+}CH_2\text{-}R}{\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}} $$

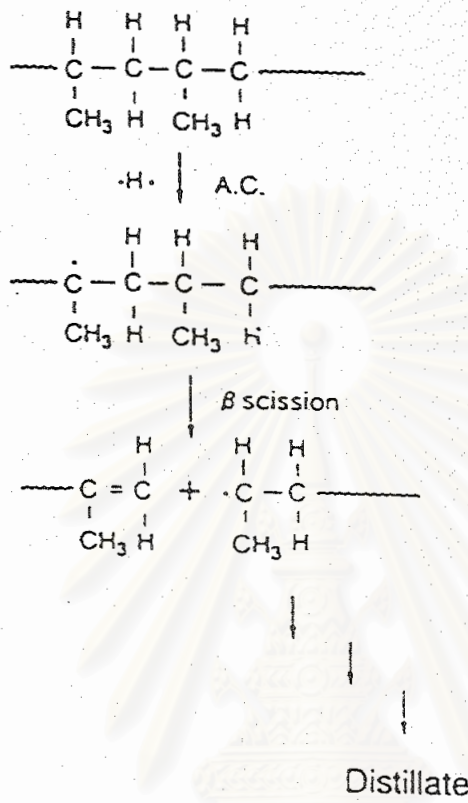**Figure 3.4** Role of Fe/AC in PP cracking.[7]

CHAPTER IV

EXRERIMENT

4.1 Raw material and chemical

    4.1.1 The plastic used in experiments were supplied from Thai Petrochemical Industry Public Company Limited. It was virgin plastics of 3-4 mm diameter pellets.

    4.1.2 The palm-oil shell for the production of activated carbon were crushed and sieved to six particle sizes of < 0.6, 0.6-1.18, 1.18-2.36, 2.36-4.75, 4.75-6.00, and 6.00-8.00 mm before being treated.

    4.1.3 Toluene 99.5%

    4.1.4 Hydrogen gas 99.5%

4.2 Apparatus

    The reaction was carried out by using apparatus (shown in **Fig 4.1**). The microreactor is a stainless steel tube SS.316 with an inner volume of 75 cm^3 , 30 mm inside diameter, (shown in **Fig 4.2**). It was heated by an electricity 450 watt, and the temperature was measured by thermocouple type R size of 1.6 mm diameter. The temperature was controlled to an accuracy of $\pm$ 5 $^{\circ}$C by means of a programmable temperature controller. The shaking of microreactor was controlled by using a control speed motor. The separation of liquid oil from solid by using the vacuum filter (shown in **Fig 4.3**). The boiling ranges of oil yield were determined by gas chromatogragh (GC Simulated Distillation) with the following conditions : Open Tubular Columns type cappiraly columns : RTX 2887 , Initial temperature 40 $^{\circ}$C , Final temperature 350 $^{\circ}$C , FID detector , Sample size 0.5 ?L , Carrier gas helium , Programming rate 10 $^{\circ}$C/min.[22]
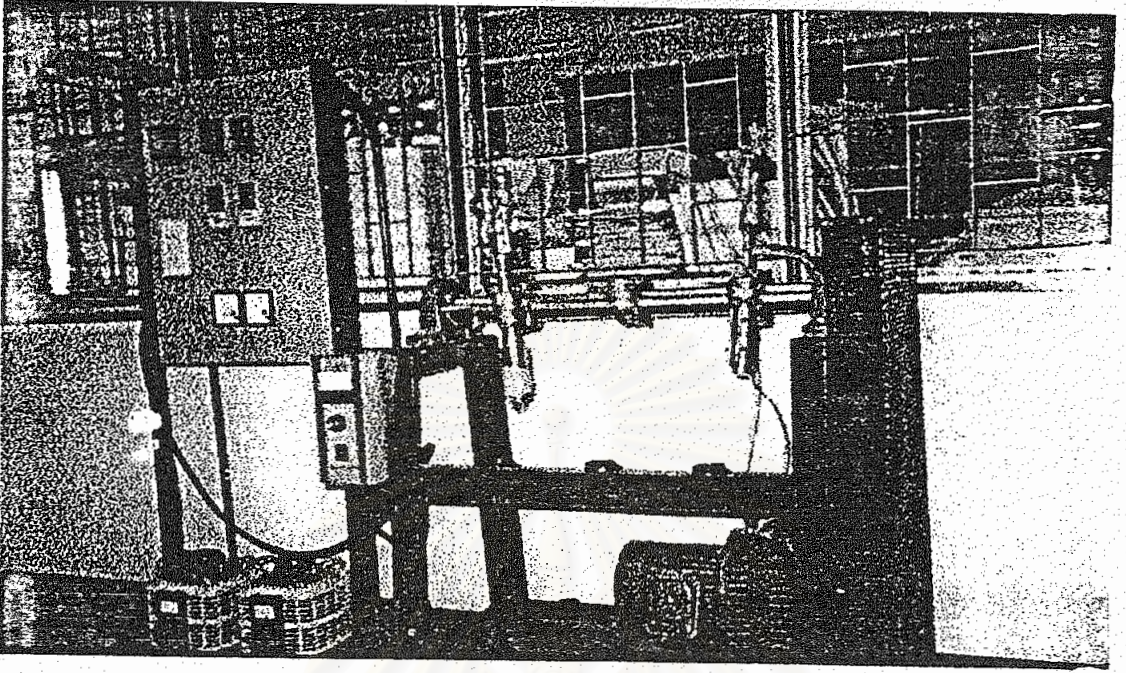
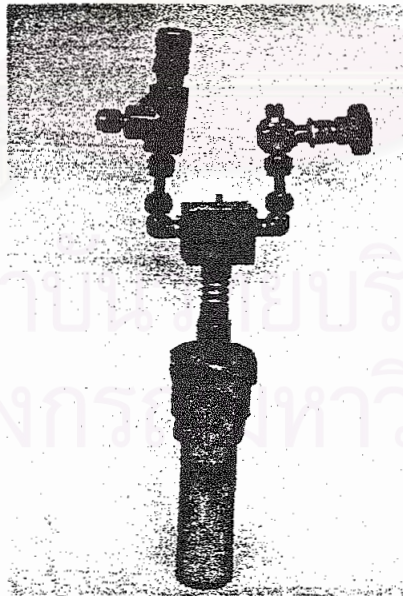Figure 4.1 The reaction experimental unit for conversion of polypropylene into oil products using Fe/Ac. Catalyst.
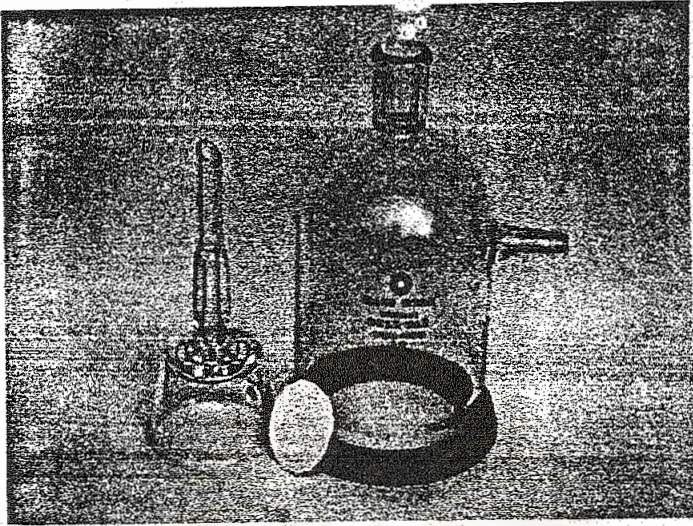

Figure 4.2 The microreactor

Figure 4.3 The vacuum filter

4.3 Processes of the experiment

4.3.1 The property and composition analysis of polypropylene

4.3.2 The processes prepared for catalyst are as follows :

- a preparation of iron on activated carbon from palm-oil shell catalyst (Fe/activated carbon) has been done through impregnation method with different percentage of iron at 1, 5 and 10 %.

- about 200 g of each type of catalyst are prepared with the following steps :

4.3.2.1 Deaeration from 2 sizes of activated carbon 0.5 mm and 1.0 mm by injecting distilled water at an equal level of a height of activated carbon in a container before allowing it to enter in vacuum equipment for 3 hours and finally air bubble will be found on its surface.

4.3.2.2 Impregnation with aqueous solution of ferric nitrate($Fe(NO_3)_3$ with required percentage of iron on deaerated activated carbon at room temperature for 2 hours.

4.3.2.3 Drying slurry with vacuum rotary evaporator to a temperature of 80 $^{\circ}$C for 3 hours, and then powdered activated carbon with $Fe(NO_3)_3$ which is in pore putting it in an oven for baking overnight to a temperature of 120°C.

4.3.2.4 The next day, calcination activated carbon with ($Fe(NO_3)_3$ which is in pore to temperature of 450°C for 3 hours for driving off nitrate, iron on surface of activated carbon will be yielded.

4.3.2.5 Reducing catalyst with hydrogen to a temperature of 400°C for 1 hour and refilling presulfation with hydrogen sulfide to a temperature of 450°C for 1 hour and keeping it cool at room temperature, catalyst usable for the intended purposes will be given.

