

CHAPTER IV

RESULTS AND DISCUSSION

This chapter is divided into 3 main parts: preliminary test, the effect of tire aging on pyrolysis products, and the effect of catalysts and their acidity on pyrolysis products and product distribution. The conditions employed on the studies in the last two parts were the appropriate conditions selected from the preliminary tests in the first part. The details of results and discussion are present in this entire chapter.

4.1 Preliminary Tests

4.1.1 DTG Experiments for Effect of Sample Weight

Figure 4.1 illustrates the effect of sample weight on pyrolysis of tire with a fixed size of 0.125 mm. All of curves are particular superimposable until the reaction is completed, confirming the sample weight has no influence on the reaction. Thus, 4 mg. of sample weight was the selected amount for studying the effect of particle size in each experiment.

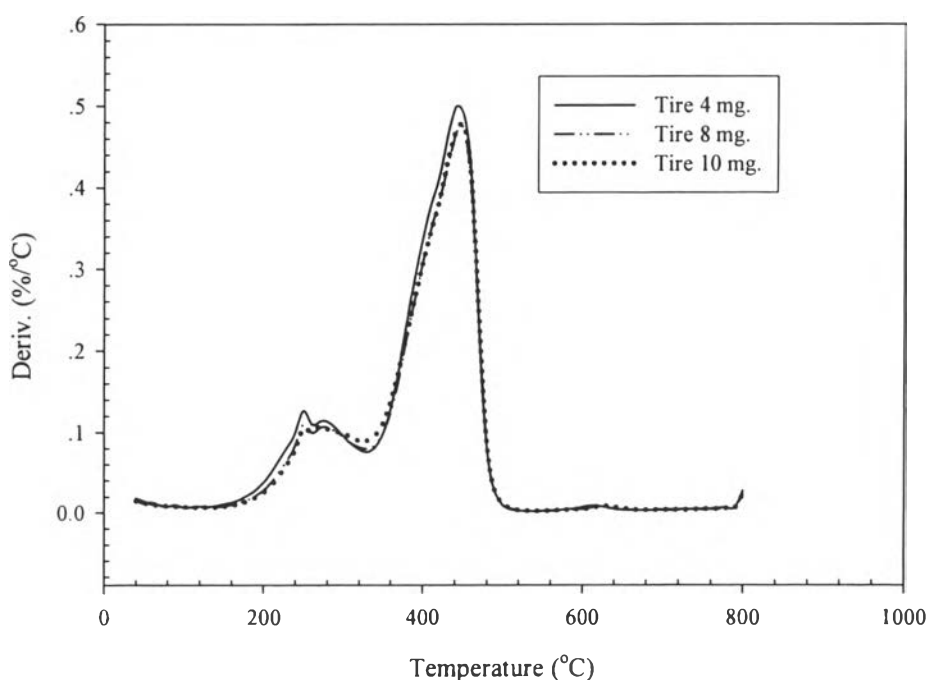


Figure 4.1 DTG curves for the effect of sample weight.

4.1.2 DTG Experiments for Effect of Particle Size

The effect of particle size is illustrated in Figure 4.2. The particle size can have a major influence on the reaction. These curves are not superimposable, so the particle size has influence on the reaction. It was generally assumed that an increase in particle size caused greater temperature gradients inside the particles, so that at a given time, the core temperature was lower than that of the surface (Encinar. *et al.*, 2000). Fixed sizes of 0.212-1 mm. were chosen to study for the next experiments.

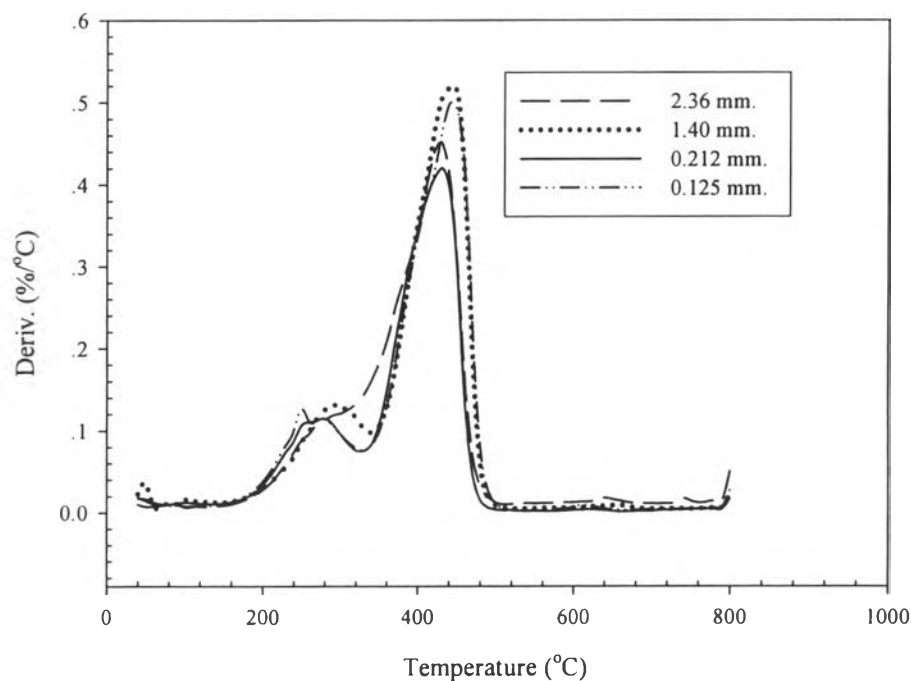


Figure 4.2 DTG curves for the effect of particle size.

4.2 Effect of Tire Aging on Pyrolysis Products

4.2.1 Physical Properties

4.2.1.1 *Crosslink density*

In general, crosslink density of rubber composites is one of the important properties of thermosets and generally restricts the degree of swelling in polymer. The impact of aging time to crosslink density is shown in Figure 4.3. The rubber compounds were aged at 70°C up to 4 weeks. The crosslink density of

1 week aged sample rapidly increases as compared to that of non-aged one. After that it slightly increases when samples were aged up to 3 weeks, and then sharply increases after 4 week aging. Usually, in a tire production the optimum cure is taken at the time which 90% or 95% of rubber is vulcanized, so about 5-10% is left out for natural vulcanization. Furthermore, with too long cure times, a surplus of vulcanizing agents may cause reduced network stability and a reduction in the properties of vulcanized rubber. The lifetime of a week aged rubber compound at 70°C in an oven is equivalent to that were storage under non-forced at room temperature for a year (นิธิอุทัยและคณะ, 1987). Hence, the rubber compounds of 4 week aging have an equivalent lifetime of 4 years under above conditions.

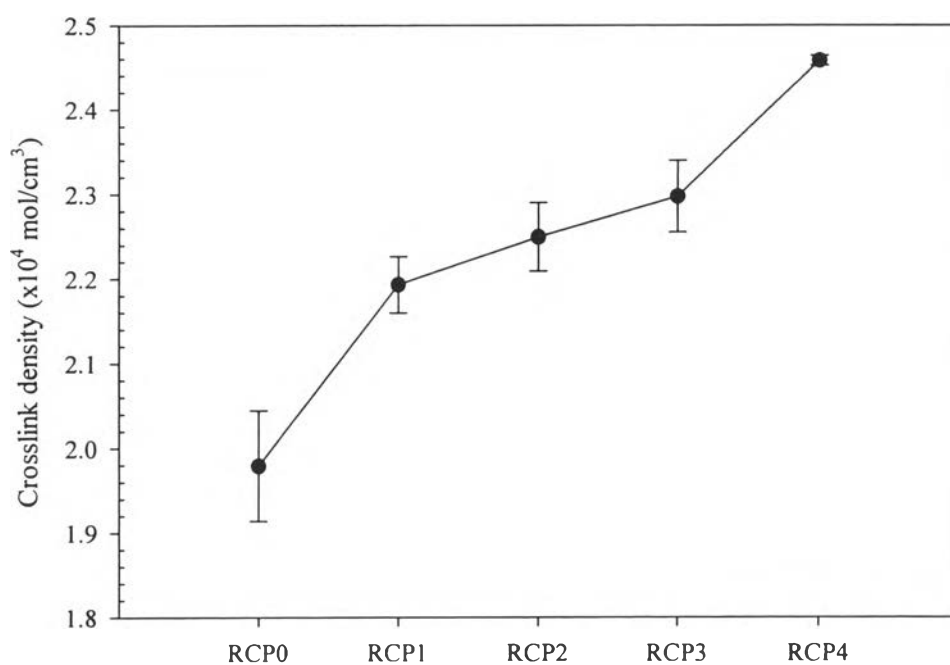


Figure 4.3 Effect of aging on crosslink density of rubber compounds.

4.2.1.2 Hardness

The crosslink density determines the physical property of vulcanizate. This is shown in Figure 4.4. The shore A hardness according to ASTM D 2240 of the various aged rubber compound samples was determined. The five series of the values increase with increasing aging time. When the crosslink is

completed, however, the effects of degradation become more pronounced, SBR compounds can actually harden, rather than soften (Rubber Engineer.

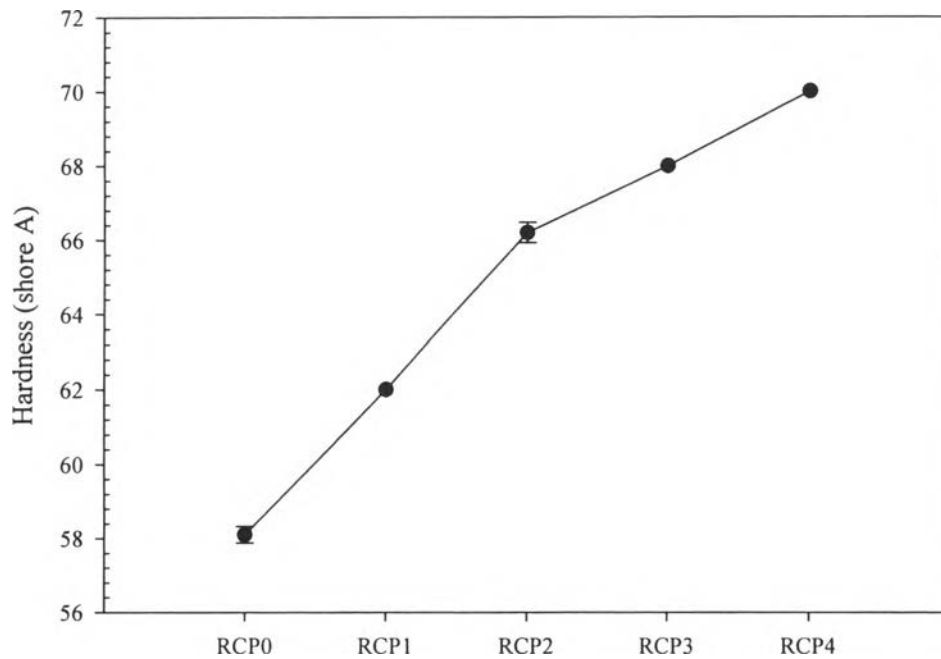


Figure 4.4 Effect of aging on rubber hardness.

