



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Tires

Almost of types of transportation vehicles such as car, truck, and airplanes use tires. The tire components are tread, belts, and sidewall. A typical tire is composed of synthetic rubbers (polybutadiene and styrene-butadiene), natural rubber (polyisoprene), sulfur, zinc oxide, silica, carbon black, inert materials, steel wire, and other additives, for examples, phenolic resin oils (aromatic, naphthenic, and paraffinic) petroleum waxes, fabric(polyester, nylon, etc.) and pigments (zinc oxide, titanium dioxide, etc). Moreover, several types of tire also have different compositions depending on the purpose of applications.

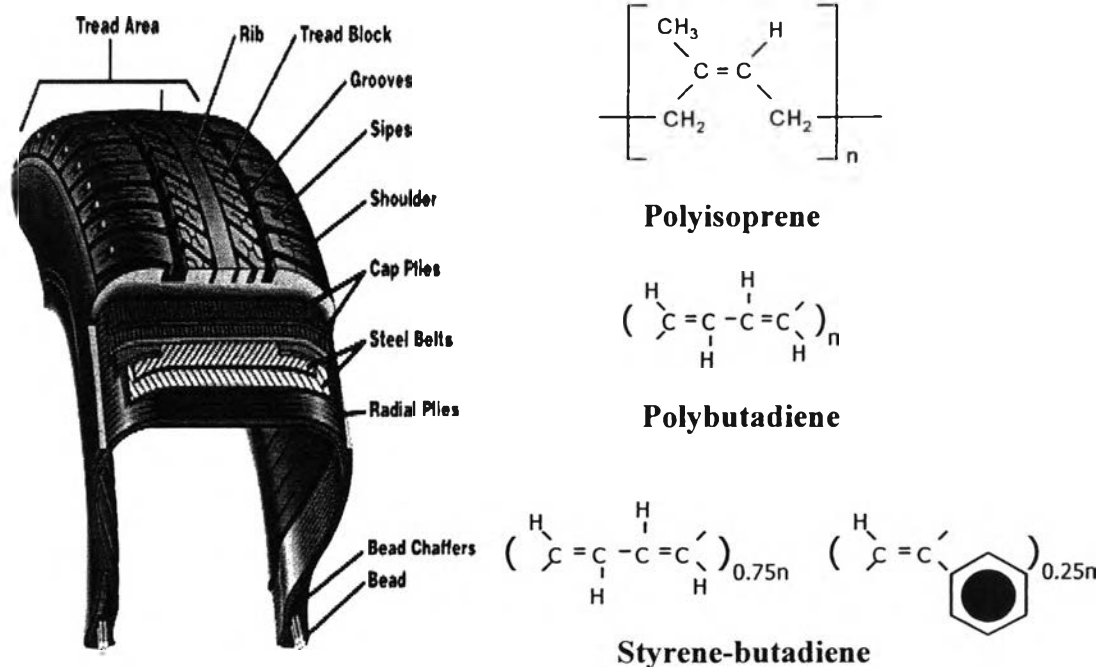


Figure 2.1 Tire component and main rubber compositions in tire (www.offroaders.com)

2.2 Pyrolysis of Tires

One recycling process which has received considerable recent attention is pyrolysis of tires. The pyrolysis is thermal decomposition process with oxygen free atmosphere. The advantage of this process is low emission to the environment. Tires are decomposed to form gas which composes of light hydrocarbons and other by-products such as hydrogen, carbon dioxide and carbon monoxide etc. Liquid product consists of very complex mixtures of organic compounds of 5-20 carbons with very high portion of aromatics, and can be used as fuel, source of chemicals, or the petrochemical feed stocks. The inorganic and inert compositions in tires such as carbon black, steel and non-volatile compounds remains as solid residue. This solid can be recycled in worth-wide applications such as activated carbon and low grade carbon black. The distribution and yields of pyrolysis product depend on type and size of tire, type and size of reactor, and operating conditions, for examples, temperatures, heating rate, pressure, and carrier gas flow rate or residue time.

2.2.1 The Influence of Operating Conditions

Many researchers have studied on pyrolysis of used tires for the influence of operating conditions. Main operating conditions that affect to the pyrolysis are shown in following section.

