CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Background

A long time ago, natural rubber original natives of Central and South America as some part of product. However, from 1893 rubber has become a popular material, especially, mostly part of the presenger car tires, as Charles Goodyear discovered that the crosslink between sulfur and polymer chain could lead to be the rubber as a result. One of the reasons is its good building track.

2.1.1 Tire

Tires contain vulcanized rubber in addition to the rubberized fabric with reinforcing textile cards, steel of fabric belts, and steel-wine bead. There are other rubbers used in tire manufacture include natural rubber (cis-polyisoprene), synthesis cis-polyisoprene, and cis-polybutadiene, and cis-polybutadiene. However, the most commonly used tire rubber is the one containing styrene-butadiene copolymer (SBR) about 25 %wt styrene.

The carbon black could help the rubbers strengthen, and also prevent abrasion. Moreover, adding aromatic hydrocarbons such as extender oil, could help the rubber soften and improve workability. In the rubber vulcanization process, sulfur is used to crosslink the polymer chain within the rubber; hardening and preventing excessive deformation at elevated temperatures. In addition, the sulfur content is up to 1.5% of rubber. The composition of a typical passenger tire by weight (data received from a well known tire company) is:

Synthetic Rubber (SBR, BR)	27%
Carbon Black	28%
Natural Rubber	14%
Oil Extender	10%
Organic Fabric	4%
Steel Wire	10%
Other Petrochemicals	4%
Fillers (S, ZnO, TiO	

2.1.2 Pyrolysis

In general, pyrolysis or thermal cracking can be defined as the decomposition of organic matter in the absence of oxygen or in an oxygen-starved atmosphere (Chang, 1996).

2.2 Pyrolysis of Tires

The primary products of pyrolysis process are pyrolytic gas (pyro-gas), oil, and char. Oil and char can undergo additional process to manufacture secondary, value-added products.

Table 2.1 Waste tire pyrolysis products

Primary product	**wt. %**	**Content**	**Secondary Products**
Pyro-gas	10-30	Hydrogen, CO_2, CO, Methane, Ethane, Propane, Propene, Butane, Other hydrocabons, app. 1% of Sulfur	Nil
Oil	38-55	High aromatic Mw 300-400 Low in sulfur (0.3-1.0%) Aromatics, Alkanes, Alkenes, Ketones, Aldehydes	Carbon Black
Char	33-38	>15% of Ash (ZnO) 3-5% of Sulfur	Activated carbon

The problems of pyrolysis process are low price of the primary products, which contain essentially low molecular weight olefins, and char and high process cost. There is an approach to reduce the problems by using the catalysts, which processing temperature and time, resulting in the increase in can result in either higher molecular weight olefins or another proportion of valuable substance.

2.2.1 Thermal Degradation

Pyrolysis of waste tires without catalysts was studied by Chang *et al.* (1995). They studied on the degradation rate using a thermal gravimetric analyzer (TGA) to measure the weight loss of waste tire and on product yield using gas chromatography (GC) in order to analyze the composition of liquid products. The results showed that the rate increased with the pyrolysis temperature. The total yield to the gas product was over 30%-58% by weight of waste tires, and increased with increasing temperature. The total yield of oil was 28-42%, and char was 14-28%.

In 1997, Cunliffe and Williams studied pyrolysis of tire in a nitrogen purges static-bed batch reactor at temperatures between 450-600 °C. They found that the oil yield decreased and the gas yield increased with increasing final pyrolysis temperature. The results showed that the derived tire oils had fuel properties similar to those of a light petroleum fuel oil. The influence of pyrolysis temperature caused an increase in the aromatic content of the oils with increasing temperature and a consequent decrease in aliphatic content.

Pyrolysis of automobile tire waste in an N_2 atmosphere was studied by Gonzalez *et al.* (2000). The compositions and properties of the different faction were determined over a range of temperatures (350-700°C) and heating rates (5–20 K/min). At higher temperatures, the gas yield increased due to strong cracking, and the increasing heating rate led to similar results to those obtained with increasing temperature. The results showed that the oil fraction yield passed through a maximum at 550-575°C, and it was a mixture of aliphatic and aromatic hydrocarbons and hydroxyl compounds, which could be used as liquid fuel. The gas fraction consisted of H_2, CO, CH_4, CO_2, C_2H_4, and C_2H_2. The results indicated that the pyrolysis process consisted of one stage for the isothermal case and three stages for non-isothermal case.