4.3.3 The physical property analysis of 1, 5, 10% Fe/AC

4.3.4 Procedure of the experiment

4.3.4.1 Weighing 15 g of polypropylene and 0.3, 0.45, 0.60 and 0.75 g of catalyst and putting it in 70 ml-reactor.

4.3.4.2 Compressing hydrogen gas at its pressure of 28, 30, 40 and 50 kg/cm^2 and checking its leakage.

4.3.4.3 Putting reactor in heater coil, covering insulator, fixing thermocouple for the measurement of internal and external temperature of reactor and finally setting its reaction temperature of 395, 415, 435 and 455°C.

4.3.4.4 Fixing reactor with shaker at 120 rpm/min when its reaction corresponds to a time set of 30, 45, 60, 75 and 90 min.

4.3.4.5 Cooling off a reactor by removing insulator and heater, blowing it with fan and keeping it cool until it goes down to a room temperature.

4.3.4.6 Filtering yielded oil, keeping some of it for analysis by distillation gas chromatograph to find out oil composition and filtering all of yielded products by using toluene as a solvent of products remaining in the reactor. Remainders in the filter are catalyst and coke or solid without any changes into the products. As a result, the data obtained from this process are used for calculating conversion percentage.

4.3.5 The composition analysis of product by gas chromatograph

The boiling ranges of oil yield were determined by gas chromatograph (GC Simulated Distillation)at PTT Research and Technology Institute for naphtha(IBN-200°C),kerosene(200-250° C),gas oil(250-300°C), and long residue (up to 350°C).[18]
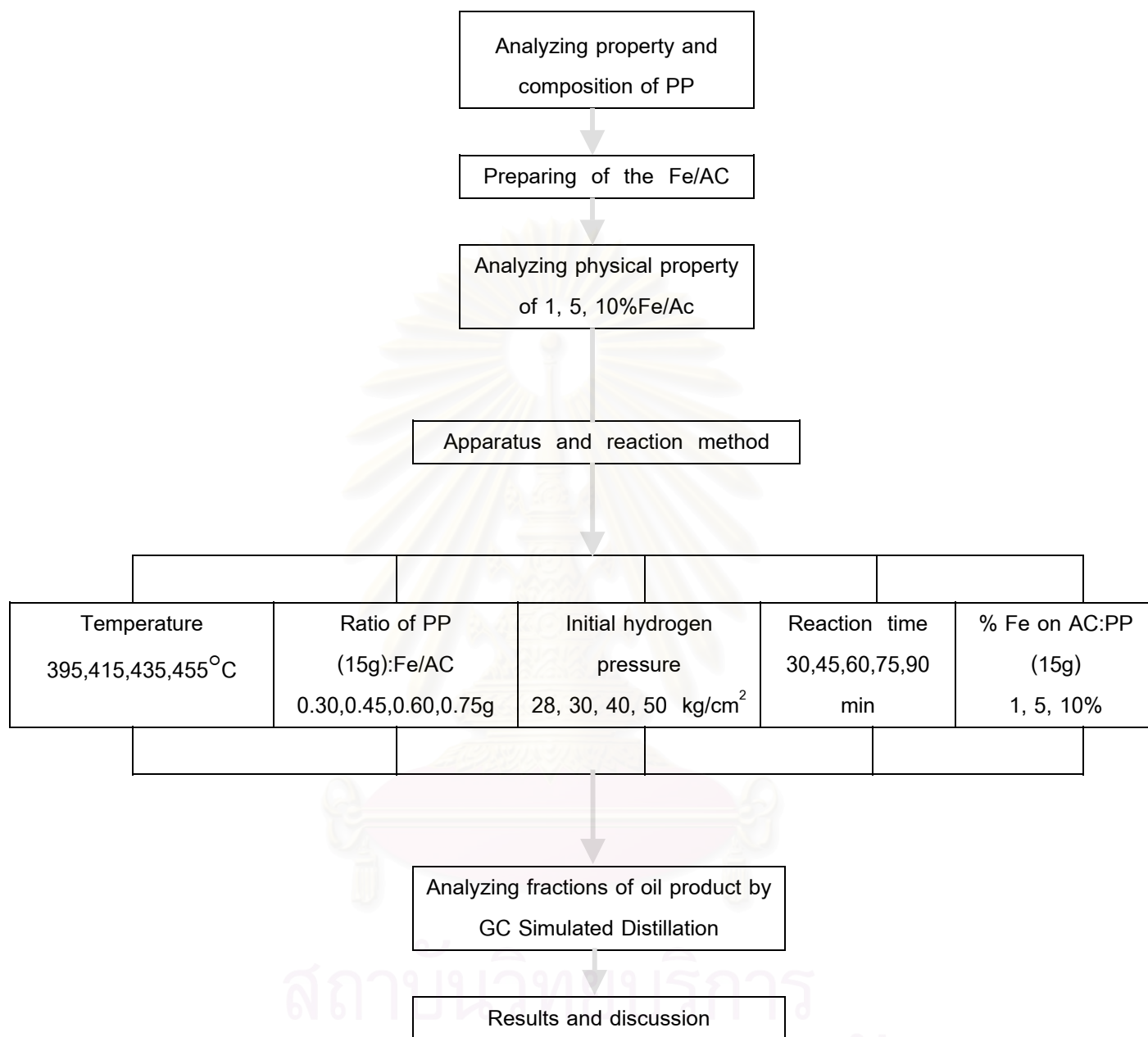
Figure 4.4 Experiment scheme of the hydrocracking of polypropylene by Fe/AC catalyst

CHAPTER V
RESULTS AND DISCUSSIONS

5.1 The property and composition of polypropylene

5.1.1 The proximate analysis

%Ash	0.5041
%Volatile matter	98.6508
%Fixed carbon	0.8451

The proximate analysis shows high percentage of volatile matters which is composed of hydrocarbon in the majority form of vapor in 950°C. In this experiment set temperatures range of 395 - 455°C, polypropylene become absolutely in the form of liquid and contacted very well with catalyst during being shaked in the reactor.

5.1.2 The ultimate analysis

%Carbon	83.510
%Hydrogen	14.203
%Nitrogen	0.8000
%Sulfur	0.0100
%Oxygen	0.973

The ultimate analysis shows the majority of carbon 83.510% and hydrogen 14.203% and some amount of sulfur and oxygen which come from initiator and unpurified polypropylene. The component of carbon and hydrogen will have the important role for being converted by hydro-cracking to oil product.

5.2 The results of research

The experimental results of hydrocracking of polypropylene by Fe/activated carbon catalyst by studying its influences to conversion percentage of the products and yielded oil composition have the following variables:, percentage of iron loading on activated carbon, temperature, a ratio of polypropylene and catalyst, initial pressure of hydrogen gas and reaction time. The results of the experiments from different conditions and those of oil composition analysis are illustrated in Table A-1. The influences of each variable above-mentioned are shown in graphs 5.1, 5.2, 5.3, 5.4, 5.5, 5.6 and 5.7 respectively.

5.2.1   Influences of percentage of iron on activated carbon on composition of oil product

The variation of percentage loading of iron 1, 5 and 10% on activated carbon using as catalyst at a fixed condition of 15 g of polypropylene, with pressure of 30 kg/cm^2, reaction time of 60 min, temperature at 415°C and 0.45 g catalyst and comparing with non catalyst at 435°C were (shown in **Fig 5.1**) It showed that a percentage of oil yield and composition were not significant different, because the percentage of gases were range of 1 to 2%, naphtha 51 to 53 %, kerosene 12 to 13%, light gas oil about 10%, heavy gas oil about 10%, long residues 10 to 11%, solid 1.0 to 2.5 % and oil yield 95.5 to 98%. While the reaction was carried out without using catalyst, the percentage of oil composition were low quality from that using catalyst. When without catalyst reaction was take place, the thermal cracking played only the important role in cracking (Fujimoto) immediately very long chains hydrocarbon to intermediate molecules and finally in the form of gases about 15.3% and oil yield about 85%.

Whereas, the catalytic reaction was simultaneously proceeded by thermal and catalytic cracking, as a result the distribution of hydrocarbon molecules was obtained the better quality of oil, namely, a increase of naphtha from 17 to 53%, kerosene 7.5 to 13%, light gas oil 8 to 10%.

In conclusion, the catalyst affected directly the oil yield and composition, whereas, the percentage of iron on activated carbon was not much affect on the oil yield and composition.