2.2.1.1 *Temperature*

The influence of temperature was studied by several researchers. Roy *et al.*, (1999) studied tire pyrolysis in the range of 350 to 700°C, and found that pyrolysis temperature did not affect to the yields over 500°C. Similarly, Rodriguez *et al.*, (2001) pyrolysed scrap tires under nitrogen in an autoclave reactor with different temperatures. They found that the pyrolysis temperatures above 500°C had no significant influence on the amount and characteristics of pyrolysis products. Thus, they concluded that 500°C was the optimum temperature for pyrolysis of tire since the rubbers were decomposed completely, and less energy was required than at higher temperatures. Laresgoiti *et al.*, (2004) reported the pyrolysis of tire produced

the liquid products mostly consisted of aromatic compounds. And over 500°C no effect of temperature on gases and liquid yields was observed.

The production of oil increases the ease of handling, storage, and transport. There are several literatures which focused on the effect of temperature on the production of the liquid or oil product with a high yield. Mastral *et al.*, (2000) studied scarp tire pyrolysis from 400 to 600°C, and found that total conversion and oil yield decreased about 10 % at the temperatures below 500°C, and remained constant at temperatures above 600°C. On the contrary, Cunliffe *et al.*, (1998) studied the influence of pyrolysis temperature, and the results showed liquid oil yield decreased with increasing the temperature to 600°C with the consequence increase in gas yield. They also reported the maximum yield was 58.2 %wt at 475°C, similar to the high yields of oil, which have been found by other researchers as shown in Table 1. It can be concluded that pyrolysis tire produced the highest yield in oil fraction. Pyrolysis yield not only depends on temperature of pyrolysed reactor, but also the flow rate of carrier gas directly related to vapor residue time inside reactor, which could influence both product distribution and composition (Mastral *et al.*, 2000).

Table 2.1 The conditions of pyrolysis of tire that give the high oil yield production

NO	Type of Reactor	Temp. (° C)	Carrier gas Flow rate	Oil yield (%wt)	Ref.
1.	Fixed bed	500	25 ml/min	55-56	Ucar <i>et al.</i> , 2005
2.	Fixed bed	570	-	57.1	William <i>et al.</i> , 2002
3.	Rotary kiln	450	0.45 m ³ /hr	36-62	Barbooti <i>et al.</i> , 2004
4.	Fixed bed	475	-	58.2	Cunliffe <i>et al.</i> , 1998

Pyrolytic oils mostly consisted of high aromatic compounds, which were affected by the operating condition. Especially, temperatures affected to the aromatic concentrations. Laresgoiti *et al.*, (2004) reported aromatic concentra-

tions were significantly increased with the temperatures in the range of 300-700°C. Likewise, Cunliffe *et al.*, (1998) showed the influence of pyrolysis temperature on aromatic content in oil. They reported that the aromatic compounds in oil increased with the increasing temperature, and the aliphatic content in the pyrolytic oil consequently decreased.

The temperature does not only affect the distributions, yields of product, and the aromatic contents in oil, but also affect the heating value of the product. Galvago *et al.*, (2002) varied the process temperatures between 550°C and 680°C, and found that higher temperatures promoted the secondary reactions of the volatile fraction. They noted that carbon content in gas phase grew with temperature. Furthermore, the calorific value of gaseous fraction also increased with temperature. Diez *et al.*, (2004) studied the influence of final temperature on the calorific value of products. They found that the liquid fraction from tire pyrolysis had high calorific value, which increased along the increasing temperature up to 40 MJ/kg. Leung *et al.* (2002) studied pyrolysis of tire powder between 500°C and 1000°C. They found that gas yield increased with increasing temperature because of thermal cracking, and also increased with residence time at temperatures above 700°C. However, the lower heating value (LHV) was decreased.

2.2.1.2 Carrier gas flow rate or residue time

Mastral *et al.*, (2000) reported that carrier gas velocity was directly related to vapor residence time inside the reactor and affected on both product distributions and compositions. However, the type of carrier gas was not important in the conversion and distribution of product. They found that the conversions and yields of oil were small with increasing gas velocity. Likewise, Barbooti *et al.*, (2004) reported oil products were increased when the N₂ flow rate was increased due to the effect on efficiency of condensation. Leung *et al.*, (2002) studied the influence of operation variables on the composition and yields of gaseous product. The results showed at a high gas residence time, gases stayed in reactor with along time, and then the product vapors were further cracked from higher heating valuable gas (C₂-C₄) into lower heating value (CO₂ and Methane). Moreover, hydrocarbons were decomposed continuously to light hydrocarbons. Similarly, Cunliffe *et al.*, (1998) also

found that hydrocarbon oils were carbonized to form carbons when the oils stayed in a hot zone for a long time.