4.2.2 DTG Experiments for the Effect of Aging Time

Figure 4.5 shows the DTG curves for the pyrolysis of aged rubber compound of 0.212-1.0 mm. diameter. All curves show two different degradation temperature regions over 30-800°C.

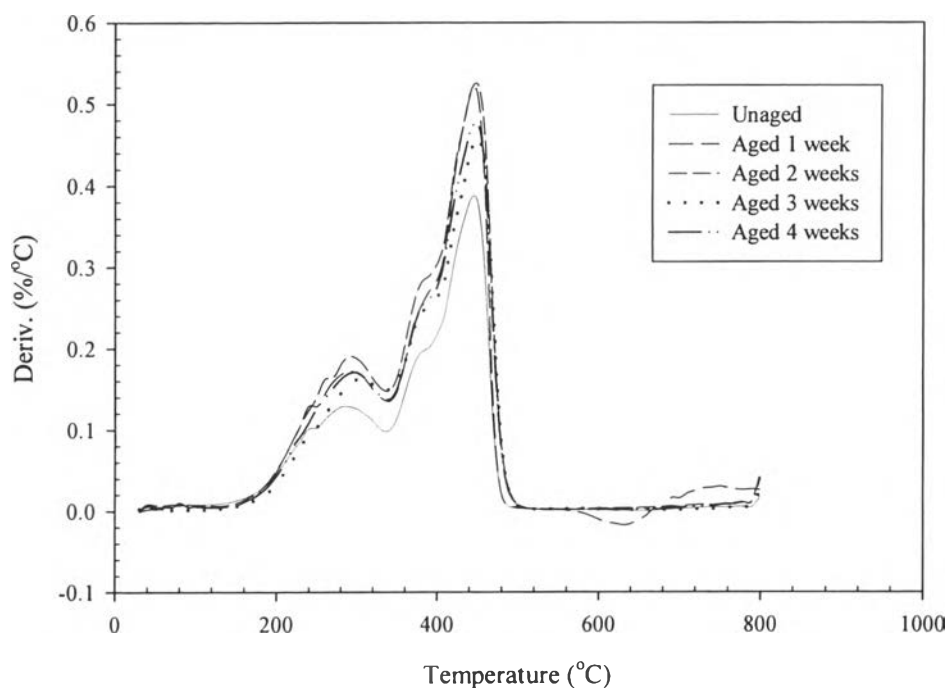


Figure 4.5 DTG curves of rubber compounds at various aging time.

Two dominant groups of peaks represent so-called primary and secondary products. In the region of 110-350°C, the primary products were generated. The secondary products appeared at higher temperatures, up to 500°C. The constituents of tires typically are natural rubber (NR), styrene butadiene rubber (SBR), butadiene rubber (BR) or their combinations, processing oil, carbon black, moisture, plasticizer, and additives. All these constituents were pyrolysed over different temperatures. At the temperature range of 150-350°C, this region is believed to be the thermal decomposition of a mixture of oil, moisture, plasticizer and additives. NR, BR, and SBR are decomposed in the range of 340-550°C (Leung *et al.*, 1998). In Figure 4.5, the peaks of aged tires, representing primary products, shift to higher temperatures than that of unaged tire. This observation may be resulted from strengthening of rubber compound matrix due to the loss of oil, moisture, plasticizer and additives along the aging process. The peaks at the second region show no difference among unaged and aged rubber compounds.

4.2.3 Product Distribution

The aged tire completely converted after the pyrolysis was completed. The pyrolysis solid residues were in the similar dimensions and shape for all samples. The liquid product represented in brown-yellow color, and its color was the more yellowish, for the longer aging time. The yields of gas, oil, and solid residue range in between 16-25%, 35-44%, and 39-40%, respectively as shown in Figure 4.6. The gas yield of these compounds decreases with aging time up to 3 weeks and then markedly increases. In the other hand, the liquid yield slightly increases after that rapidly decreases. The free chain length of NR between crosslink points and thermodynamic stability in terms of Bond Dissociation Energy (BDE) can explain these observations. These points will be discussed later for more details. Moreover, the aging time has no significant effect on the solid yield. The obtained solid residue was mainly carbon black.

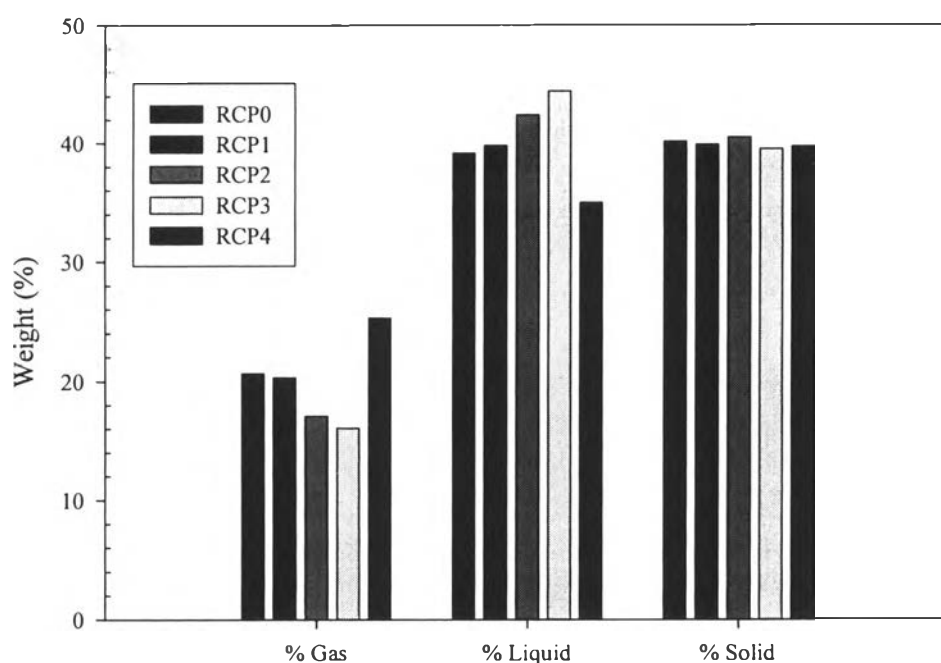


Figure 4.6 The effect of aging time on gas, oil, and solid residue yield.

4.2.4 Components in Gas Product

Figure 4.7 shows the components of gas produced from pyrolysis of aged rubber compounds at various aging times up to 4 weeks. A gas sample from each experiment was collected in one Tedlar bag along reaction and analysed by gas chromatography.

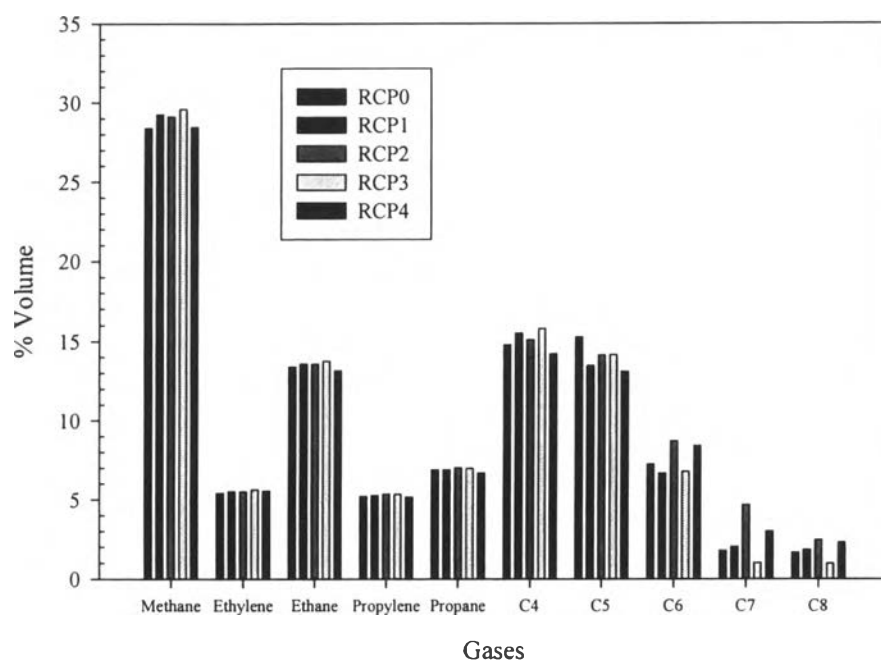


Figure 4.7 The gas compositions from pyrolysis of aged rubber compounds.

The pyrolysis gas was composed of methane, ethylene, ethane, propylene, propane, C₄-, C₅-, C₆-, C₇-, and C₈- hydrocarbons. The volume percentage of CH₄ exhibited a maximum value. It can be generated by both the direct breakdown of the polymer and secondary reactions including char reduction, tar cracking, shift reaction, etc. High amounts of ethane, C₄, and C₅ were also produced but not as much as that of methane. The volume fractions of C₄ and C₅ are comparable. Little amounts of C₇ and C₈ were produced as a trace in gas phase. C₄ and C₄⁺ came from the depolymerization of styrene-butadiene rubber, which normally is the main component of automotive tire (Laresgoiti *et al.*, 2000). No significant differences in lighter hydrocarbons were observed for tires aged at various aging time, but heavy hydrocarbons were. At aging time of 2 and 4 weeks, the obtained products were copious in the range of C₆-C₈ because of the wider distance of double bonds in polymer chain.