After studying the influence of percentage loading of iron on activated carbon , it decided to choose 10% loading of iron on activated carbon using as catalyst for studying others variables. The preparation of 10% loading of iron gave higher precision than 1 or 5% loading, because after impregnation of iron nitrate on surface activated carbon and after drying, observing some iron nitrate at the surface of bottom flask. So if it prepared 1% loading of iron, it would not be sure that it was correct , and 10% loading of iron on activated carbon was prepared in a large amount for this experiment.
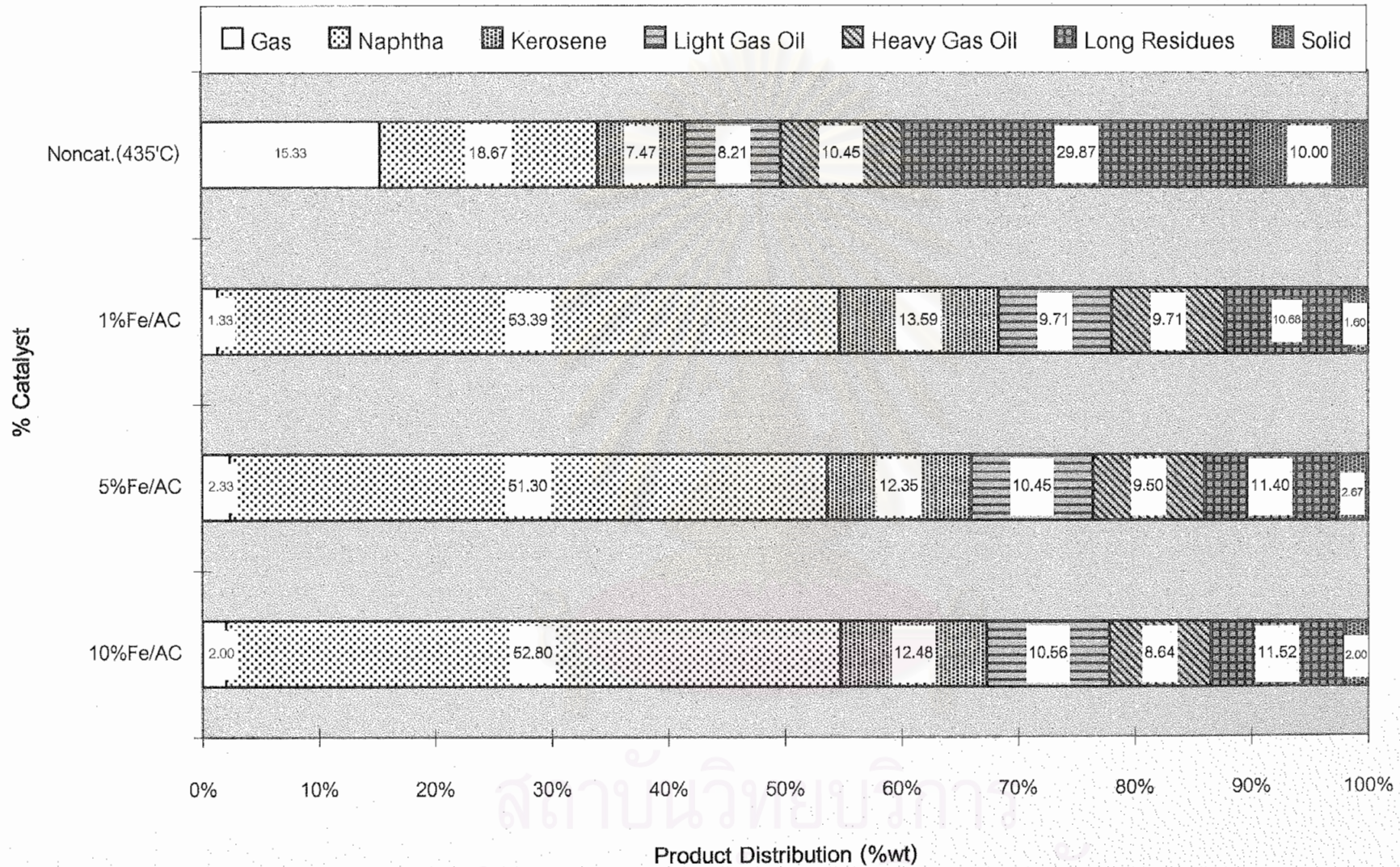
Figure 5.1 Polypropylene conversion with various percentages of catalyst.

Reaction conditions : 15 g of PP, 30 kg/cm^2, 60 min and 0.45 g of catalyst, 415 'C

5.2.2 Influences of reaction temperature on composition of oil product

The reaction temperatures of 395, 415, 435 and 455°C were varied with a fixed conditions at 10% Fe/AC, 15 g of polypropylene, hydrogen pressure at 30 kg/cm^{2}, 60 min reaction time and 0.45 g of catalyst (shown in **Fig 5.2**). It is found that when the temperature increases, a percentage of oil was increased from 90.08 to 94.94%. This is because an increase in temperature induces a larger amount of thermal cracking of polypropylene. At the same time, a higher temperature also increases more catalytic cracking that will give higher composition of naphtha increasing from 36.03% at 395°C to 62.62% at 435°C and its value staying unchanged at temperature of 455°C accounted as 66.66%. Other compositions such as kerosene, gas oil have a trend to be stable while long residues and solid have a trend to be little decreased. This occurrence is caused by thermal cracking of polypropylene chains and its changes in sizes to a low molecular weight suitable for being changed by catalytic cracking into naphtha or kerosene. It is found that there is very little amount of gas accounted as only 1 to 3% in each experiment.

Although, the oil composition at 435°C yields higher percentage than 415°C, but this two temperatures caused a small difference of naphtha about 9% and long residues about 7% and the rests remaining stable. And because of the 415°C was the temperature that the reaction would be approaching steady in composition of oil. We decided to work the experiments of the remaining variables at 415°C for uncomplicated operation the lower temperature of reaction and carried out some experiments at 435°C for comparison of oil product and composition.

In conclusion in case of temperature, the suitable temperature of 435°C yields percentage value of naphtha, kerosene, light gas oil, heavy gas oil, long residues and solid at 62.62, 13.49, 8.67, 6.74, 4.82 and 1.33% respectively.
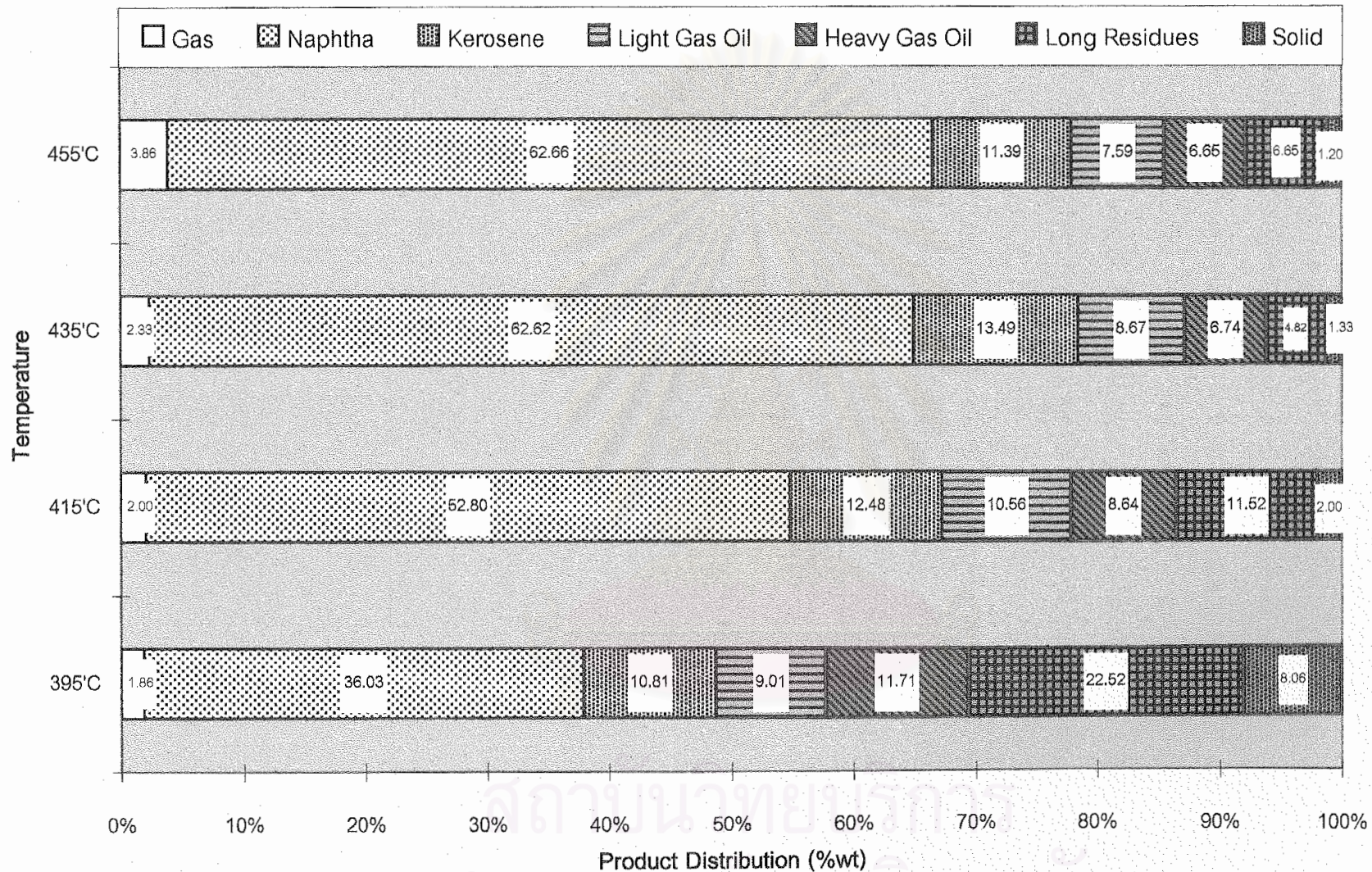
Figure 5.2 Polypropylene conversion on 10%Fe/AC (1mm) catalyst with various reaction temperatures.

Reaction conditions : 15 g of PP, 30 kg/cm^2, 60 min and 0.45 g of catalyst.

5.2.3 Influences of ratio of polypropylene to catalyst on composition of oil product

The variation of weight catalyst from 0.30, 0.45, 0.60 and 0.75 g at a fixed conditions of 10% Fe/AC, with 15 g of polypropylene, hydrogen pressure at 30 kg/cm^2, 60 min reaction time and at temperature of 415°C was (shown in **Fig 5.3**) It is found that a higher mass (lower ratio of polypropylene to catalyst) of catalyst induced a slight increase in percentage of oil from 94.67% to 96.33% including compositions of gas, naphtha, gas oil, long residue and solid being stable. Normally the larger quantity of used catalyst, the higher percentage in oil product and composition. This experiment showed that the contacts between reactant and catalyst of different ratio of polypropylene to catalyst having the same pattern give similar oil composition because of very well shaking in reactor to cause entirely catalytic cracking. However it was observed in the case of reaction with and without catalyst that there was significantly different between them.