Influence of process variables on oil from tire pyrolysis and hydropyrolysis in a swept fire bed reactor was studied by Mastral *et al.* in 1999. The products were the combination of oil and gas together with a solid that corresponds to the unconverted carbon black. The conversion was close to the maximum possible at 500°C, and the oil yield was higher than 40%. High yield of limonene was obtained in the all conditions investigated, and it was attributed to a cyclization reaction of the isoprene liberated.

In 2001, Rodriguez *et al.* studied pyrolysis of scrap tires under nitrogen in an autoclave at 300-700°C. The pyrolysis liquids were complex mixtures of C_5-C_{20} organic compounds with great proportions of aromatics. Pyrolysis gases were composed of hydrocarbons of which C_1 and C_4 are dominant, together with some CO, CO_2 and H_2S. Tire pyrolysis residues had the same dimensions as the original tire portion, and were easily disintegrated into powder and pieces of steel cord.

In 1995, Chaala and Roy studied the production of coke from scrap tire vacuum pyrolysis oil. The primary function of a coking unit is to upgrade the heavy crude oil fraction. They pyrolyzed the scrap tire under the vacuum at 500°C and total pressure of 20 kPa in a Process Development Unit. Then, the heavy oil product from this process was passed to coking process at temperatures of 480 – 500°C under the partial pressure formed by the vapors and gas produced in the process. The results showed that the coke obtained from scrap tire vacuum pyrolysis derived oil contained low sulfur, low ash and low metal contents, including a low vanadium concentration. Coking of the tire derived pyrolysis oil yielded high percentages of by-products with high commercial value, for examples a combustible gas with high heating value, a naphtha faction with a high aromatic content, a light gas oil rich in aromatic hydrocarbons, and a heavy gas oil that can be recycled during the coking process.

In 2000, Dai *et al.* used a circulating fluidized bed (CFB) reactor to pyrolyze waste tires. The pyrolysis of tire powder was carried out at various pyrolysis temperatures, particle sizes of tire powder, and feed position. The effects of temperature, residence time, and heating rate were studied. They found that high temperature and long residence time yielded more CH_4, H_2, C_2H_4, and CO, and less heavy hydrocarbon gas. The pyrolysis temperature, heating rate and residence time had greater effect on the oil yield, but the particle size had less effect on the gas composition. The most dominant composition in pyrolysis oil was aromatics, followed by alkanes, non-hydrocarbons, and asphalt.

Gonzalez *et al.* (2001) found that the effect of temperature was similar to the effect of heating rate. As the temperature increased, the yield of char decreased and the yield of gas increased. The yields of char oil and gas were 37-49%, 55%, and 4-11%, respectively. A gas chromatography (GC) with a thermal conductivity detector was employed to analyze the gas composition, mainly H_2, CO, CH_4, CO_2, C_2H_4, and C_2H_6. The liquid fractions were aliphatic, aromatic and hydroxyl compounds characterized by FTIR function group analysis and chromatography. The kinetics of the thermal decomposition of the feedstock was studied using isothermal and non-isothermal thermo gravimetric method at different temperatures (400-600°C) and heating rates (5-50 K/min). The particle sizes (0.2-2.6 mm. diameter) had an influence on the reaction, but the nitrogen flow rate and initial sample weight had no effect.

In 1999, Choi studied pyrolysis patterns of SBR with different microstructures characterized by pyrolysis gas chromatography. Butadiene, 4-VCH, and styrene were the major volatile pyrolysis products. The relative abundance of the styrene peak increased with increasing in the styrene unit content in SBR. The peak intensity ratio of 4-VCH/butadiene decreased with increasing in the 1, 2-unit content, but it increased with an increase in the cis-1, 4, or trans-1, 4-unit content.

Many researchers attempted to apply catalysts to overcome the faults of thermal cracking and received more useful chemicals with narrow distribution.

2.2.2 Catalytic Degradation

The influence of operation variables on the composition and yields of gaseous product from pyrolysis of tire powder was studied by Lueng *et al.*, (2002). The pyrolysis rate increased with increasing temperature in the range of 500-1000°C. It was found that high temperature and long residence time increased the gas volume. Maximum heating value of the gas was achieved at temperatures between 700°C and 800°C. The gas product from pyrolysis contained H_2, CO, CO_2, H_2S, and hydrocarbons. When dolomite and limestone were used as catalysts, they both have significant effect on the pyrolyzed products and have the capability of absorbing H_2S. However, their lifetime was limited. The product distribution was about 38% gas, 28% oil, and 34% char at the temperature of 900°C with the use of dolomite catalyst.