4.2.5 Carbon Number Range in Liquid Products

The evolved effluents from pyrolysis experiment were condensed in a series of ice-NaCl and ice-acetone vial condensers before analyzed by a SIMDIST gas chromatography. Figure 4.8 shows the carbon number range of pyrolysed liquid of aged rubber compounds. Non-aged rubber compound gives quite wider distribution of carbon numbers. When the aging time was longer, liquid oil was produced in narrower carbon number distribution, and the peaks tend slight shift to lower carbon number. After aging for 4 weeks, the peak shifted to higher carbon number, but not relevant. It seems that aging up to 4 weeks did not change much the distribution shape, but it caused the narrower distribution of liquid hydrocarbons. Upon aging process, the number of entangled molecules increased with a decrease in the number of free chain lengths as indicated by the increase of crosslink density. Pyrolysis of non-aged rubber gave wider distribution of carbon number, possibly due to having more free chain lengths to be broken down independently. On the other hand, aged rubber compounds are comprised of crosslinked chain pyrolyzed simultaneously as a group of molecules.

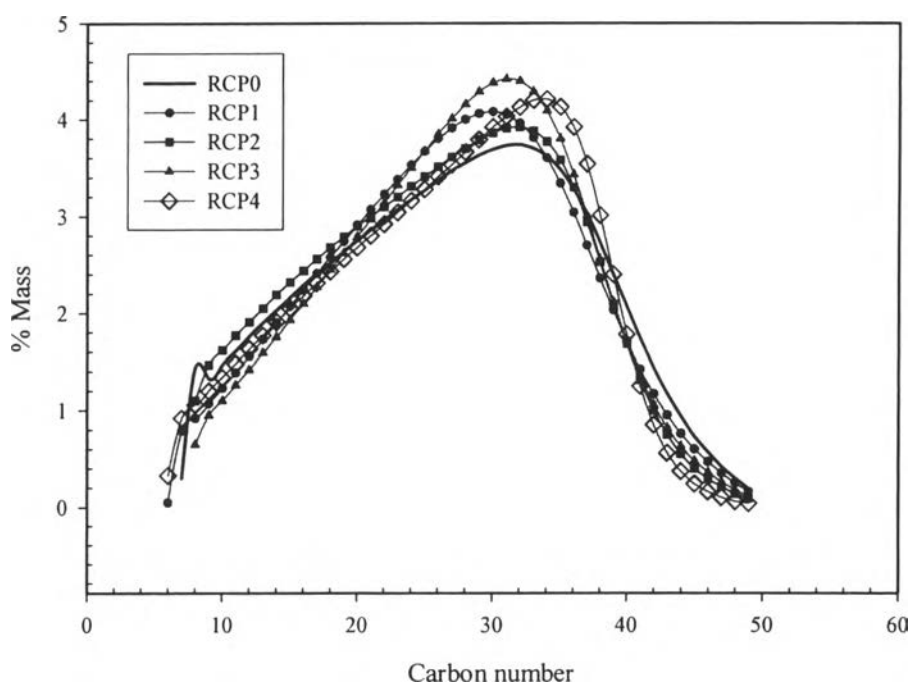


Figure 4.8 The effect of aging time on carbon number.

4.2.6 Oil Fractions in Liquid Product

Figure 4.9 shows distillation of oil fractions comprised of gasoline (<149°C), kerosene (149-232°C), gas oil or diesel (232-343°C), fuel oil (>343°C), and heavy vacuum gas oil. Each fraction was classified according to its boiling point range. As a consequence, there were no significant differences on the mass percentage of each fraction from various aging time.

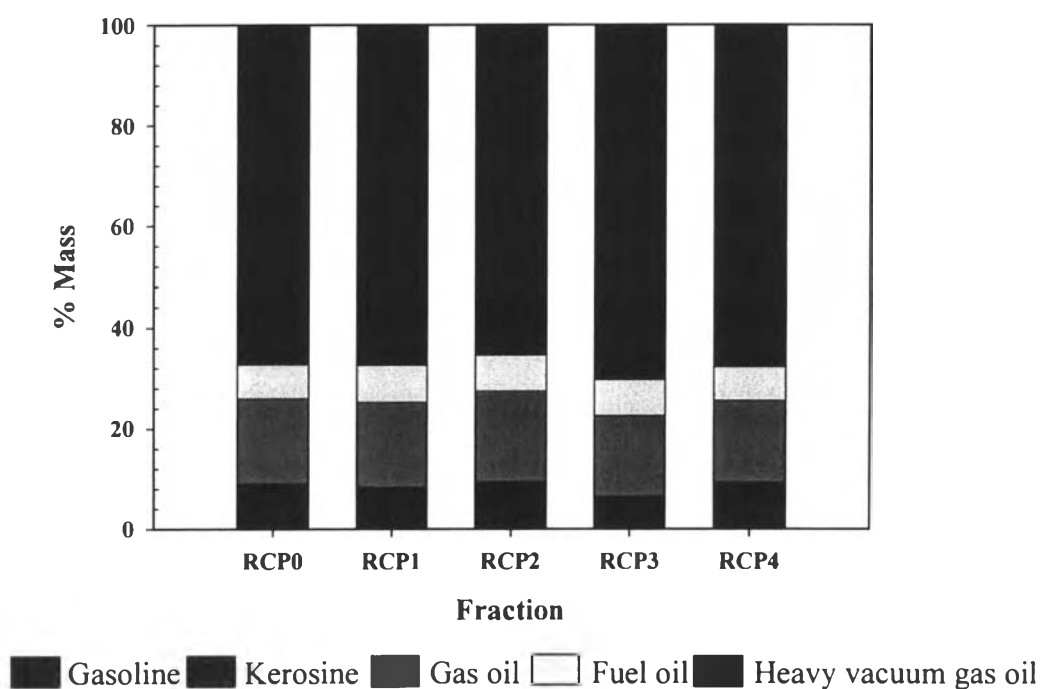


Figure 4.9 The oil fraction of pyrolysed aged rubber compound.

4.2.7 The Carbon Content in Solid Residue

The solid residues, after thermal cracking of aged rubber compounds, were washed with THF and performed TGA in air atmosphere, up to 800°C. The amounts of carbon content in solid residues at each aging time, left after thermal pyrolysis are shown in Figure 4.10. No significant difference in the amount of organic carbons was observed from the sample aged up to 4 weeks. The residue remaining in the pan of TGA experiment was inorganic filler in rubber compounds of about 8% weight. González *et al*, 2001 reported the pyrolyzed solid, with a medium higher heating value (HHV) of 28 MJ Kg⁻¹, can be used as a solid fuel.

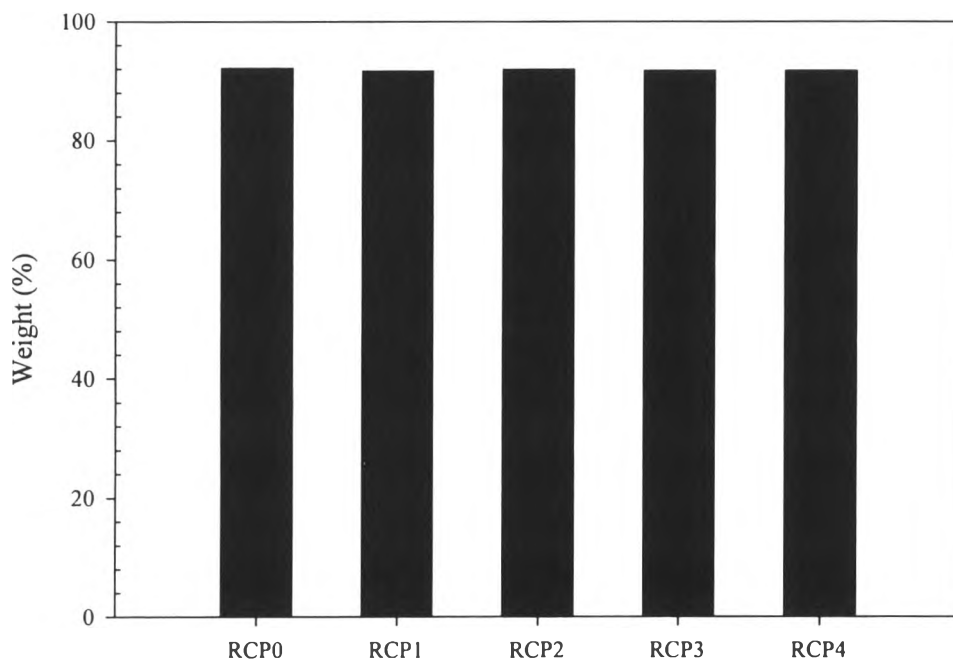


Figure 4.10 Carbon content in solid residues from pyrolysis of aged rubber compounds.

4.2.8 The Purposed Model of Aging Time

Aging is a collection term for changes in properties of materials that occur on longer storage without the action of chemicals that lead to partial or completed degradation. In NR polyisoprene, there is one double bond for each isoprene unit. These double bonds and the α -methylene groups are reactive groups for vulcanization reactions with sulfur. Thus, the double bonds are prerequisite for the sulfur vulcanization reaction. Vulcanization is the conversion of rubber molecules into three dimension networks by the formation of crosslinks. By crosslinking, the rubber changes from the thermoplastic to the elastic state. The effect of aging on structural vulcanizate as shown by purposed model in Figure 4.11.