In conclusion, catalyst weights do not much affect cracking reaction in the range of 0.30 to 0.75 g of catalyst to 15 g of polypropylene.
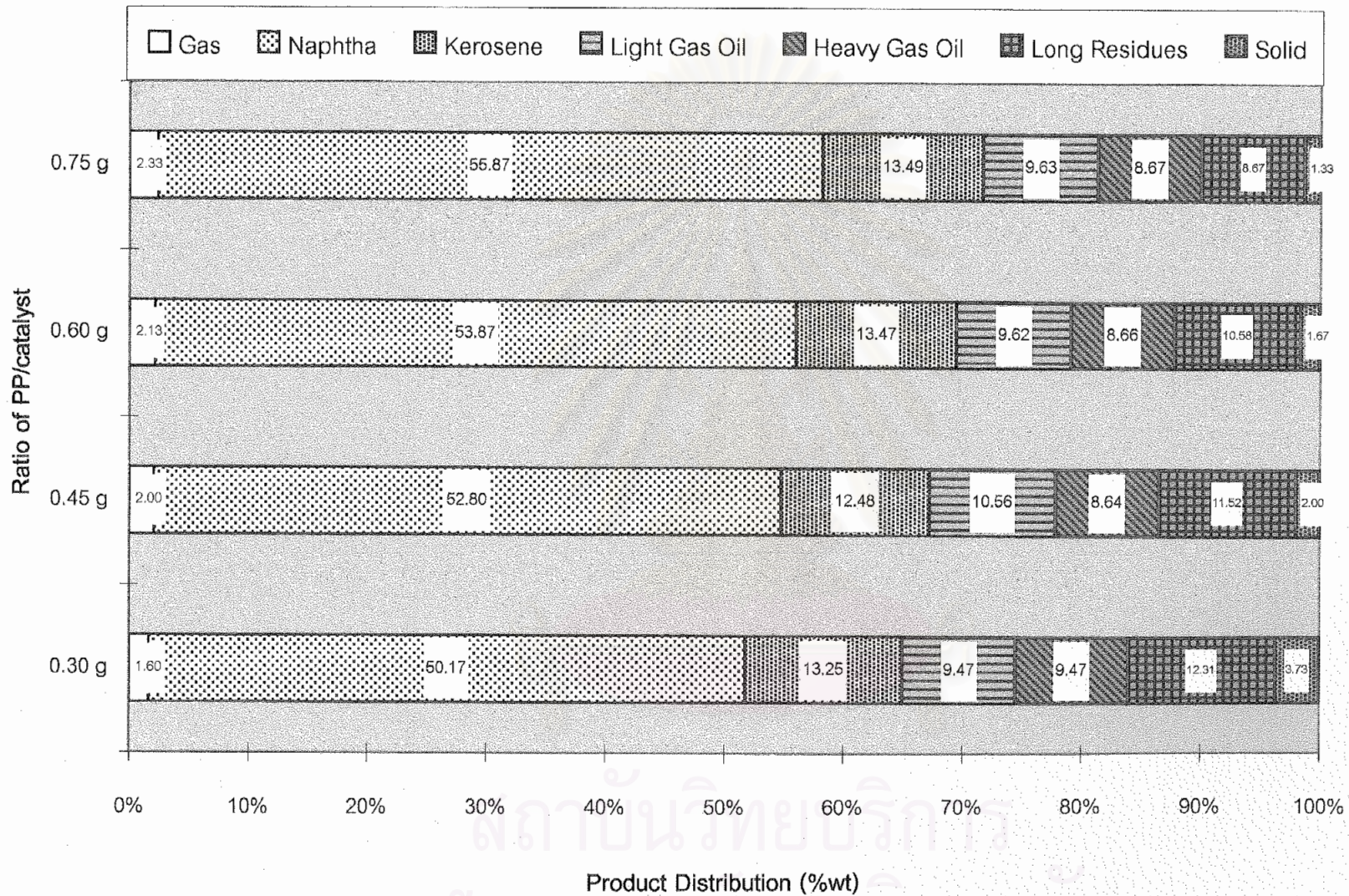
Figure 5.3 Polypropylene conversion on 10%Fe/AC (1mm) catalyst with various ratios of PP per catalyst.

Reaction conditions : 15 g of PP, 30 kg/cm^2, 60 min and 415 'C for reaction temperature.

5.2.4 Influences of initial pressure of hydrogen gas on composition of oil product

The variation of initial pressure of hydrogen gas from 28, 30, 40 and 50 kg/cm^2, with a fixed condition at 10% Fe/AC, 15 g of polypropylene, 60 min reaction time, two temperatures of 415°C and 435°C, and 0.45 g catalyst was (shown in **Fig 5.4, 5.5**.) At temperature of 415°C it was found that a higher pressure of hydrogen causes a slight increase in amount of oil product from 93.00% at 28 kg/cm^2 approaching to stable oil of 96.00% with pressure over 30 kg/cm^2. The comparison at a temperature of 435°C had the same pattern giving a similar oil composition as one at 415°C. During an experiment at stable temperature, thermal and catalytic cracking should be proceeded in the same manner. However, an increase in amount of hydrogen helps to stimulate cracking reaction and causes higher catalytic cracking. This is conformed in the theory of spill over of hydrogen on catalyst, namely during the reaction some hydrogen at the surface of catalyst is consumed, so the higher pressure of hydrogen, the more mass transfer from gas phase to solid surface of catalyst. Therefore it causes high conversion and more higher quantity of percentage composition. So it showed a higher trend of naphtha from 50.02 to 57.11%. Other compositions are stable while solid dramatically reduces from 5.13 to 1.01 %.

In conclusion, amount of hydrogen has an impact on amount of naphtha and solid both 415°C and 455°C with its suitable hydrogen pressure at 30 kg/cm^2.

Figure 5.4 Polypropylene conversion on 10%Fe/AC (1mm) catalyst with various initial hydrogen pressure.