2.2.2 The Type of Feed (Tire)

The effect of different type of tires; passenger and truck tires was investigated in a fixed-bed reactor by Ucar *et al.*, (2005). They found that the composition of gaseous products of both tires were similar and contained mainly C1-C4. The truck tire which contained styrene-butadiene rubber, natural rubber, and butadiene rubber gave higher yield of oil product than the passenger car tire which contained only natural and butadiene rubber. The pyrolytic oil was composed of lighter hydrocarbons than diesel, but heavier than naphtha. Moreover, they found the tire containing a high percentage of butadiene rubber (BR) and low percentage of natural rubber (NR) gave the high aromatic content in oil fractions due to Diel-Alder reaction of alkene from butadiene rubber or limonene precursor, which might react with pyrolysis product from butadiene compound.

2.2.3 Catalytic Conversion

The catalytic conversions of hydrocarbon become interesting and more commercial because a catalyst can modify product yields and compositions of hydrocarbon products. Several works have been focused on catalytic conversion or catalytic pyrolysis.

2.2.3.1 *Zeolites*

Several researches studied the effect of zeolite in catalytic conversion or pyrolysis of waste tires. Williams *et al.*, (2003) studied the effect of ZSM-5 and Y Zeolite with different pore sizes and Si/Al ratios. The results showed that the oil products had high single ring aromatic compounds, such as toluene, benzene, and xylene when the Y zeolite with low Si/Al ratio was used. They also found that lower pore size zeolite (ZSM-5) produced lower aromatic compounds as compared with large pore size (Y-zeolite). Similarly, Boxiang *et al.*, (2003) reported the concentration of single ring aromatics in oil products increased when ZSM-5 and USY zeolites were used in pyrolysis of tire. Beta zeolite provided lower aromatiza-

tion capacity because of weaker acid sites. They also studied the mesostructure materials (AL-MCM-41 and Al-SBA-15), and found that these catalysts generated very wide range of alkylaromatics. Fan *et al.*, (2005) studied a novel catalyst having excellent olefin reduction without loss in octane number of gasoline. They reported the series of zeolites (SAPO-11/HMOR/beta/ZSM-5 zeolites) gave higher liquid yields, improved gasoline RON because of high iso-paraffins (C₅-C₆) and arene (C₈-C₁₀), and lowered amount of coke deposit on catalysts. They also reported HMOR, H-beta, and SAPO-11 were good catalysts for hydroisomerization, while HZSM-5 was good for aromatization. Moreover, they investigated that the stronger acidity favored aromatization at high temperatures, but had lower stability because of coke formation.

2.2.3.2 Beta Zeolite

Beta zeolite has a three-dimensional large pore size with intersecting channel system as shown in Figure 2.2. Two perpendicular straight channels, each with a cross section of 0.76 x 0.64 nm, run in the a- and b-directions, and sinusoidal channels of 0.55 x 0.55 nm run parallel to the c-direction. Beta zeolite is a kind of high silicon zeolite with 12-ring orifice. It has the alumina atom which can produce Bronsted as well as Lewis acidity. Bronsted acidity presents on both internal and external surface. Lewis acidity is predominantly present on the internal surface.