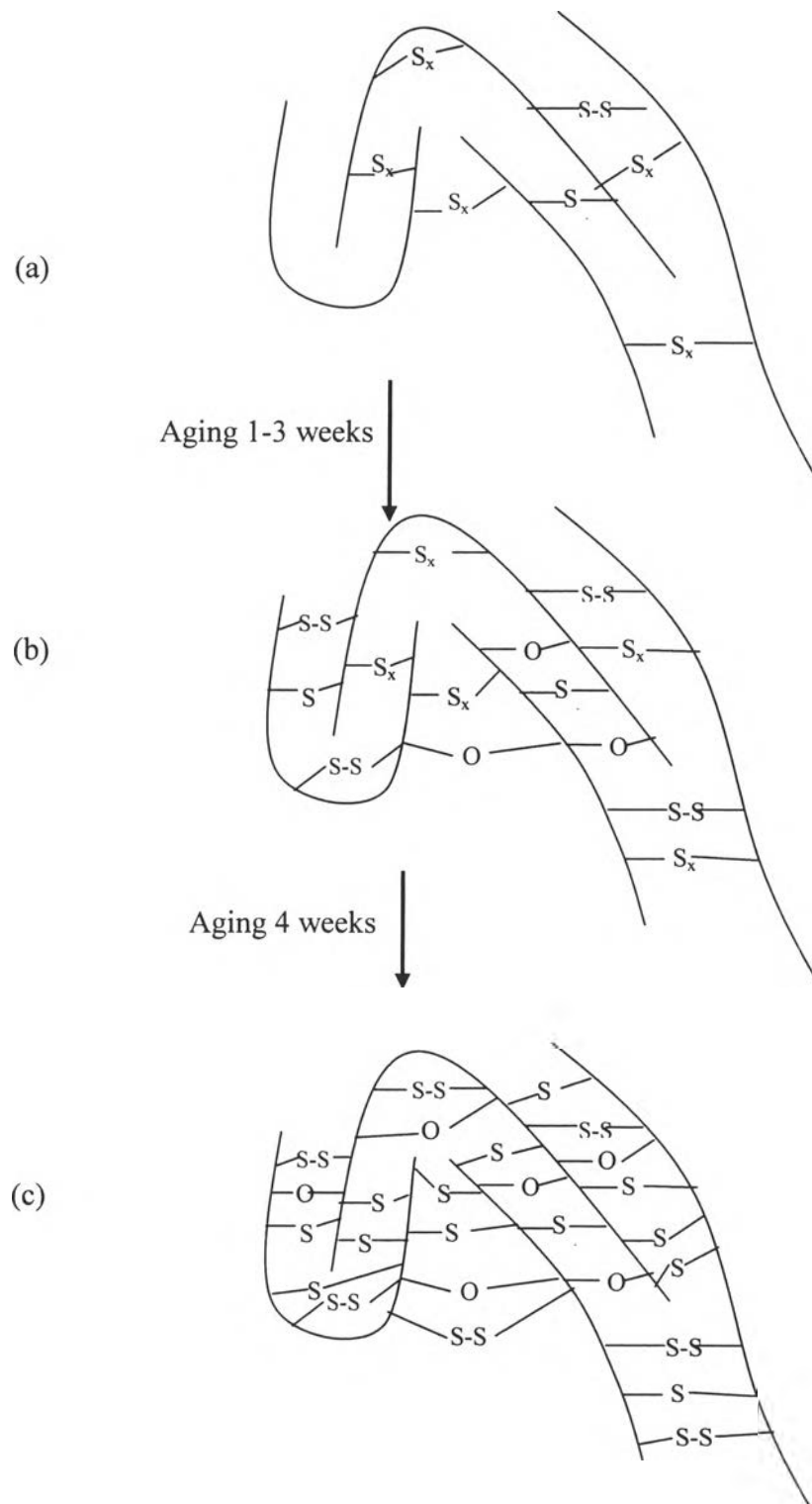


Figure 4.11 Purposed model of crosslink density (a) non-aged rubber compound (b) after aged 3 weeks rubber compound (c) after 4 weeks aging.

Uncured and cured rubbers are especially prone to such aging effects. The unsaturated groups in diene rubbers make it possible to cure with sulfur, but at the same time present sensitivity toward oxygen from the air and other added reactive materials during storage that is partially bound to the vulcanizate. Reactions occurring during the exposure are chain reaction and active radicals. During oxidation the first product is H_2O that again decomposes into free radicals, that start new chain reaction and also can react with double bonds of the rubber (autocatalytic reaction) as mention by Rubber Technology Handbook. In general, additional network chain could result from crosslinking by: 1) residual curatives, sulfur and accelerator 2) rearrangement of crosslinked sulfur 3) oxidative coupling (Hamed *et al.*,1999). The last effect is proportionate to the aging time. The oxygen absorption changes to autocatalytic one. Relatively small amounts of bound oxygen lead to deep seated changes in the structure of the vulcanizate, not only on the surface but also in the bulk of the vulcanizate. Oxygen can cause crosslinking whereby a higher crosslink density is affected. The crosslink density of aging up to 3 weeks gained that of non-aged as shown in model (b). Even after vulcanization, free double bonds are still sensitive to the remaining crosslink agents. The model (c) shows for the case at longer reaction time up to 4 weeks. During vulcanization the crosslinks initially formed are mainly the thermally unstable polysulphidic bonds and they are transformed into di- and mono- sulphidic bonds as the aging progresses, so-called maturation of sulfur crosslinks. The samples contain more mono- and di- sulphidic bonds. It can be implied that the number of crosslink density increases dramatically at 4 week aging.

Non-aged rubber compound is suggested to be in the form as appeared in model (a). It resulted in higher gas yield but smaller liquid yield as compared to the aged rubber compounds up to 3 weeks suggested to appear as in model (b). These results included wider distribution of carbon number in liquid products. It can be explained that the heat introduced by pyrolysis is capable to crack the free chains. According to Bond Dissociation Energy (BDE); thermodynamic stability of chemical bonding is in a sequence as the following, C-C (607 kJ/mol) < C-S (699 kJ/mol) < C-O (1076.5 kJ/mol). It appeared of that the crosslink was not tremendous after rubber compounds were aged up to 3 weeks, as illustrated in model (b). The applied

heat prefers being used in free chain scission (C-C bond) rather than to crosslink cleavage (C-S or C-O bond) due to BDE. This is the reason attributes to the gaining in liquid yield but declining in gas yield of narrower product distribution of rubber compounds with aging time up to 3 weeks. As Choi, *et al*, 1999 mentioned, the free chain length of NR between crosslinks in the vulcanizates became shorter as the crosslink became higher. These reasons correspond to the narrow distribution of carbon number. The model (c) can justify the rubber compound of 4 weeks aging time. Its gas yield suddenly increased but liquid yield suddenly reduced. This means that it contains the highly networked structure as indicated by the abrupt increase of crosslink density. All pyrolysis heat prefers cracking the weakest C-C bonds to other bonds such as C-S and C-O bonds.

4.3 Effect of Catalyst Acidity

4.3.1 Catalyst Characterization

4.3.1.1 Crystallinity

From the catalyst preparation, the amount of loaded sulfate was varied up to 8%. The XRD patterns of $\text{ZrO}_2/\text{SO}_4^{2-}$ are shown in Figure 4.12. The patterns of unimpregnated and impregnated catalysts show no difference. Thus, the sulfate loading did not have impact on the structure of ZrO_2 . In addition, monoclinic phase of $\text{ZrO}_2/\text{SO}_4^{2-}$ was formed.

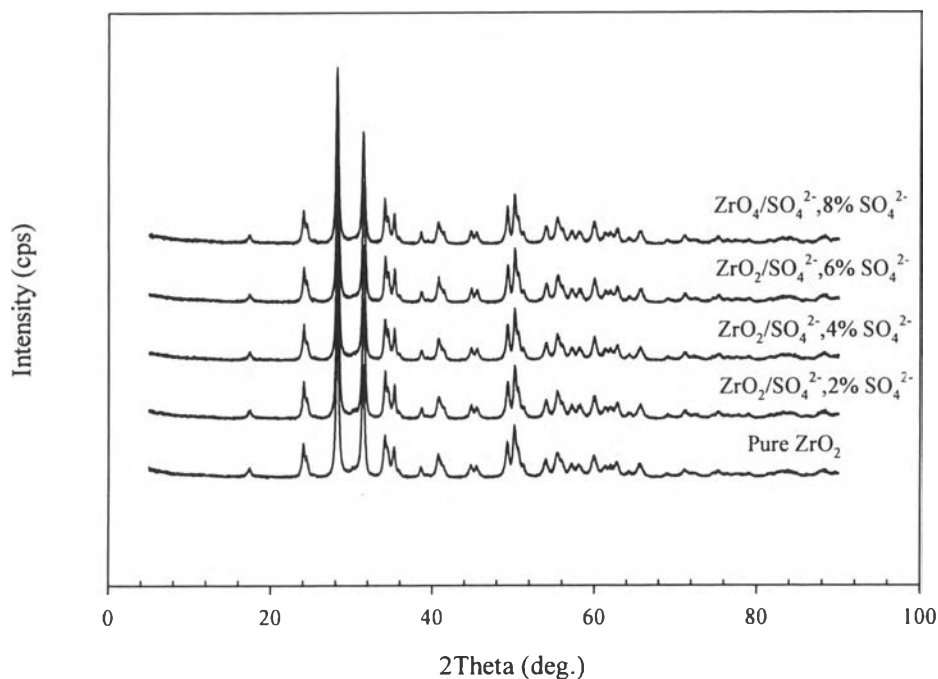


Figure 4.12 XRD patterns of ZrO_2/SO_4^{2-} at various SO_4^{2-} loadings.

4.3.1.2 Thermal stability

In studying the thermal stability, TGA technique was employed. The curves of ZrO_2/SO_4^{2-} in Figure 4.13 showed 2 regions of weight loss. For the first region, derivative peaks are located at 30 to 300°C due to moisture and excess sulfate decomposition (for high loading case) or sulfate on weaker sites. The adsorption of water can inhibit the strong acidity. The water can be removed by drying at 100-200°C for 3-4 hours as mentioned by MEL CHEMICAL. Moreover, ZrO_2/SO_4^{2-} lost some components proportionally to sulfate amount at about 550°C, which was probably caused by the decomposition of sulfate on the surface to form SO_3 , as mentioned by Snipes *et al.*, 1979. These observations guarantee that at the conditions employed in pyrolysis experiments, SO_4^{2-} ions and superacidity were still maintained on the surface of catalysts.