Aromatic chemicals from the catalytic pyrolysis of scrap tires were examined by Williams and Brindle (2002). They pyrolyzed scrap tires in a fix bed reactor, and the evolved pyrolysis gas was passed through a secondary catalytic reactor in order to maximize the concentration of single ring aromatic compounds. Three types of zeolite catalysts that they used were ZSM-5, Y-zeolite (CBV-400) and Y-zeolite (CBV-780) catalyst with different surface acidity and pore sizes. The results showed that the influence of the presence of either catalyst was to reduce the yield of oil with a consequent increase in the gas yield and the formation of coke on the catalyst. The yield of aromatic hydrocarbons in the derived oils was related to the different properties of three catalysts such as pore size which influenced selectivity. The lower pore size of ZSM-5 as compared to that of Y-zezolite resulted in a lower production of aromatic compounds. As well-known, the silica/alumina ratio influences the number of catalytically active sites on the catalyst surface. The Y-zeolite (CBV-400) with the lower silica/alumina ratio and therefore higher surface activity due to higher alumina surface concentration produced an oil with a higher aromatic hydrocarbon content as compared to the Y-zeolite (CBV-780) having higher silica/alumina ratio.

From the literature reviews above, acidic zeolites are powerful catalysts for catalytic cracking and pyrolysis, so the series of ITQ zeolites was selected as catalysts in this work.

2.3 ITQ-zeolites

ITQ-7 is a three-dimensional twelve-membered ring zeolite which presents double four-membered ring units (D4MR) in its structure. There is isomorphic substitution of Ge to Si atoms in the double four-membered ring units stabilizes such small cages. The zeolite with tri-directional system of channels has the pore diameters between 6.1 and 6.3 Å (Corma *et al.*, 2005).

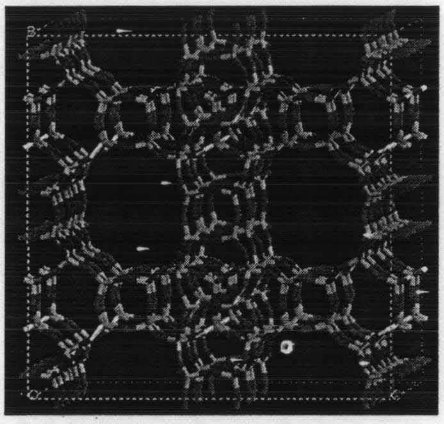

Figure 2.1 The structure of ITQ-7 (Cormal *et al.*, 2005).

ITQ-13 shown in Figure 2 is a single crystalline phase which has a unique three-dimensional channel system comprising of three sets of channels. In particular, ITQ-13 comprises of the first set of generally parallel channels each of which is defined by a ten-memberd ring of tetrahedrally coordinated atoms each has cross-sectional dimensions of about 4.8 Å by about 5.5 Å, whereas the second set of generally parallel channels which are also defined by ten-membered rings of tetrahedrally coordinated atoms each has cross-sectional dimensions of about 5.5 Å by 5.7 Å. The third set of generally parallel channels defined by a nine-membered ring of tetrahedrally coordinated atoms each has cross-sectional dimensions of about 4.0 Å by about 4.9 Å (Corma *et al.*, 2003).

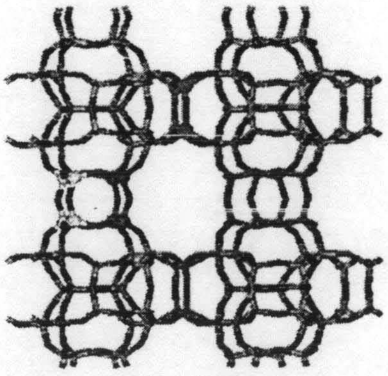

Figure 2.2 The structure of ITQ-13 (Corma *et al.*, 2003).