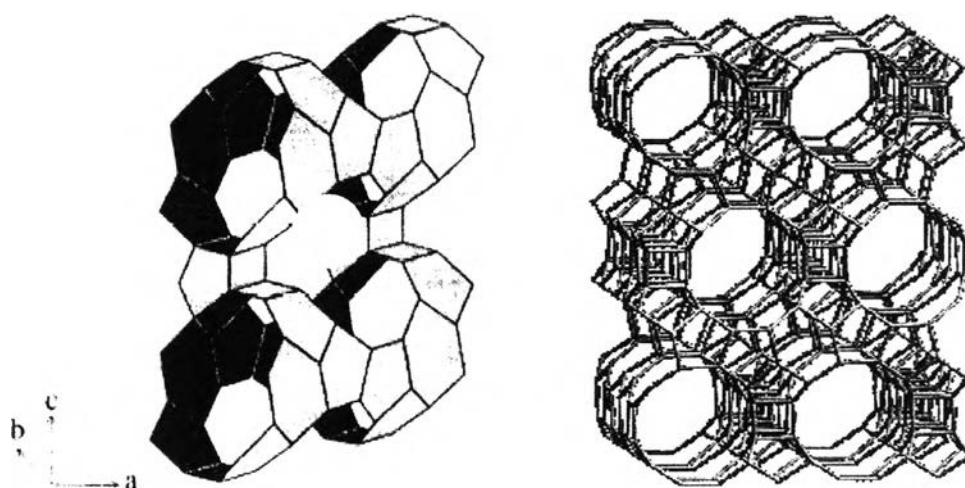


Figure 2.2 Beta zeolite: (a) channel system, (Jansen, *et al.*, 1997) and (b) structure (www.chemistry.nus.edu.sg)

This zeolite has good selectivity on chain hydrocarbon cracking, and used in several applications. Examples of successful applications of Beta zeolite include aromatic alkylation, aromatic acylation, indole synthesis, aromatic nitration, and aliphatic alkylation (Jansen *et al.*, 1997). For the application in petrochemical or petroleum refinery industry, Beta zeolite was used as a catalyst in aromatic alkylation, isomerization, hydrocracking, and catalytic cracking due to the advantages of zeolite studied by several researchers.

In 2002, Du *et al.*, studied on alkylation of benzene with ethylene to ethylbenzene over Beta zeolite catalyst by *in situ* IR. They found that Beta zeolite had a good performance for benzene alkylation in liquid phase, and can to be an active selective catalyst for alkylation of benzene with ethylene. The isomerization reaction was studied by Halgeri *et al.*, (1998). They reported that the advantage H-Beta was due to the large pore size catalyst, which isomerization of large molecule could be occurred. In 1999, Corma *et al.*, studied catalytic cracking of n-heptane on MCM-22, and compared with ZDM-5 and Beta Zeolites. The results showed that Beta zeolite gave the high ratios of alkane / alkene and iso-butane/total butane. Similarly, Bonetto *et al.*, (1992) showed Beta zeolite produced relatively high iso-butane yield in gas oil cracking process. In 2006, Marcilla *et al.*, studied catalytic pyrolysis of LDPE over H-Beta and HZSM-5 zeolites in dynamic conditions. They found that Beta zeolite gave higher selectivity to produce C₄ and C₅ compounds in the different temperature (300-500°C). Beta zeolite does not only give high alkane / alkene ratio, but also has ability in cracking naphthenes or aromatic-naphthanic rings. In 2001, Corma *et al.*, had accomplished some interested research by using Beta zeolite in cracking tetraline and decaline. The results showed that the large pore size, Beta zeolite was a suitable catalyst for cracking naphthenes and fused aromatic-naphthenic ring in light cycle oil, and be better suited for hydrotreating light cycle oil.

Beta zeolite has good properties, but there has been a few of research that used this zeolite in catalytic pyrolysis of tire. In 2006, Miguel *et al.*, studied the effect of five acid solid in the conversion of tire rubber into hydrocarbon products They found that Beta zeolite produced high single aromatic content in oil product, but it provided lower aromatic capacity due to weaker acid site as compared with other zeolites

2.2.3.3 Supported Palladium Catalysts

The production of clean transportation fuels has been significant attention due to environmental concerns and more stringent limits on the amount of aromatic in gasoline and diesel. The pyrolysis of tire produces the oil product which has the similar properties of commercial oils, but it contains with high aromatic concentration. Thus, the pyrolytic oil needs the technology that can reduce aromatic compounds. The hydrotreating and hydrogenation are two commercial proven refining technologies in the high aromatic oil (Pillai *et al.*, 2004). The supported palladium catalysts were widely used as the catalyst for hydrogenation reaction. This reaction depended on the acidity of supports and types of metal. The noble metal supported on zeolites had higher activity for aromatic hydrogenation as compared with that supported on alumina or titania. The higher acidity of the support could be attributable partly to the better dispersion of metal on zeolites (Song, 2000). Similar to Chupin *et al.*, (2000) studied the gas phase hydrogenation of toluene by using Pt/Al₂O₃, Pt- and Pd-/HFAU zeolite in a fixed bed reactor at 110 °C. The results showed the Pd / HFUA had a high activity and initial hydrogenation activity than Pd/ Al₂O₃, due to the acidity of support which had a positive effect to toluene hydrogenation. The effect of metal type was studied by Song *et al.*, (1996). They studied the hydrogenation of a model fuel containing 20% naphthalene at 200 °C over Pd-and Pt on H-Mordenite and H-Y zeolite. They reported the Pd/ Y zeolite or Mordenite were more active than platinum on the same supports at the same loading level. Moreover, Ahmed *et al.*, (2005) studied the effect of Pt, Pd, Ir and Re supported on H-ZSM-5 on hydroconversion of cyclohexene. They found that Pd gave higher hydrogenation/dehydrogenation activity than all metals in this research, and Pd was the most active catalyst in cyclohexene conversion, even at low temperatures.