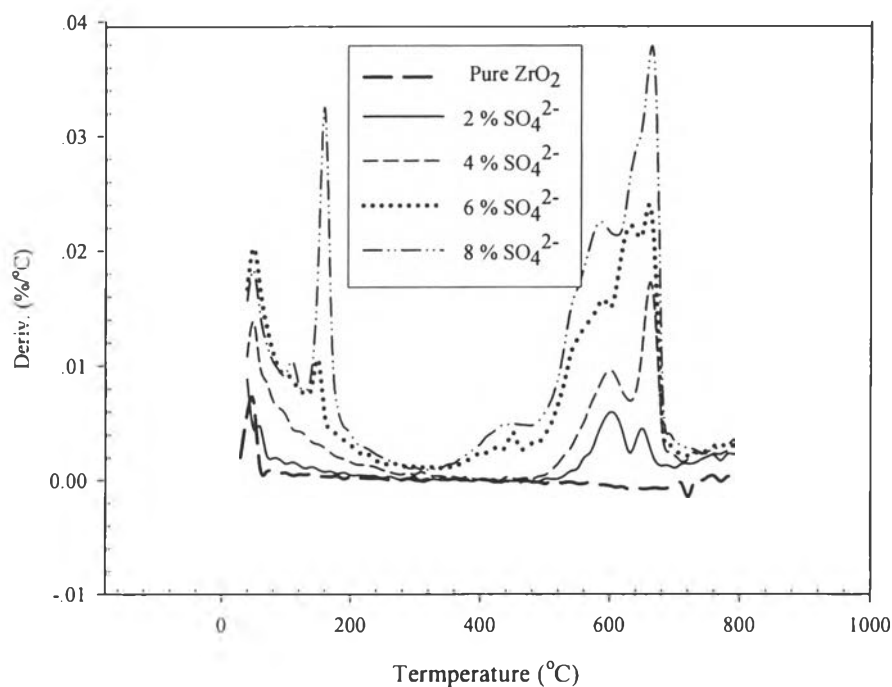


Figure 4.13 Weight loss of $\text{ZrO}_2/\text{SO}_4^{2-}$ at various SO_4^{2-} loadings.

4.3.1.3 Specific surface area

The surface area of catalysts was measured by using BET technique on Autosorb-1 instrument. The surface area of catalysts decreases with the increase of sulfate amount impregnated on the surface as displayed in Table 4.1.

Table 4.1 BET surface areas of $\text{ZrO}_2/\text{SO}_4^{2-}$

Catalyst	% SO_4^{2-}	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (\AA)
$\text{ZrO}_2/\text{SO}_4^{2-}$	0	6.680	1.182×10^{-2}	70.77
	2	3.588	4.196×10^{-3}	46.78
	4	3.784	2.880×10^{-3}	30.54
	6	1.028	1.480×10^{-3}	57.62
	8	1.963	3.178×10^{-3}	64.76

4.3.2 DTG Experiments for the Effect of Catalyst on Pyrolysis

Figure 4.14 reveals the effect of catalysts on pyrolysis of tire. $\text{ZrO}_2/\text{SO}_4^{2-}$ provided two groups of products; primary and secondary. When the amount of impregnated sulfate increases, the derivative peaks in both of the first and the second regions slightly shift to the right (to the higher temperature). This indicates that catalysts have the effect on pyrolysis process.

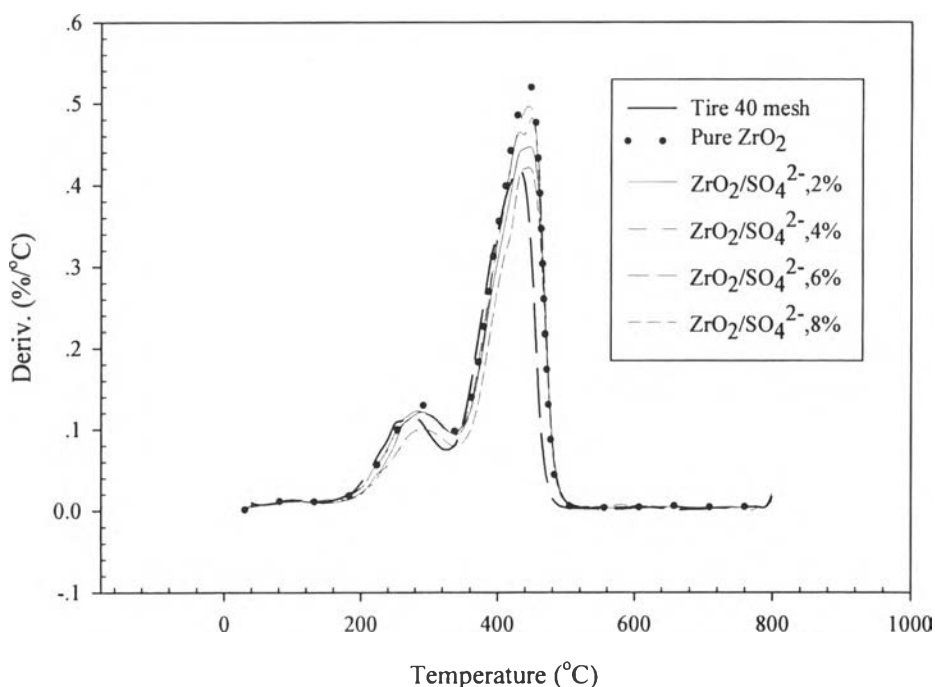


Figure 4.14 DTG curves of tire co-pyrolyzed with various $\text{ZrO}_2/\text{SO}_4^{2-}$.

4.3.3 Effect of Loaded Sulfate on Pyrolyzed Products

4.3.3.1 Product distribution

Catalyst to tire ratio of 0.50 was selected for studying the effect of loaded sulfate on pyrolyzed waste tire in contact mode. The total weight of sample was 1.00 gram. The obtained conversion in catalytic pyrolysis of waste tire can be considered as a completed one. The liquid obtained in tire-catalytic pyrolysis which was usually termed as oil. It was dark-brown-colored products which resembled petroleum fractions. The obtained solid-pyrolysis was a piece of equal dimensions and shape as those of original tire portion. The color of catalysts represented in dark-gray color, as demonstrated by Sassi *et al.* 1999, deactivation of

sulfated zirconia was closely related to the accumulation of coke precursors on the surface. The effect of % SO_4^{2-} loaded on the surface of ZrO_2 on gas, liquid, and solid residue was shown in Figure 4.15. The pyrolysis in the absence of catalysts produced gas yield of 19.2%, liquid yield of 39.8%, and char yield of 41.0%. Catalysts affected on all product yields. They sharply increased gas yield, rapidly decrease liquid yield and slightly decreased in solid residue as compared to those from non-catalytic case. Productions from the catalytic cracking was approximately 29-31 % gas, 30-34 % liquid, and 37.0-39 % solid residue. As the amount of sulfate increased, liquid yield was slightly increased with small decrease in gas and solid residue yields. The results of the presence of catalysts differed markedly from non-catalytic case.

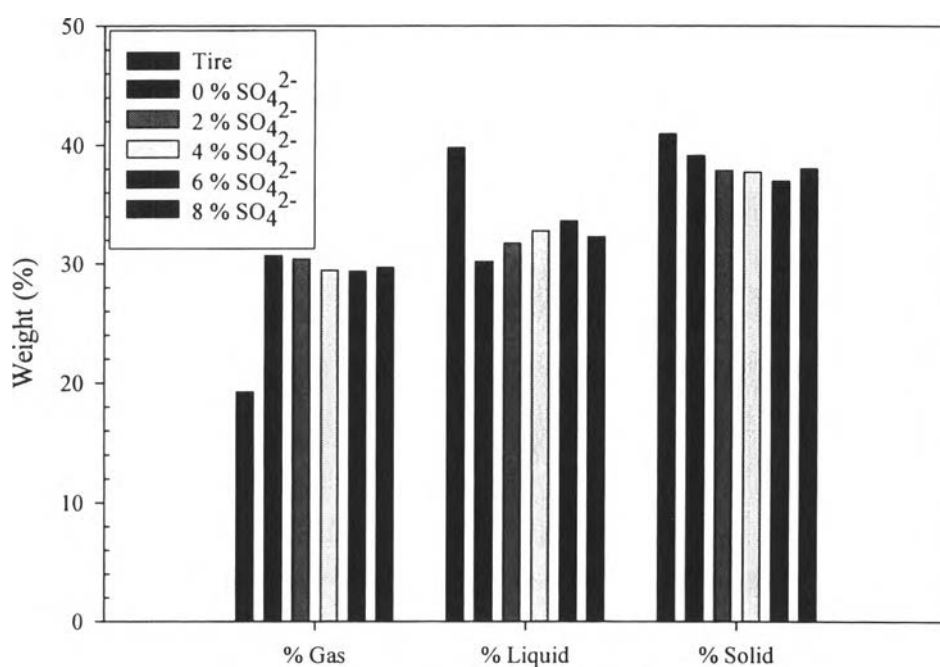


Figure 4.15 Effect of SO_4^{2-} loaded amount on gas, oil, and solid residue yield.

4.3.3.2 Components in gas product

Gaseous products leaving the reactor were captured in a Tedlar bag. Gas compositions of tire pyrolysis with $\text{ZrO}_2/\text{SO}_4^{2-}$ at various % SO_4^{2-} loaded are shown in Figure 4.16. Gases are comprised of methane, ethylene, ethane, propylene, propane, C_4 -, C_5 -, C_6 -, C_7 -, and C_8 - hydrocarbons. Methane demonstrates the maximum volume whereas ethane, C_4 , and C_5 are the minor components. Ethane

and C₅ are comparable but not in as high volume as C₄. Methane and C₂ can be produced by both the breakdown of the polymer and secondary reactions such as tar cracking. The presentation of C₅ can be explained by referring to Cho, S.S., 1999. The monomer (repeat unit) of the polymer is the most abundant of the volatile products formed by pyrolysis. The % SO₄²⁻ loaded impacts the volume of methane, C₄, and C₅. Amount of loaded sulfate increased, consequently decreasing methane but increasing C₄ and C₅. There is no significant difference on the amounts of other components produced from various percentages of loading.