Reaction conditions : 15 g of PP, 60 min , 415 'C and 0.45 g of catalyst
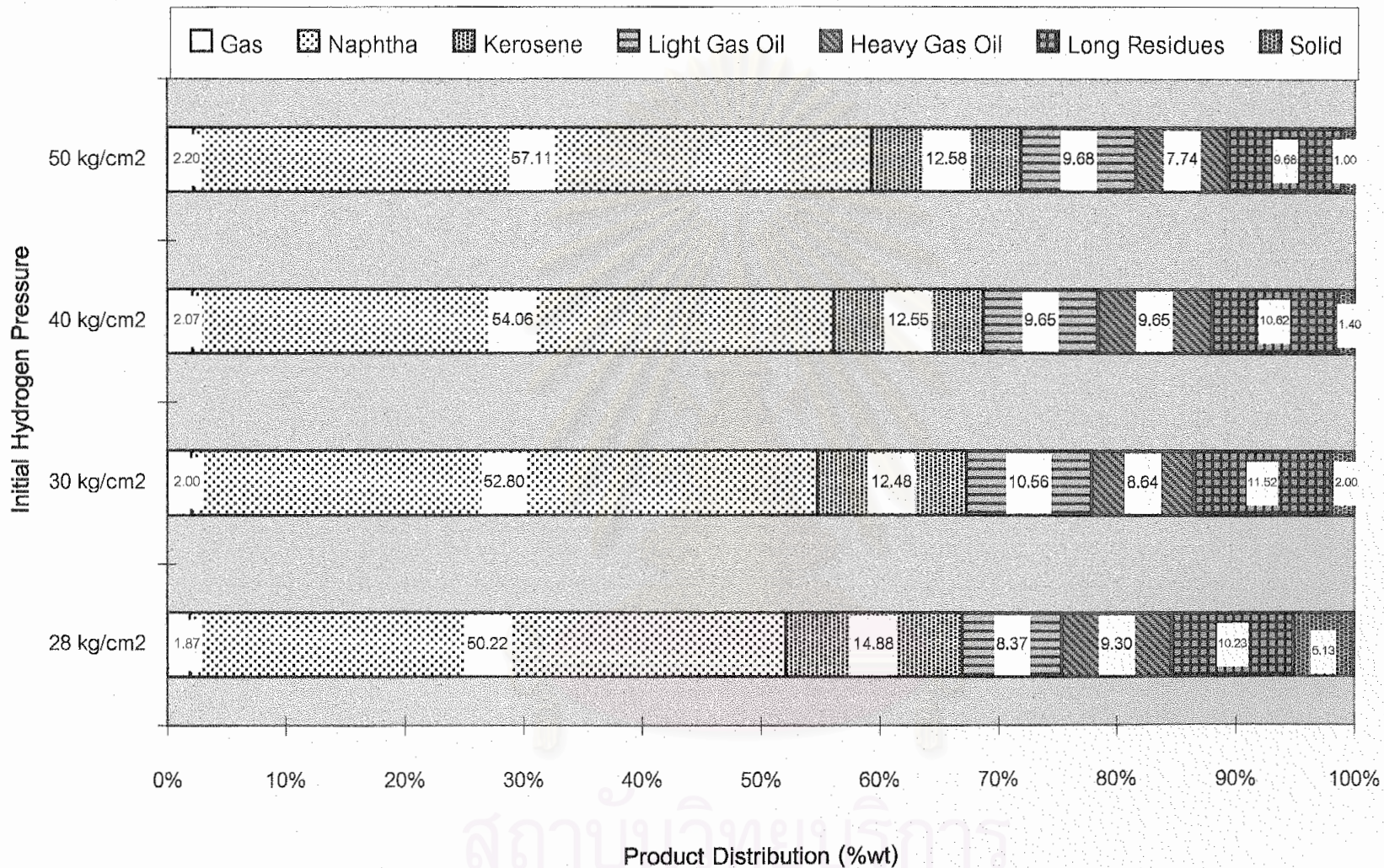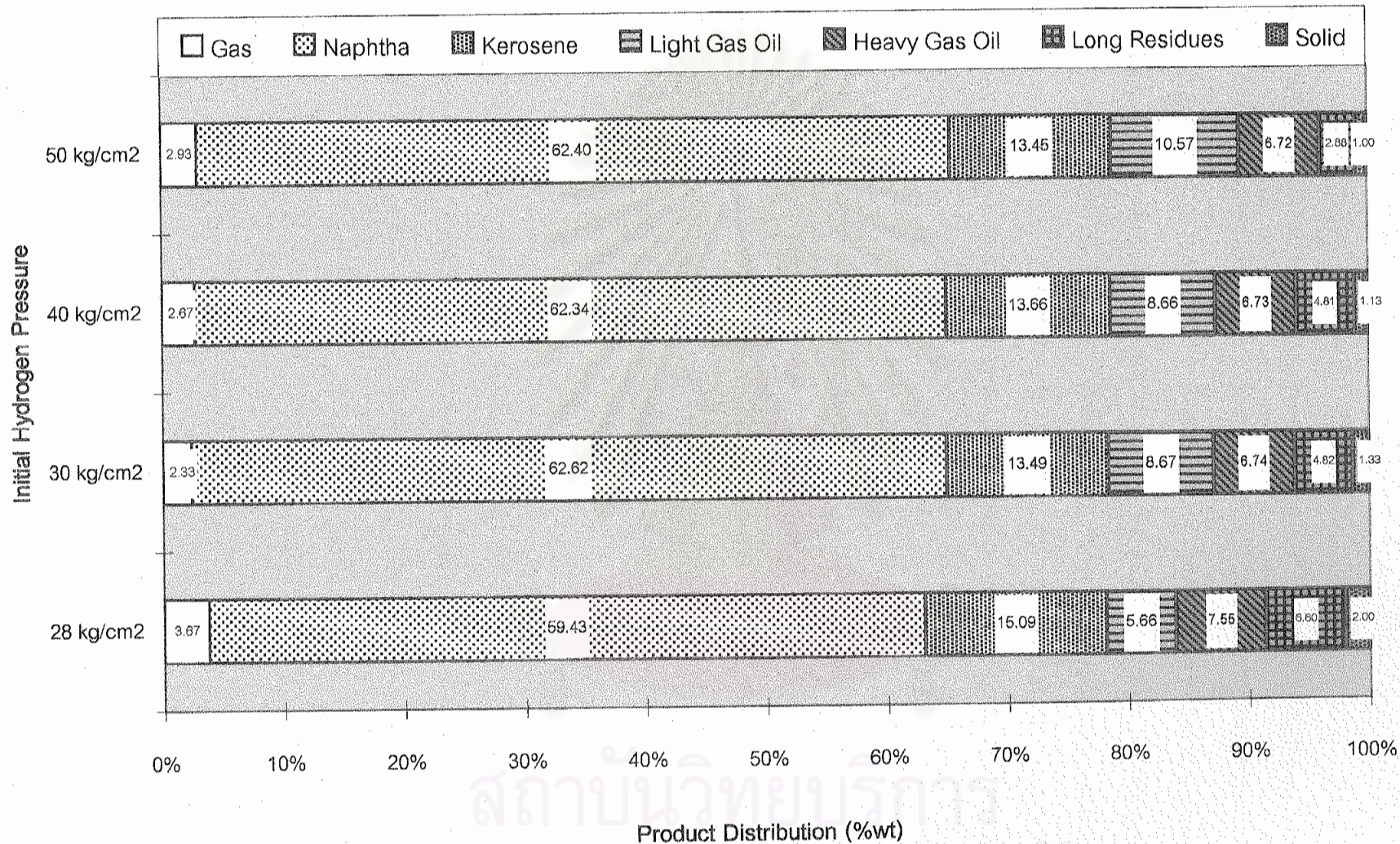
Figure 5.5 Polypropylene conversion on 10%Fe/AC (1mm) catalyst with various initial hydrogen pressure.

Reaction conditions : 15 g of PP, 60 min , 435 'C and 0.45 g of catalyst

5.2.5 Influences of reaction time on composition of oil product

The variation of reaction time from 30, 45, 60, 75 and 90 min, by fixing condition at 10% Fe/AC, 15 g of polypropylene, pressure at 30 kg/cm^2 , two temperatures of 415°C and 435°C and 0.45 g catalyst were (shown in **Fig 5.6, 5.7**). It is found that for the temperature of 415°C, an increase in reaction time induced an increase in percentage of oil yield from 89.81% to 92.13% and being stable at 96.00%. At the reaction time were 60 min and over, It was also found that percentage of naphtha increased in the same direction from 41.31% to 45.15%. A percentage trends to be stable at 54.00% while that of kerosene and gas oil kept almost constant. Conversely, value of long residues and solid has been dramatically reduced because longer time is allowed more thermal cracking than catalytic cracking. For the comparison at a temperature of 435°C, the results had the same pattern of oil composition. Thermal cracking takes place before catalytic cracking (Fujimoto). However, thermal cracking has still occurred in a continual manner. Longer thermal cracking can change heavy hydrocarbon into low hydrocarbon, as a result there is a clear reduction in values of long residues and solid. At the same time, catalytic cracking of low hydrocarbon yields higher amount of naphtha.

In conclusion, a suitable reaction time is 60 min in both 415°C and 455°C. For 415°C the percentage of yielded oil is 96.00%. Percentages of light gas oil, heavy gas oil , long residues and solid are 52.80, 12.48, 10.56, 8.64, 11.52 and 2.00% respectively.

Figure 5.6 Polypropylene conversion on 10% Fe/AC (1mm) catalyst with various reaction time.

Reaction conditions : 15 g of PP, 30 kg/cm^2, 415 'C and 0.45 g of catalyst
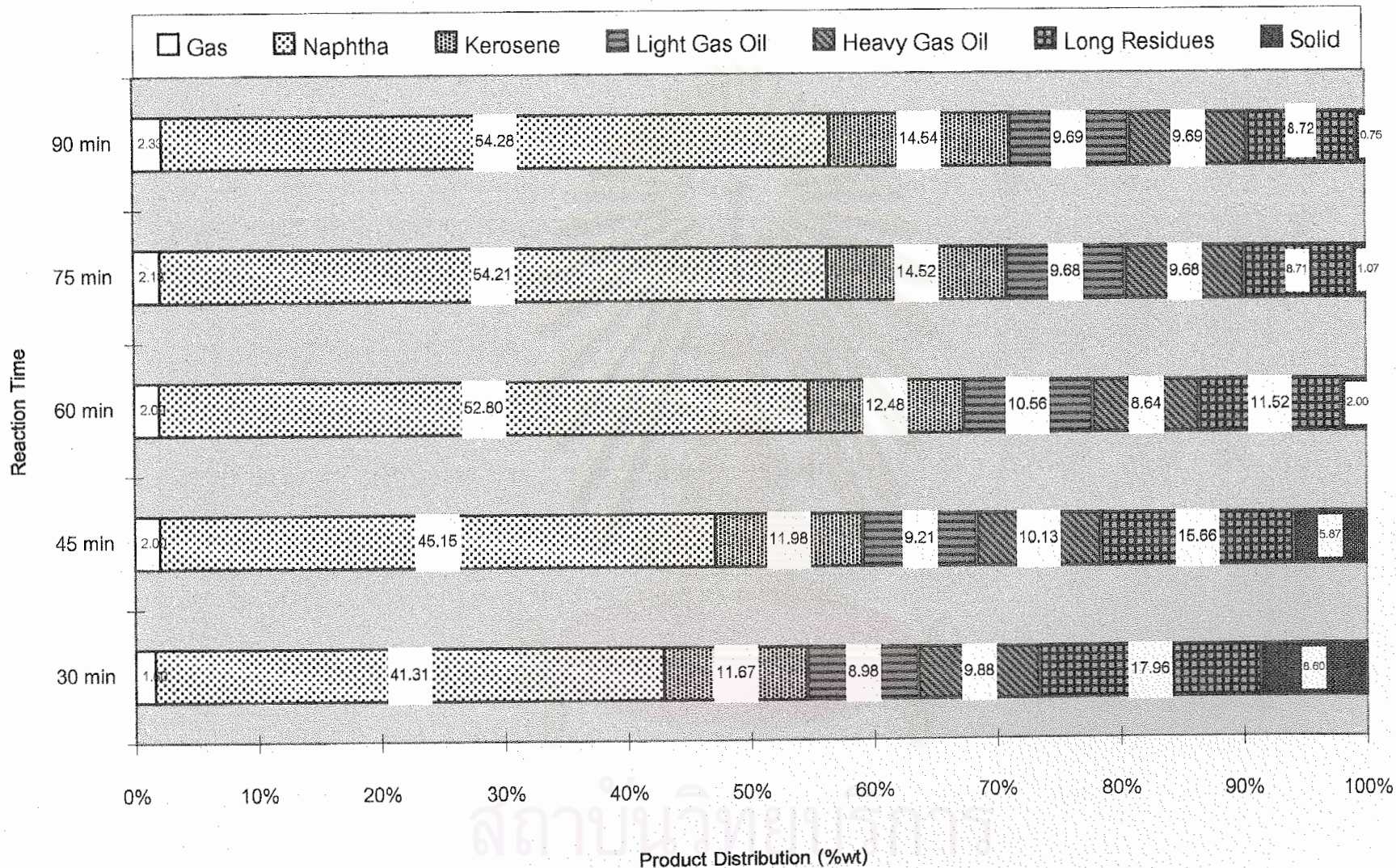
Figure 5.7 Polypropylene conversion on 10% Fe/AC (1mm) catalyst with various reaction time.