The hydrogenation and ring opening of polycyclic aromatic hydrocarbon were the one of reaction performed to enhance the quality of the pyrolytic oils and other oil products by using bifunctional catalysts. Weitkamp *et al.*, (2001) studied the production of C₂₊ alkane from aromatic compounds by using noble catalysts. They reported that aromatic compounds converted to alkane in two routes. First, a direct route utilizing bifunctional catalysts, and second, a two-stage

route comprises hydrogenation and cracking. The results showed that the Pd/H-ZSM-5 was the good catalyst to produce C₂₊ alkane in a direct route.

The octane number decreased with reducing aromatic compounds in gasoline. Therefore, another way was chosen to boot the octane number of gasoline. Increasing the content of branched alkanes in the gasoline was the most suitable way. Because, it was more environmentally alternative way compared with oxygenates and aromatics addition (Liu *et al.*, 2005). Bifunctional catalysts with the novel metals (basically, platinum and palladium) provided the hydrogenating- dehydrogenating function, and had a high activity and selectivity of hydroisomerization. Sánchez *et al.*, (2006) studied the hydroisomerization of n-hexane, n-heptane, n-octane, cyclohexene, and benzene. They found that Pd/Beta zeolite suppressed the conversion of cyclohexene toward dehydrogenation to benzene in the hydroisomerization of cyclohexane. Lui *et al.*, (2005 and 2006) studied the direct iso-paraffin synthesis from synthesis gas via Fischer-Tropsch (FT) routes in a dual reactor system, The Fischer-Tropsch was carried out over Co/SiO₂ catalyst in the upper reactor, and the FT hydrocarbon were converted by Pt and Pd over Beta zeolite in the lower bed reactor. The 0.5%wt Pd/Beta showed stable performance in iso-paraffin selectivity. It had a high ratio of iso-butane/ total butane. They found that the main hydrocarbon products were C₃-C₅, similar to those obtained by Hickey *et al.*, (1989.) and Blomsma *et al.*, (1995). Moreover, Lui *et al.*, (2006) reported that Pd/Beta catalyst still showed high activity in production of gasoline range iso-paraffin even at a low temperature (280 °C).

The amount of metal loading in catalysts affected to the selectivity and conversion in isomerization reaction. Blomsma *et al.*, (1995) studied the isomerization on Pd/H-Beta with different palladium loading (0.1-1.0 %). This different metal loading gave the conversion between 10-50 % and the selectivity toward mono branching, multi-branching and cracking. Especially, 0.1 and 0.25%wt of Pd / H-Beta showed the high selectivity for multi-branching and cracking but low selectivity in mono-branching. Lui *et al.*, (2006) reported the effect of metal loading. They reported that the increase Pd loading on Pd/Beta catalyst enhanced the selectivity of C₄-C₈ normal paraffins, and decreased in selectivity of olefins C₄-C₈ normal olefins. Lucas *et al.*, (2005) studied the effect of the palladium and platinum loading over

beta agglomerated zeolite based catalysts in the hydroisomerization of n- octane. The results showed that the strong acid density of momo-metallic catalyst decreased with increasing the metal contents, due to the acid sites partial covered by metal particles. Lui *et al.*, (2006) reported the balance of metallic function and acidic function of the catalyst played important roles in the activity and stability of bifunctional catalysts.