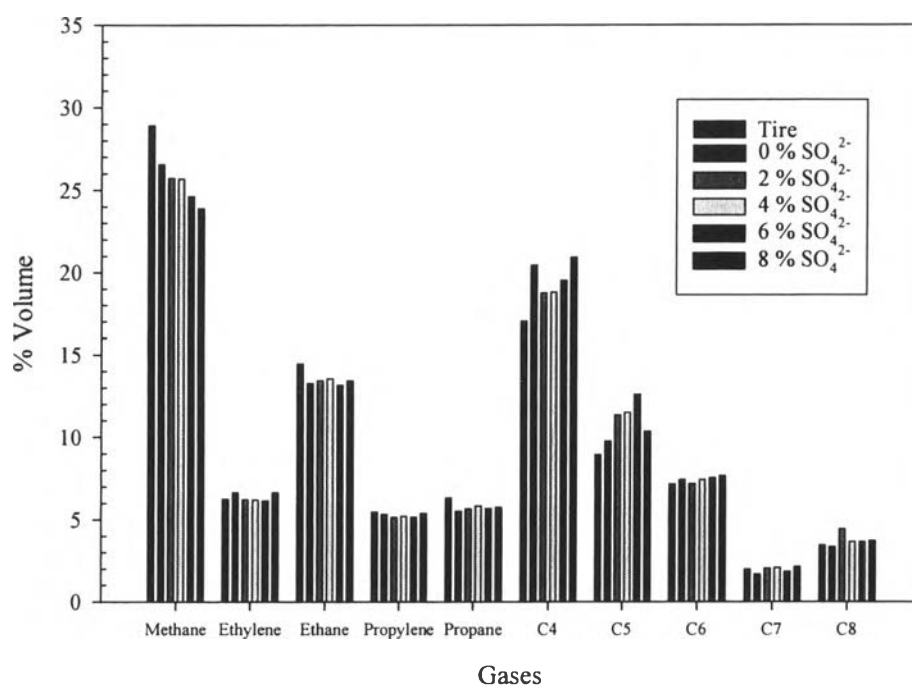


Figure 4.16 The gas composition of tire pyrolysis with ZrO₂/SO₄²⁻.

4.3.3.3 Carbon number range in liquid product

Figure 4.17 indicates the effect of ZrO₂/SO₄²⁻ at various percentages of SO₄²⁻ on the carbon number range in liquid products, which were trapped in condensers and analyzed by a SIMDIST gas chromatography. It can be seen that, as expected, pyrolysis oils derived from tire are a very complex mixture containing a wide variety of organic compounds of 8-49 carbons. In the absence of a catalyst, a wider carbon number of higher complexity was produced as compared to the catalytically pyrolyzed oils. Loading more sulfate, the range of carbon number

shifts to small carbon number range and presents narrow distribution at about 22-26 carbon. From the specific surface area analysis, the pore size of pure ZrO_2 showed the largest size whereas the loaded sulfate 4% gave the smallest. Therefore, organic compounds produced by pure ZrO_2 shift to high carbon numbers but the loaded 4% sulfate produced organic compounds in small range carbon number. It may be possible that two kinds of reactions, i.e. cracking of tar and synthesizing of alkenes, coexist in the process. As Leung *et al.*, 2002 mentioned, it seems that the latter reaction was dominant at the temperature was lower than 800°C .

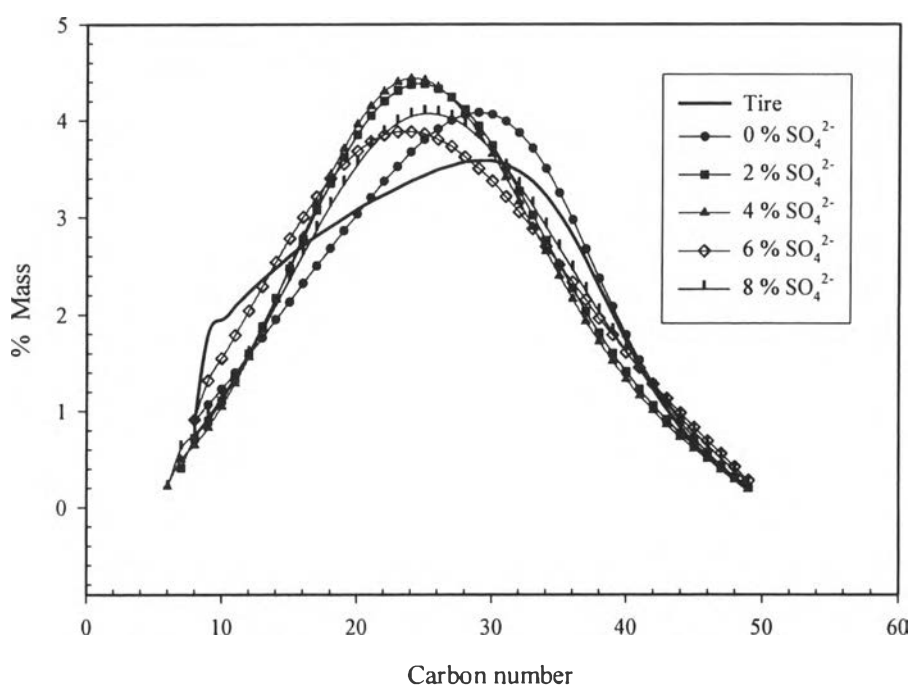


Figure 4.17 The effect of $\text{ZrO}_2/\text{SO}_4^{2-}$ on carbon number.

4.3.3.4 Oil fraction in liquid product

The oil derived from the uncatalysed and catalysed pyrolysis of used tire undertaken at 500°C are very complex containing a wide variety of mainly gasoline, kerosene, gas oil or diesel, fuel oil, and heavy vacuum gas oil. In the thermal degradation, the heavy vacuum gas oil was cracked to valuable petroleum in small amounts of gasoline, kerosene, and fuel oil. The abundant fraction was gas oil. The influence of the percentage of loading sulfate on the fraction of gasoline, kerosene, gas oil, fuel oil, and heavy vacuum gas oil is also

shown in Figure 4.18. The percentage sulfate was varied from 0 to 8 %. Gasoline, gas oil, and fuel oil do not continuously increase, however, ranging from 1.92 to 2.46, 17.54 to 20, and 7.61 to 8.77 % by mass, respectively. The last two fractions dominate with the maximum at 6% sulfate whereas gasoline is maximum with 8% sulfate. However, no significant change in kerosene fraction was observed until loading with 6% sulfate. Kerosene can be used as feedstock for hydrotreatment and catalytic reforming units for the production of gasoline by reason of it represented as medium naphtha (Handbook of petroleum product analysis).

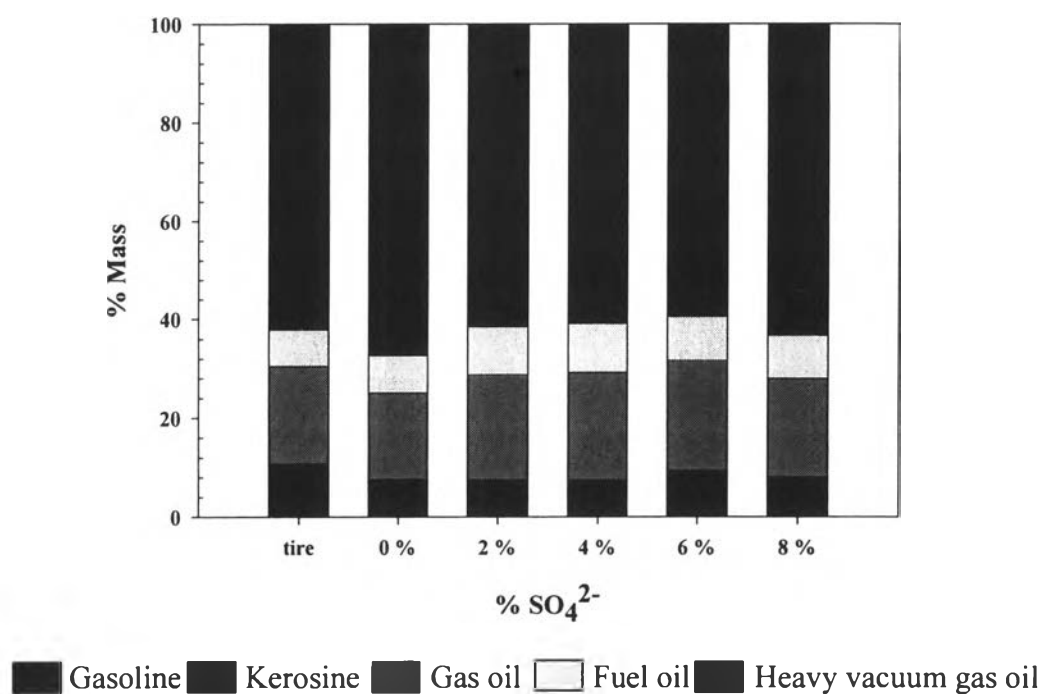


Figure 4.18 Oil fractions of tire co-pyrolised with various ZrO_2/SO_4^{2-} .

4.3.3.5 Carbon content in solid residue

The carbon content in solid residues after catalytic cracking of waste tire are shown in Figure 4.19. All of the carbon contents obtained in solid residue are not significantly different.