Reaction conditions : 15 g of PP, 30 kg/cm^2, 435 'C and 0.45 g of catalyst
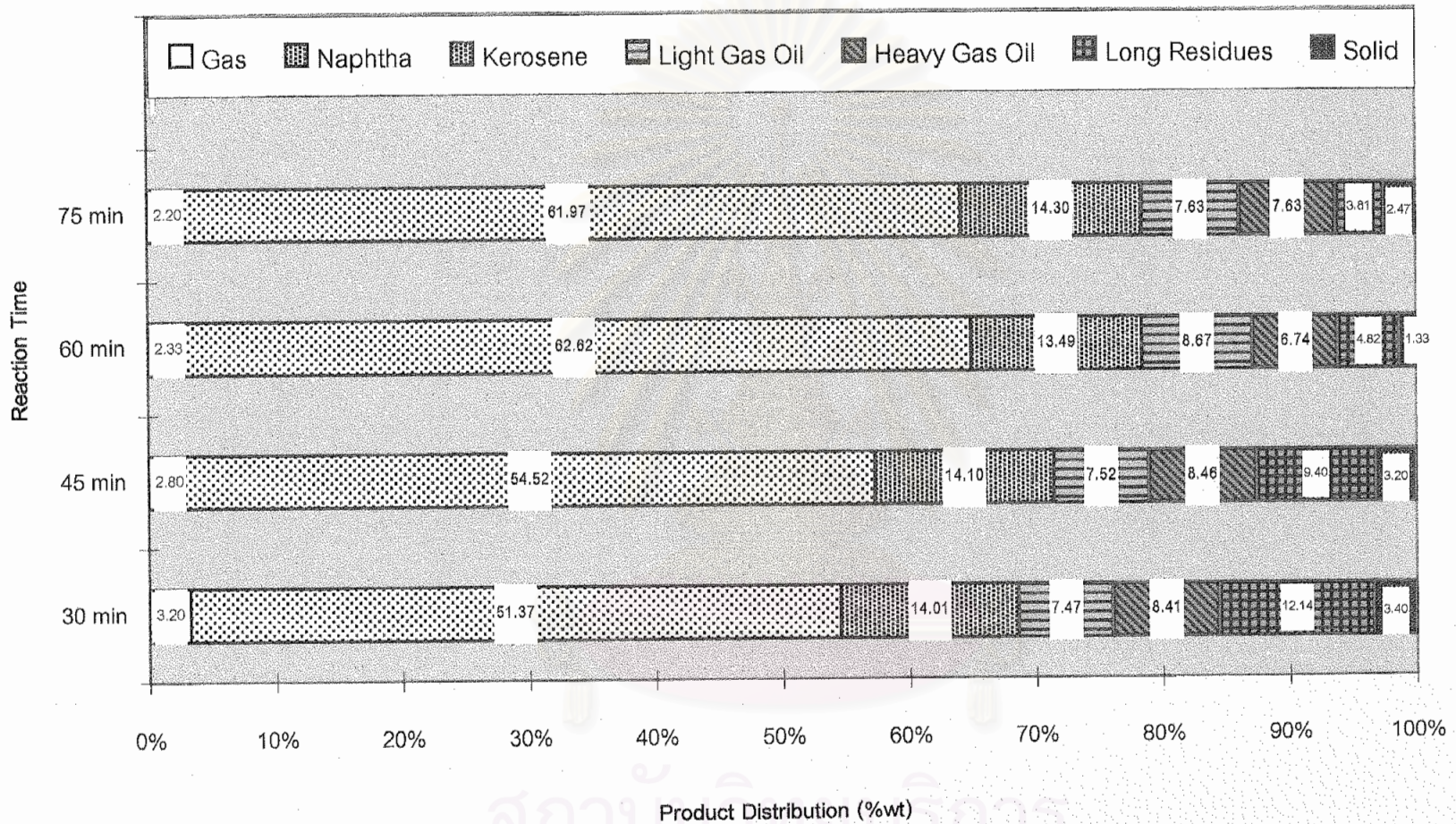
5.2.6 Characterization of iron on activated carbon before and after using in reaction

Characterization of iron on activated carbon before and after using in reaction show by the surface specific area (BET) of catalyst.

Table 5.1 Surface specific area (BET) of pure activated carbon and any loading of iron on activated carbon of particle size 1mm. Before and after using catalyst in reaction at 415°C 30 atm

Percentage loading of iron % by weight	Surface specific area m^2/g before reaction	Surface specific area m^2/g after reaction
Pure activated carbon	746	-
1% Fe/ activated carbon	719	46
5% Fe/ activated carbon	692	37
10% Fe/ activated carbon	706	52

Table 5.1 shows the surface specific area before and after in this experiment. It found that when iron was impregnated on the surface of pure activated carbon, the surface decreased slightly about 5.3%, it mean that the iron metal crystals in the pores of activated carbon, and it no affect of percentage loading of iron on surface area. The surface area of each type of percentage loading iron was not significant different, it implied that all percentage loading of iron caused the same covering of metal crystal all the pores of activated carbon. So all the percentage loading of iron on activated carbon in this experiment, there was no effect of surface area on the oil yield and composition.

Table 5.1 shows also the surface specific area of catalyst after using in reaction. It found that the surface area was decreased largely after being carried out reaction by 94%. This was because of some small amount of unconverted polypropylene covering the surface of catalyst verifying by comparison of pure and used catalysts shown by SEM in (Fig. 5.8, 5.9).

Figure 5.8   The surface specific area of catalyst before using in reaction

Figure 5.9   The surface specific area of catalyst after using in reaction

5.3 Comparison of this work with other work

The comparison of this work with that of Kaoru Fujimoto [7] (1996) was presented with fractions of gases, oils and solids and expressed in term of wt% in **Table 5.2**

Table 5.2 Comparison of this work with Kaoru Fujimoto et al. (1996)

Description	This work	Kaoru Fujimoto' s
Plastic	Polypropylene	Polypropylene
Catalyst	Fe/AC (Palm oil shell)	Fe/AC (Yallourn coal)
Conditions		
Temperature	435 $^\circ$C	400 $^\circ$C
Reaction time	60 min	60 min
Results		
Oils (%wt)	96.33	92.00
Gases (%wt)	2.34	2.50
Solids (%wt)	1.33	5.50
Naphtha (%wt)	62.62	38.46
Kerosene (%wt)	13.49	15.09
Light gas oil (%wt)	8.67	20.06
Heavy gas oil (%wt)	6.74	15.27
Long residues (%wt)	4.83	3.12

Kaoru Fujimoto et al. studied catalytic cracking of polypropylene. Polypropylene cracking was conducted in a batch apparatus using a conventional shaking autoclave with an inner volume of 75 cm^3.

The reaction conditions were : temperature ; 380 - 400 °C, reaction time ; 60 min, initial hydrogen pressure; 3.0 MPa, polypropylene:10 g, catalyst, (5% Fe/AC Yallourn coal), 0.3 g,CS_2 ; 0.03 g. From **Table 5.2**, Kaoru Fujimoto et al. obtained 92.00% of oil yield , naphtha 38.46%, kerosene 15.09%, light gas oil 20.06%, heavy gas oil 15.27% and long residues 3.12%   whereas this work obtained 96.33 % of oil yield , naphtha 62.62%, kerosene 13.49%, light gas oil 8.67%, heavy gas oil 6.74% and long residues 4.82% This result can be explained that activated carbon from palm oil shell would transfer free radical more than activated carbon from Yallourn coal[7]. And this work was carried out higher temperature than that of Fujimoto which higher temperature (better thermal cracking) would support catalytic cracking (high percentage of oil yield and quality showing in the former experiments).

CHAPTER VI
CONCLUSIONS AND SUGGESTIONS

The following conclusions from this study have been drawn :

1. Catalyst used for hydrocracking of polypropylene into oil products is iron on activated carbon (Fe/AC) catalyst.
2. This work aims to study the hydrocracking of polypropylene by using iron on activated carbon catalyst in microreactor, the temperature was varied from 395-455°C, 28-50 kg/cm^2 of initial hydrogen pressure and 30-90 min of reaction time. Analyses of the products were performed using GC Simulated Distillation.
3. From the experimental results obtained from this study, it may be concluded that, suitable conditions are as follows :

    3.1 Suitable temperature is 435°C

    3.2 Catalytic weight dose not much affect cracking reaction

    3.3 Hydrogen pressure is 30 kg/cm^2

    3.4 Time for reacting is 60 min

    3.5 Percentage of iron on activated carbon dose not affect oil composition

At temperature 435 $^{\circ}$C, hydrogen pressure 30 kg/cm^2 , reaction time 60 min with 10%Fe/AC the oil yield, gas, naphtha, kerosene, gas oil, long residues and solid were 14.45, 2.33, 62.62, 13.49, 15.41, 4.82, 1.33%

<u>Suggestions</u> :

From the research of S.R. Palmer tetralin was filled for being used as hydrogen donor solvent, and the aromatic structure of tetralin, which makes it a good solvent for polypropylene liquefaction. So an addition of tetralin helps to stimulate cracking reaction, therefore tetralin may be filled as well for getting more product.