There are the large amounts of sulfur in the pyrolysis of tire. This compound causes the poison of catalyst and reduces the activity or selectivity of catalyst. Thus, there were some researchers having focused on high sulfur tolerance catalysts. Song, (2000) reported that the mordenite-supported Pd catalyst was more active and more sulfur-resistant than the same metal supported on Y-zeolite, at the same metal loading level. Pt supported on the same mordenite had less sulfur resistance than Pd supported catalyst. Therefore, he concluded that the structure of zeolite and the type of metal are important for the sulfur tolerance. Moreover, Jongpattiwut *et al.*, (2003), studied the effect of bimetallic Pt and Pd on sulfur resistance in hydrogenation of polyaromatic hydrocarbons. They reported that acidic supports could affect to the electron withdrawing ability, metal particles, and the formation of metal – sulfur interaction. Matsui *et al.*, (2005) also studied the effect of noble metal particle size on the sulfur tolerance of monometallic Pd and Pt catalysts supported on high silica USY zeolite. They found that particle size of metal significantly affected to sulfur tolerance of both Pt and Pd/USY zeolite. Pd particles with the diameter less than 20 Å showed the highest sulfur tolerance because the sulfidation proceeded from surface sulfidation to bulk phase sulfidation, and the catalyst had the residual Pd metal phase co-existed with Pd sulfide phase at the surface of small particles.

The properties of the metal particle depended on the catalyst preparation techniques, such as methods for introducing a metal into supported/zeolite, and the condition for pre-treatment and reduction (Lui *et al.*, 2007). These could affect to the selectivity, activity of catalyst, and the particle size of the metal, related to the sulfur tolerance of the catalyst. The metal component could be loaded by several methods, the most widely used being ion exchange and impregnation. The ion exchange technique is the simple technique, and the zeolite with negatively charged porous framework and mobile cations sitting in the pore were prepared this technique. Lui *et al.*, (2007) showed that the ion-exchange metal/zeolite

catalyst generally gave higher dispersion of metal on zeolite than an impregnated catalyst due to the different metal –support interactions. Furthermore, the impregnated technique gave bigger particles of metal than the ion exchanged technique. These gave the less efficient hydrogen spillover than promoting hydroconversion reaction on zeolite and higher selectivity of heavy hydrocarbon molecules. Canaizare *et al.*, (1998) showed Pd metal atoms loaded by ion-exchange techniques were anchored by the zeolite protons. Pd atoms could not migrate during the reduction step. Therefore, the metals formed small particles inside the zeolite crystals. However, if a high Pd content was loaded by ion exchange, a certain quantity of Pd was not anchored by the mordenite protons, and migrated to the external surface of the Mordenite zeolite. If Pd was loaded by impregnation, large particles located outside the zeolite crystals were obtained. Therefore, they concluded that the different forms of metal particles with different preparation techniques affected to contribution of component quality and quantity of the pyrolytic oils.

From several research works, the catalyst and operating condition can affect to the upgrading reaction and the product in pyrolysis of used tire. This research work will be the studies on the influence of operations in the condition in reaction zone (reaction temperature and nitrogen gas flow rate) and effect of palladium (Pd) metal loading and catalyst preparation technique (incipient wetness impregnation and ion-exchange method) on the quantity and quality of oil product in pyrolysis of used tire.

The objectives of this research work were: (1) to synthesis the bifunctional catalysts, palladium over Beta zeolite with different metal loading, (2) to study the effect of operating conditions of pyrolysis (catalytic temperature and residence time) on quality and quantity of products, (3) to study the effect of catalyst preparation (incipient wetness impregnation and ion-exchange method) on the quality of product, (4) to investigate the quantity and quality of oils and other products from using the different catalysts

The scope of this research work covers: (1) pyrolysis of scrap tires (> 50,000 km) was performed in a bench-scaled autoclave reactor, (2) using palladium (0.25, 0.5, 0.75, 1.25 % wt) supported on H-beta zeolite, (3) the catalyst preparation techniques were incipient wetness impregnation and ion exchange, (4) particle size, hold-

ing time, N₂ flow rate, heating rate, the amount of sample and catalysts were fixed at 8-18 mesh, 90 min, 30 ml/min, 10 min/°C, 30 g and 10g, respectively, (5) the pyrolysis liquid products was separated using liquid chromatography column, (6) the boiling point distillation of liquid products was determined by a SIMDIST GC (FID), and gas products composition was determined by a GC, and (7) catalyst characterization was performed using the following techniques: BET, XRD, AAS, TEM, and TPO.