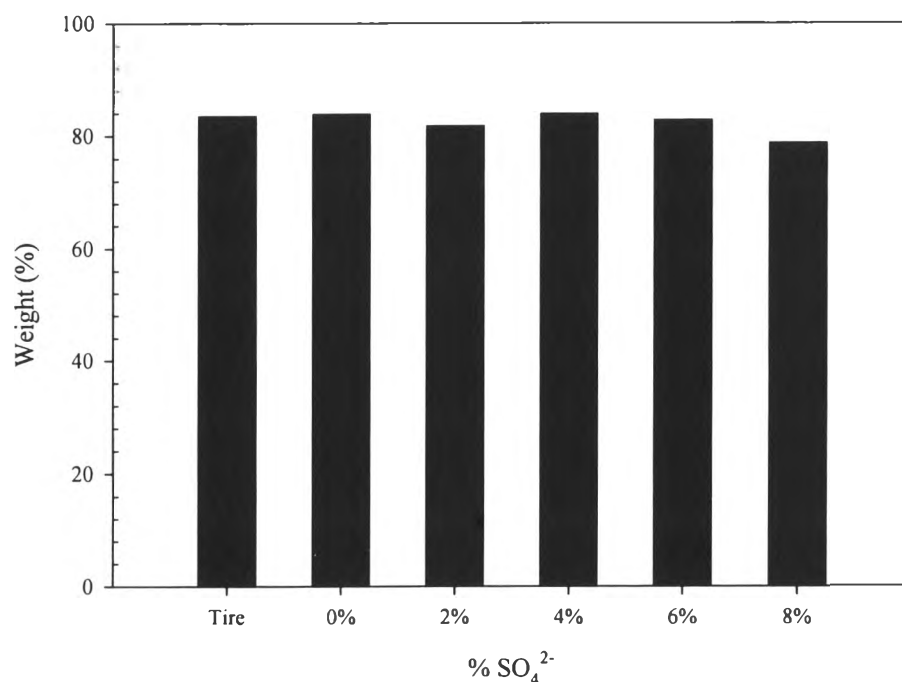


Figure 4.19 Carbons content in solid residue from tire pyrolysis with various $\text{ZrO}_2/\text{SO}_4^{2-}$.

4.3.4 Effect of Catalyst to Tire Ratios

4.3.4.1 *Product distribution*

In this experiment, the influence of catalyst to tire ratio was examined. $\text{ZrO}_2/\text{SO}_4^{2-}$ with 4% SO_4^{2-} was inspected using the catalyst to tire ratio of 0.00, 0.11, 0.25, 0.50, and 1.00. The 4% sulfate loaded was selected due to the thermal stability. There was no moisture and excess sulfate decomposed before 500°C. The total weight of sample was fixed at 1.00 gram. The obtained solid pyrolysis residue was a piece of equal dimensions and shape as in the original tire portion. The results show that the influence of the amount of catalysts was to reduce the yield of liquid and solid residue with a consequent increase in the gas yield. The yields of product from the pyrolysis of tire at various catalyst to tire ratios are shown in Figure 4.20 that the yields of oil and solid residue decrease from 40-33 % and 41-36 %, respectively. There is a corresponding increase in the yield of gas from 19-29%. The change in char yield may be attributed to the secondary reaction of carbon black with CO_2 and/or to the decomposition of inorganic components retained in solid char and/or the strong acidity of catalyst.

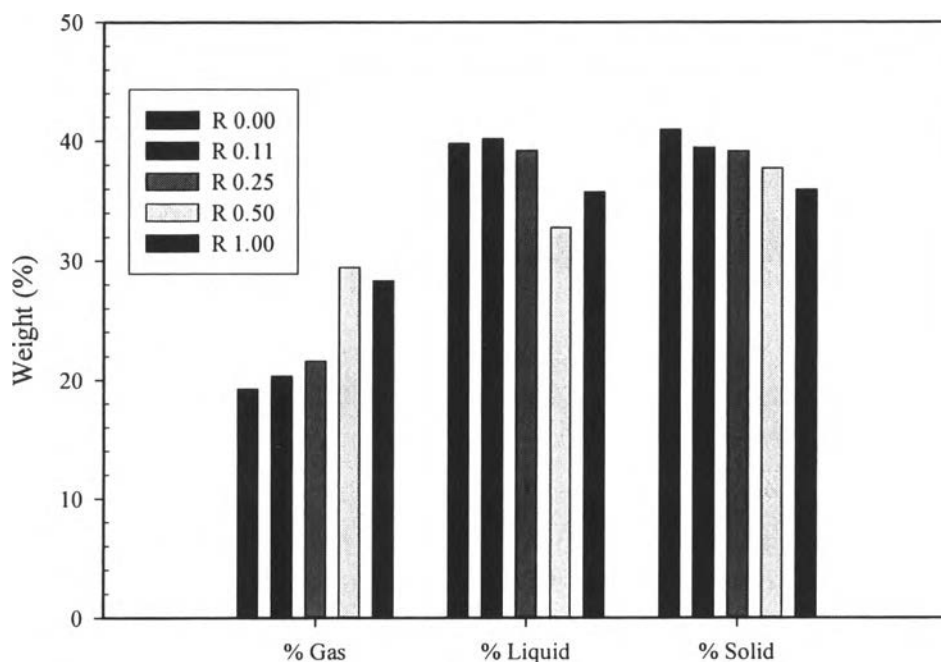


Figure 4.20 The effect of catalyst to tire ratio on pyrolysed products.

4.3.4.2 Components in gas product

Figure 4.21 shows the components of gas produced from catalytic degradation with various ratios of catalyst to tire from 0.00, 0.11, 0.25, 0.50, and 1.00. Non-condensable gases were analyzed off-line by a gas chromatography. The gases were identified as methane, ethylene, ethane, propylene, propane, C_4 -, C_5 -, C_6 -, C_7 -, C_8 - hydrocarbons, which were the same components as mentioned in the previous section. With the addition of catalyst, the volume percentage of methane is the dominant, followed by C_4 and ethane, respectively and with lower volume of other hydrocarbon gases. Methane and ethane can be used as a combustible gas with a high heating value as mentioned by Chaala *et al.*, 1996. Furthermore, the light hydrocarbons (C_3 -) slightly decrease while the heavy hydrocarbons (C_4 -) slightly increase, with increasing amount of catalysts. C_7 and C_8 are exhibited as a trace, possibly because the mechanism of tire depolymerization includes a pattern in which large fragments are detached from the polymeric matrix of rubber and are then efficiently fragmented to light hydrocarbons as the pyrolysis proceeds (Murena *et al.*, 1996).

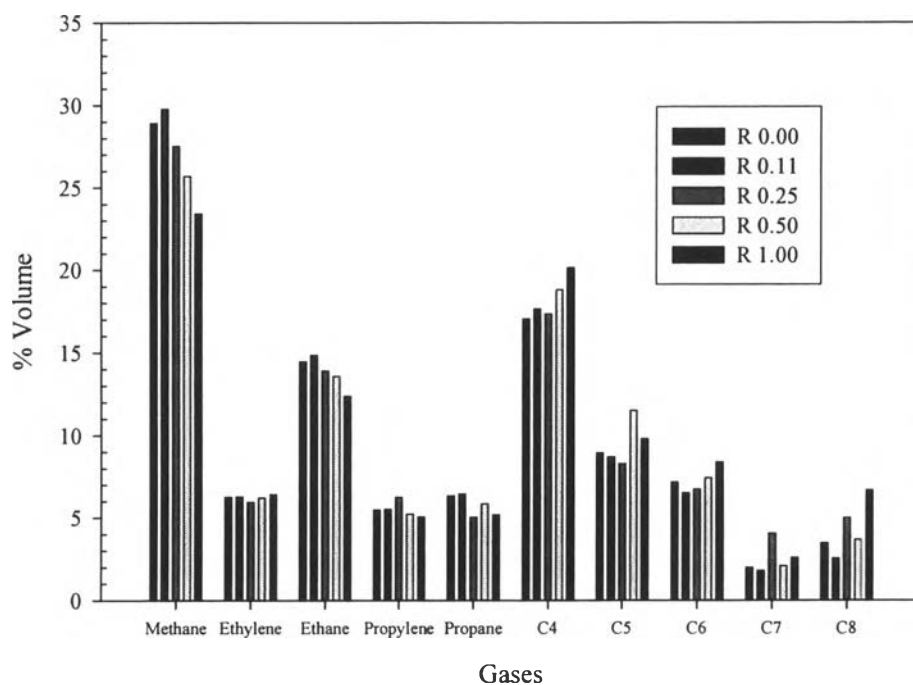


Figure 4.21 The gas composition from tire pyrolysis at various catalysts to tire ratios.

4.3.4.3 Carbon number range in liquid products

Carbon number ranges of tire pyrolysis oil obtained at various catalyst to tire ratios are illustrated in Figure 4.22. The carbon number range of oil from thermal pyrolysis is presented in wider distribution while with the addition of catalysts, the range of carbon number shifts to smaller carbon number range. Furthermore, thermal pyrolysis favors a high yield of C_{10} hydrocarbons, such as D,L-limonene, postulated to be the thermal degradation product of polyisoprene elastomer (Benallal *et al.*, 1995). The maximum of distribution curves shifts from the right to the left until the catalyst to tire ratio changes to 0.25, indicating that higher amount of lighter hydrocarbons are produced with the ratios increasing to 0.25. However, when higher ratio is higher than 0.25, the maximum of the curves shifts backward to higher carbon number, meaning that heavier hydrocarbons are reproduced. Hence, the optimum ratio to produce more valuable lighter products is 0.25.

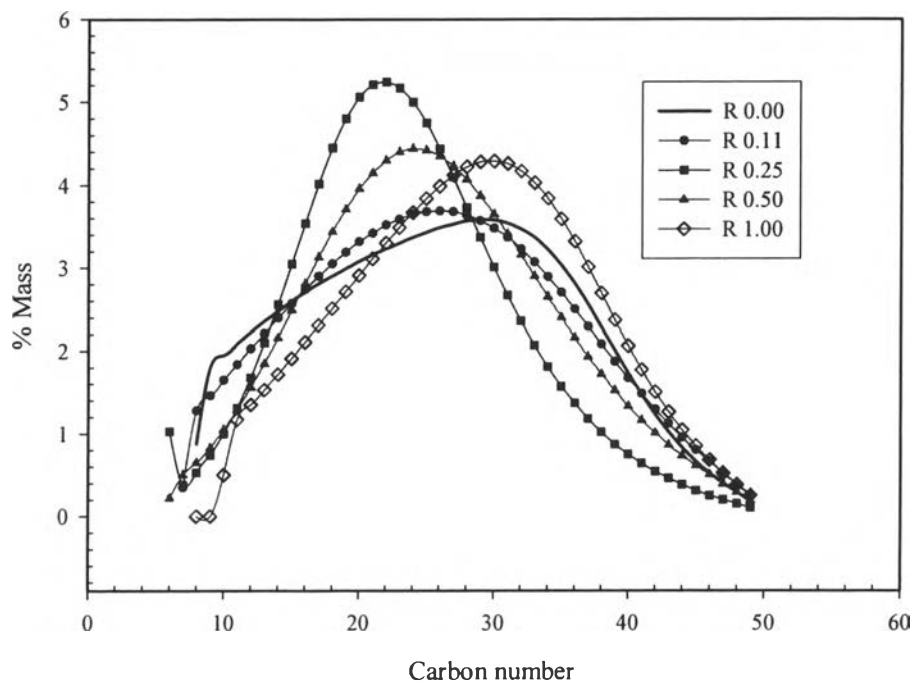


Figure 4.22 The effect of catalyst to tire ratio on carbon number.