ITQ-21 contains a three-dimensional channel system of fully interconnected large cavities and containing Si, Ge, and optionally Al as framework cations. This material presents a unique pore topology formed by nearly spherical large cavities of 1.18 nm diameter joined to six other neighboring cavities by circular twelve-ring pore windows with an aperture of 0.74 nm (Corma *et al.*, 2002).

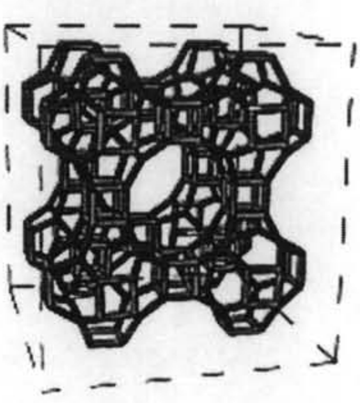

Figure 2.3 The structure of ITQ-21 (Cormal *et al.*, 2002).

ITQ-22 has a three-dimensional channel system comprising three sets of channels. The first set of eight-membered ring channels each has cross-sectional dimension of 12.72 Å. The third set of twelve-membered ring channels each has cross-sectional dimensions of 41.69 Å (Corma *et al.*, 2002).

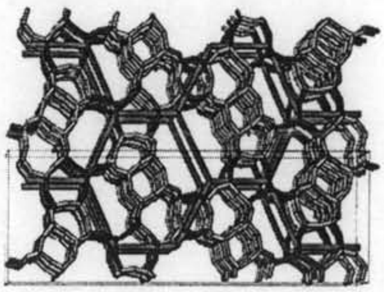

Figure 2.4 The structure of ITQ-22 (Corma *et al.*, 2002).

ITQ-24 as depicted in Figure 5 is an orthorhombic unit cell which has a three-dimensional pore system of intercrossing twelve-membered ring and ten-membered ring channels. The first set of generally parallel channels each of which is defined by a twelve-memberd ring straight runs perpendicularly with a pore aperture of 7.2 Å by 5.6 Å, where as the second set of generally parallel channels which are also defined by twelve-membered rings sinusoidal channels with a pore aperture of 7.2 Å by 6.2 Å. The third set of generally parallel channels which defined by a ten-membered rings channel system that intersects perpendicularly to both twelve-membered ring channel system with a pore opening of 5.6 Å by 4.8 Å (Corma *et al.*, 2003).

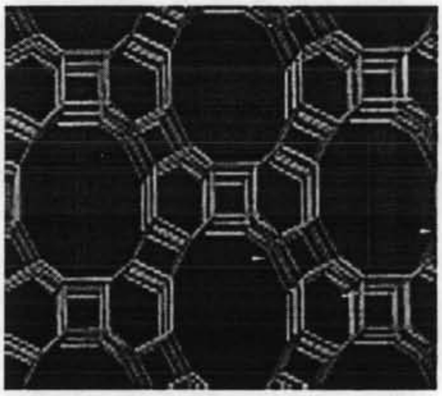

Figure 2.5 The structure of ITQ-24 (Corma *et al.*, 2003).

Mordenite zeolite is an orthorhombic crystal structure with straight 12-membered ring channels (6.5 x 7.0Å) and crossed 8-membered ring channels (2.8 x 5.7Å). The picture of mordenite is shown in Figure 2.6.

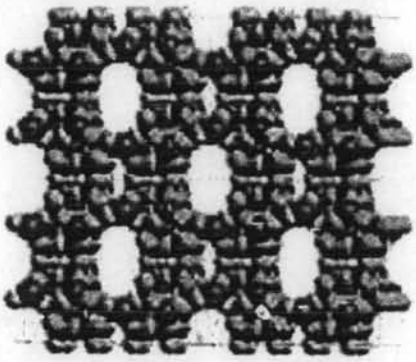

Figure 2.6 The structure of mordenite.

In 2000, Corma used ITQ-7 as a FCC zeolitic additive. The results showed that ITQ-7 zeolite had a good properties as an additive of USY zeolite for gasoil cracking and gave higher ratios of propylene/propane, butenes/butanes and isobutene/isobutane than Beta zeolite. ITQ-7 produced higher gasoline yield, with lower aromatics and higher olefin yield with an important increase in isoamylenes. The results were indicated that the lower content of aromatics for ITQ-7 gasoline decreased the research octane number (RON) of produced gasoline. However, the decrease in RON was compensated by the increase in isoparaffins and iso-olefins when using ITQ-7.