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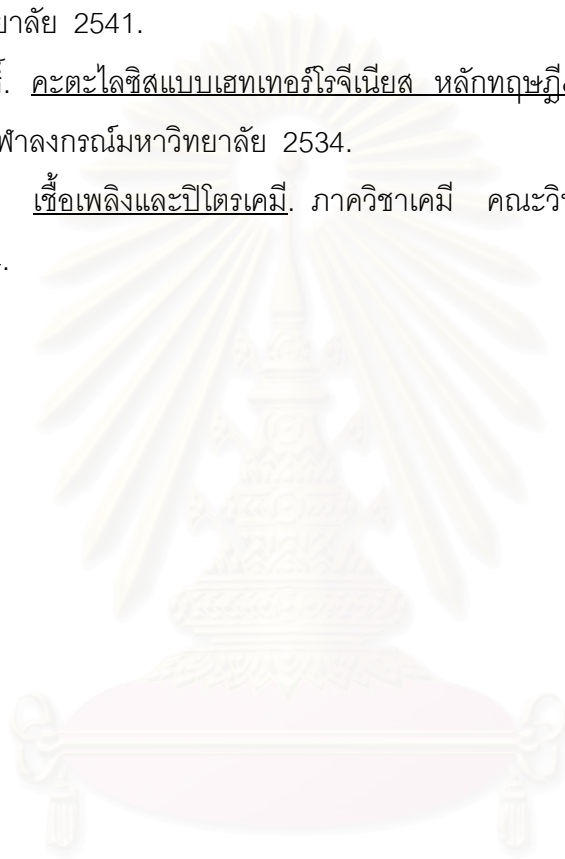
APPENDICES

APPENDIX A

DATA FROM THE STUDY OF HYDROCRACKING OF
POLYPROPYLENE USING IRON ON ACTIVATED CARBON FROM
PALM OIL SHELL

Table A-1 Product distribution of all conditions.

No.	Raw Material	Catalyst	H_2 (kg/cm²)	Temp. (°C)	Time (min)	Solid (g)	% Solid	Oil Yield (g)	% Yield	Gas (g)	% Gas	% Naphtha 65-200 °C	% Kerosene 200-250 °C	% Light Gas Oil 250-300 °C	% Heavy Gas Oil 300-350 °C	% Long Residues > 350 °C
PS-1	PP = 15.02 g.	10% Fe/Ac (1 mm) = 0.45 g	30	395	60	1.21	8.06%	13.53	90.08%	0.28	1.86%	36.03%	10.81%	9.01%	11.71%	22.52%
PS-2	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	30	415	60	0.30	2.00%	14.40	96.00%	0.30	2.00%	52.80%	12.48%	10.56%	8.64%	11.52%
PS-3	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	30	435	60	0.20	1.33%	14.45	96.33%	0.35	2.33%	62.62%	13.49%	8.67%	6.74%	4.82%
PS-4	PP = 15.01 g.	10% Fe/Ac (1 mm) = 0.45 g	30	455	60	0.18	1.20%	14.25	94.94%	0.58	3.86%	62.66%	11.39%	7.59%	6.65%	6.65%
PS-6	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.30 g	30	415	60	0.56	3.73%	14.20	94.67%	0.24	1.60%	50.17%	13.25%	9.47%	9.47%	12.31%
PS-7	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.60 g	30	415	60	0.25	1.67%	14.43	96.20%	0.32	2.13%	53.87%	13.47%	9.62%	8.66%	10.58%
PS-8	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.75 g	30	415	60	0.20	1.33%	14.45	96.33%	0.35	2.33%	55.87%	13.49%	9.63%	8.67%	8.67%
PS-9	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	28	415	60	0.77	5.13%	13.95	93.00%	0.28	1.87%	50.22%	14.88%	8.37%	9.30%	10.23%
PS-12	PP = 15.01 g.	10% Fe/Ac (1 mm) = 0.45 g	30	415	30	1.29	8.59%	13.48	89.81%	0.24	1.60%	41.31%	11.67%	8.98%	9.88%	17.96%
PS-13	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	30	415	45	0.88	5.87%	13.82	92.13%	0.30	2.00%	45.15%	11.98%	9.21%	10.13%	15.66%
PS-14	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	30	415	75	0.16	1.07%	14.52	96.80%	0.32	2.13%	54.21%	14.52%	9.68%	9.68%	8.71%
PS-15	PP = 15.00 g.	5% Fe/Ac (1 mm) = 0.45 g	30	415	60	0.40	2.67%	14.25	95.00%	0.35	2.33%	51.30%	12.35%	10.45%	9.50%	11.40%
PS-16	PP = 15.00 g.	1% Fe/Ac (1 mm) = 0.45 g	30	415	60	0.24	1.60%	14.56	97.07%	0.20	1.33%	53.39%	13.59%	9.71%	9.71%	10.68%

No.	Raw Material	Catalyst	H_2 (kg/cm^2)	Temp. ($^{\circ}$C)	Time (min)	Solid (g)	% Solid	Oil Yield (g)	% Yield	Gas (g)	% Gas	% Naphtha 65-200 $^{\circ}$C	% Kerosene 200-250 $^{\circ}$C	% Light Gas Oil 250-300 $^{\circ}$C	% Heavy Gas Oil 300-350 $^{\circ}$C	% Long Residues > 350 $^{\circ}$C
PS-17	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	40	415	60	0.21	1.40%	14.48	96.53%	0.31	2.07%	54.06%	12.55%	9.65%	9.65%	10.62%
PS-18	PP = 15.02 g.	10% Fe/Ac (1 mm) = 0.45 g	50	415	60	0.15	1.00%	14.54	96.80%	0.33	2.20%	57.11%	12.58%	9.68%	7.74%	9.68%
PS-20	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	30	415	90	0.11	0.73%	14.54	96.93%	0.35	2.33%	54.28%	14.54%	9.69%	9.69%	8.72%
PS-21	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	28	435	60	0.30	2.00%	14.15	94.33%	0.55	3.67%	59.43%	15.09%	5.66%	7.55%	6.60%
PS-22	PP· = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	40	435	60	0.17	1.13%	14.43	96.20%	0.40	2.67%	62.34%	13.66%	8.66%	6.73%	4.81%
PS-23	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	50	435	60	0.15	1.00%	14.41	96.07%	0.44	2.93%	62.40%	13.45%	10.57%	6.72%	2.88%
PS-24	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	30	435	30	0.51	3.40%	14.01	93.40%	0.48	3.20%	51.37%	14.01%	7.47%	8.41%	12.14%
PS-25	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	30	435	45	0.48	3.20%	14.10	94.00%	0.42	2.80%	54.52%	14.10%	7.52%	8.46%	9.40%
PS-26	PP = 15.00 g.	10% Fe/Ac (1 mm) = 0.45 g	30	435	75	0.37	2.47%	14.30	95.33%	0.33	2.20%	61.97%	14.30%	7.63%	7.63%	3.81%
PS-27	PP = 15.00 g.	—	30	435	60	1.50	10.00%	11.20	74.67%	2.30	15.33%	18.67%	7.47%	8.21%	10.45%	29.87%

APPENDIX B

GRAPH OF PRODUCT FROM GAS CHROMATOGRAPH

(GC Simulated Distillation)

PTT RESEARCH AND TECHNOLOGY INSTITUTE

PETROLEUM AUTHORITY OF THAILAND

Analytical and Petrochemical Research Department

71 Moo 2 Phahonyothin Rd.,Wangnoi, Ayutthaya, 13170 Thailand. Tel. 537-3000 Ext. 2402-3 Fax. 537-3000 Ext. 2401

CERTIFICATE OF ANALYSIS

CERT NO.   :   36/1/2543   [Page :1/2]   REF NO.   :   85/43

SAMPLE NAME   :   PS-1 (Batch 1)   SAMPLING DATE :   -

SAMPLE ID.   :   FU051/43   SAMPLE CONDITION : Good

SAMPLE FROM   :   Chulalongkorn University   RECEIVED DATE :   23/05/43

SAMPLING LOCATION :   -   ANALYSIS DATE :   1-2/06/43

Test Item	Method	Unit	Result
Boiling Range Distribution	ASTM D2887-93 (Modified Method)	$^{\circ}F$	
% Recovered			
IBP			168
5			180
10			236
15			267
20			271
25			278
30			326
35			367
40			391
45			443
50			463
55			512
60			551

THIS CERTIFICATE OF ANALYSIS IS REFERED TO ONLY SUBMITTED SAMPLE(S) . IT IS YOUR RESPONSIBLE TO USE HERE IN RESULTS IN ANY PURPOSES. EXCEPT IN FULL , THIS CERTIFICATE SHALL NOT BE REPRODUCED WITHOUT THE WRITTEN APPROVAL OF THE DIVISION MANAGER OR DEPARTMENT DIRECTOR.

FR-ฝวญ.-001(1/1)   Revision 1-19/10/42

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CERTIFICATE OF ANALYSIS

CERT NO. : 36/1/2543 [Page :2/2]

Test Item	Method	Unit	Result
% Recovered (Cont.)			
65			596
70			649
75			704
80			770
85			834
90			903
95			977
FBP			1050

REMARK : IBP (Initial Boiling Point) - the temperature at which a cumulative corrected area count

equal to 0.5% of the total sample area

FBP (Final Boiling Point) - the temperature at which a cumulative corrected area count
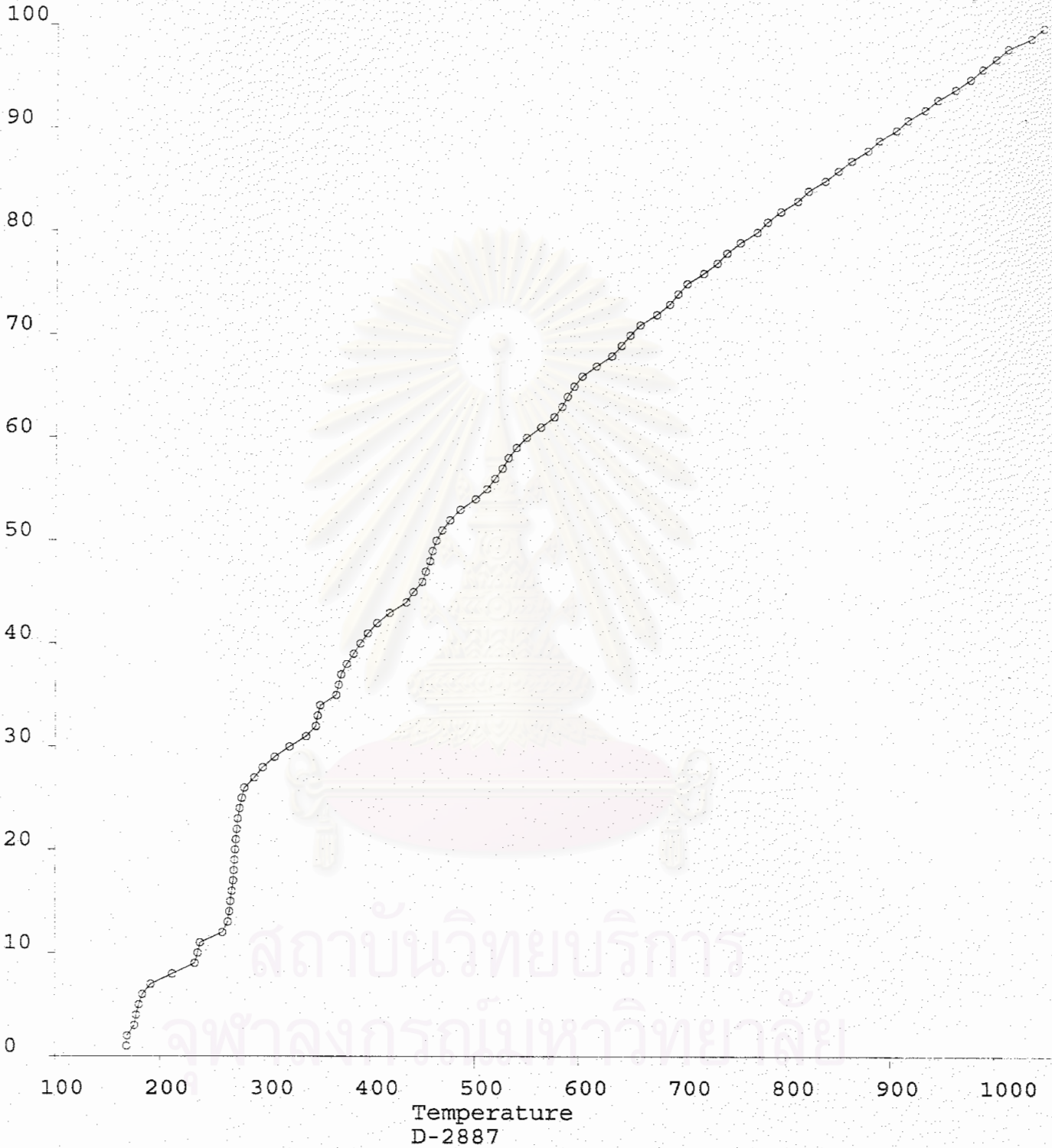
equal to 99.5% of the total sample area

APPROVED BY : *C. Tanher*

(Mr. Chatree Tonkunakorn)

POSITION : Division Manager

DATE OF ISSUE : 12 / 06 / 43

FR-ฝวญ.-001(1/1)   Revision 1-19/10/42

% Off

Temperature
D-2887

Sample Name   : "FU051/43 (1)"
Data File   : C:\TC4\D2887\OIL_093.arn
Operator   : "supot"
Date Collected   : 6/1/00 @ 12:53:35 PM
Sim Dis Calculated   : 6/12/00 @ 10:56:44 AM

Sim Dis Method   : c:\sd\2887\ptt_3.287
Last stored on 6/12/00 @ 10:55:42 AM by supot

Sample Name : PS-1

88
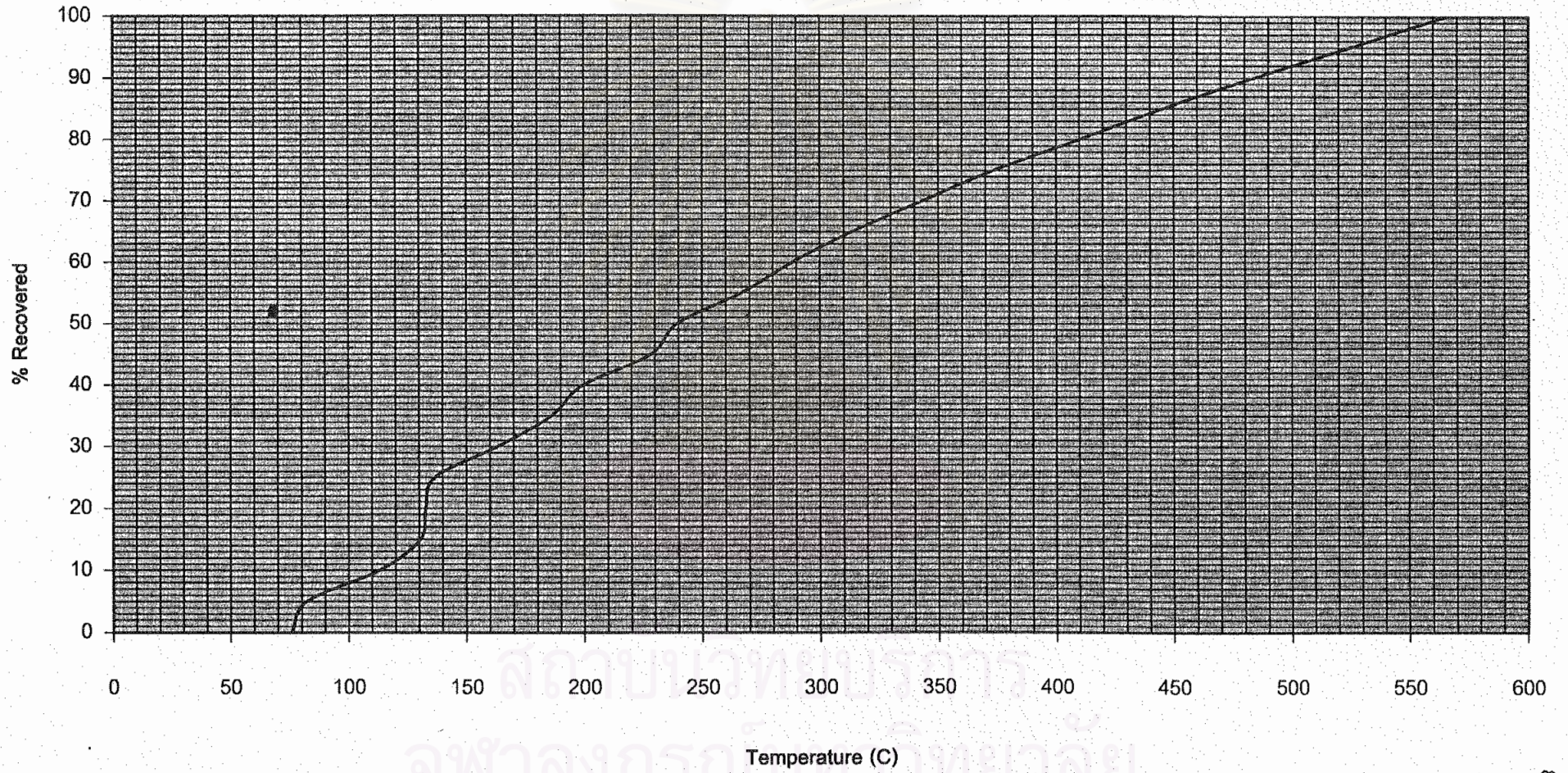
VITA

Miss Poonsuk Phungtum was born in Ayutthaya , Thailand on October 22, 1972. She received her Bachelor's Degree of Science from Chemistry, Faculty of Science, Khon Kaen University in 1995. She continued her Master's study at the Program of Petrochemical and Polymer Science, Faculty of Science, Chulalongkom University in 1998.