4.3.4.4 Oil fraction in liquid product

Figure 4.23 displays the influence of catalyst to tire ratio. About 40 % wt. of liquids is the heavy fraction with boiling points of 15-370°C, which is the boiling point range specified for atmospherically distilled petrol. The catalyst to tire ratios have the impact on every fraction. Indeed, catalyst to tire ratio at 0.25 appears to be the optimum ratio, since at this ratio, the most valuable products was produced with the least heavy fraction.

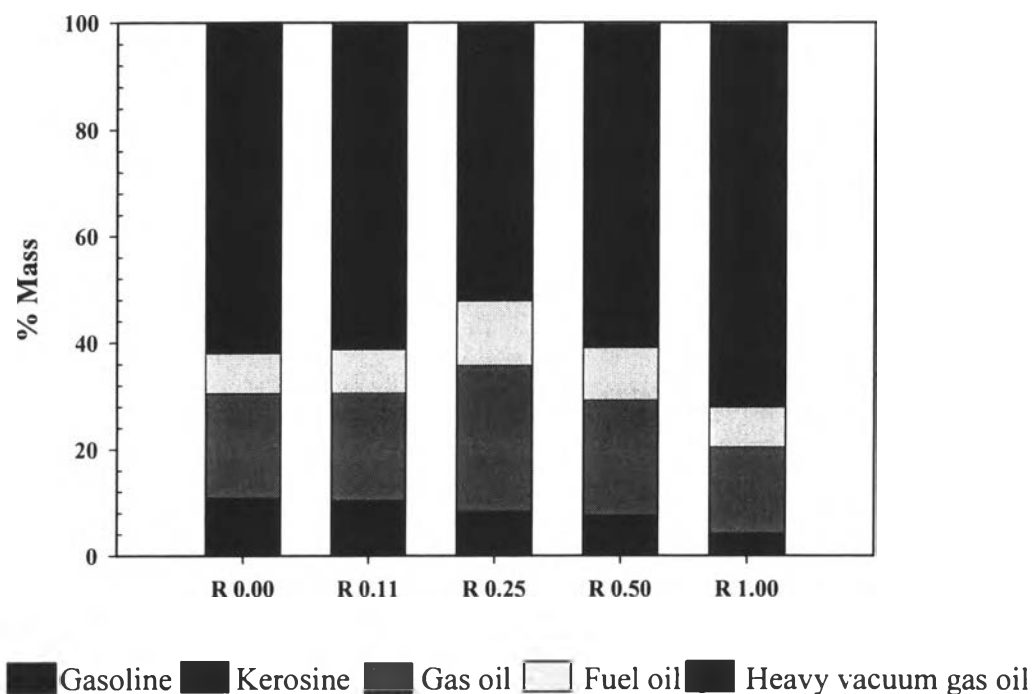


Figure 4.23 Oil fractions from pyrolysis of tire with various catalysts to tire ratios.

4.3.4.5 Carbon content in solid residue

Figure 4.24 illustrates the influence of dissimilar amount of catalyst on pyrolysed solid residues. There are no differences of the whole carbon content obtained at different ratios. The carbon content should be original carbon black earlier added into rubber compound. This observation confirms that tire were completely converted to products with 100% conversion.

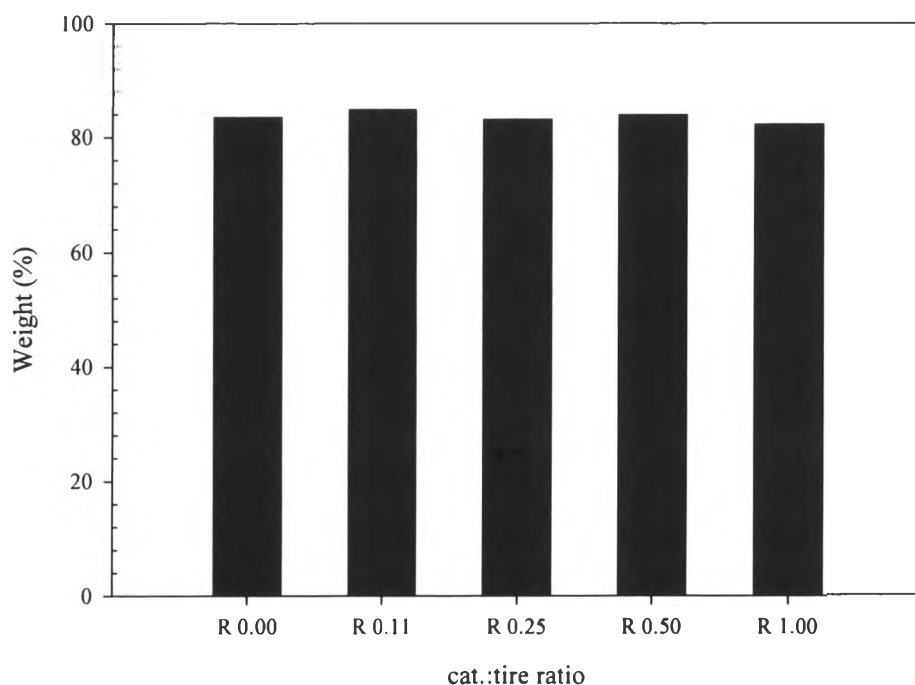


Figure 4.24 Carbon contents in solid residue from tire pyrolysis with various catalysts to tire ratios.

4.3.5 The Purposed Matters of Pyrolysis

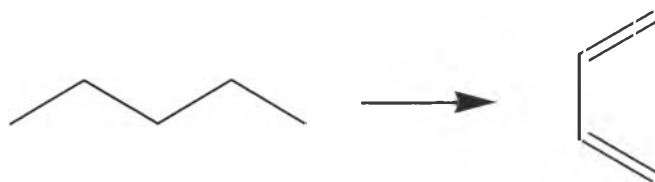
4.3.5.1 *Thermal pyrolysis*

In the thermal cracking, the rubbers used in tire manufacture are characterized by carbon-carbon double bonds, and that thermal decomposition produces highly reactive free radicals, which are often sub-units of the original rubber molecules. One of the “early” products is 1,3-butadiene or isoprene. Isoprene is formed during the thermal decomposition of natural rubber. A portion of the isoprene dimerizes to form limonene (dipentene, C₁₀), a high value chemical used, for example, as an industrial solvent, and an additive to gasoline.

Typical aromatization and condensation reactions may take place to large aromatic molecules and finally to a coke-like material. A general reaction scheme of Diels-Alder reaction mechanism for the aromatization of alkenes compounds to aromatic compounds. Pyrolysis of tires leads to production of ethane, propene, and 1,3-butadiene, which react to form cyclic alkenes. Dehydrogenation of the cyclic alkenes compounds with six carbon atoms occurs to produce single ring

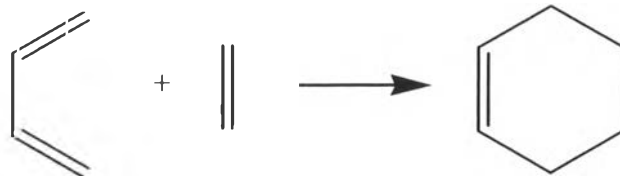
aromatic compounds and as a result, subsequent association reactions leads to the formation of polycyclic aromatic hydrocarbons (PAH) as mentioned by Cunliffe, *et al.*,1998.

i) Dehydrogenation of Alkanes to Alkenes/Dienes



1,3-Butadiene

ii) Cyclisation



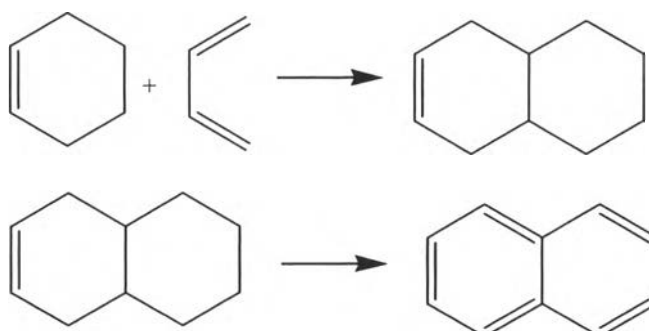
Cyclohexene

iii) Aromatisation



Benzene

iv) Example Formation Route For PAH



Naphthalene

Figure 4.25 Diels-Alder reaction for the formation of polycyclic aromatic hydrocarbons in thermal pyrolysis (Cunliffe, *et al.*,1998).

This postulation can quote to the high production of liquid in tire pyrolysis without catalyst. Including, the quality of liquid oil exhibited wider distribution and shifted to higher carbon number. The impact of added catalyst on product yields was increasing gas yield but reducing liquid yield due to product selectivity. This can be elucidated by the opportunity of catalytic and free radical kinetic. The final product of free radical mechanism is methane which undergoes random cracking and free radical adds rapidly up huge molecules, whereas that of catalytic one is ethane suffering carbenium ions.

4.3.5.2 Catalytic pyrolysis

The classical cracking mechanism involves carbenium ion chain carrier that react with the alkane reactants to abstract hydrides and generate carbenium ions that undergo β -scission. The products include alkanes and alkenes, but not methane, ethane, or H_2 , because protolytic cracking gives alkenes products, which are much stronger bases than alkanes. However, high amount of methane and ethane represent in gas phase for both effect of loaded sulfate and catalyst to tire ratio. The degradation of the tire component is due both to thermal and catalytic cracking in this reaction. The relative importance depends on the sulfate loaded amount and catalyst to tire ratio. The volume percentages of methane and ethane decrease with both amount of loaded sulfate and catalyst increase whereas the effect of loading sulfate represents only methane. The presumed acidic catalytic cracking mechanism with rubber chain is shown as the following.

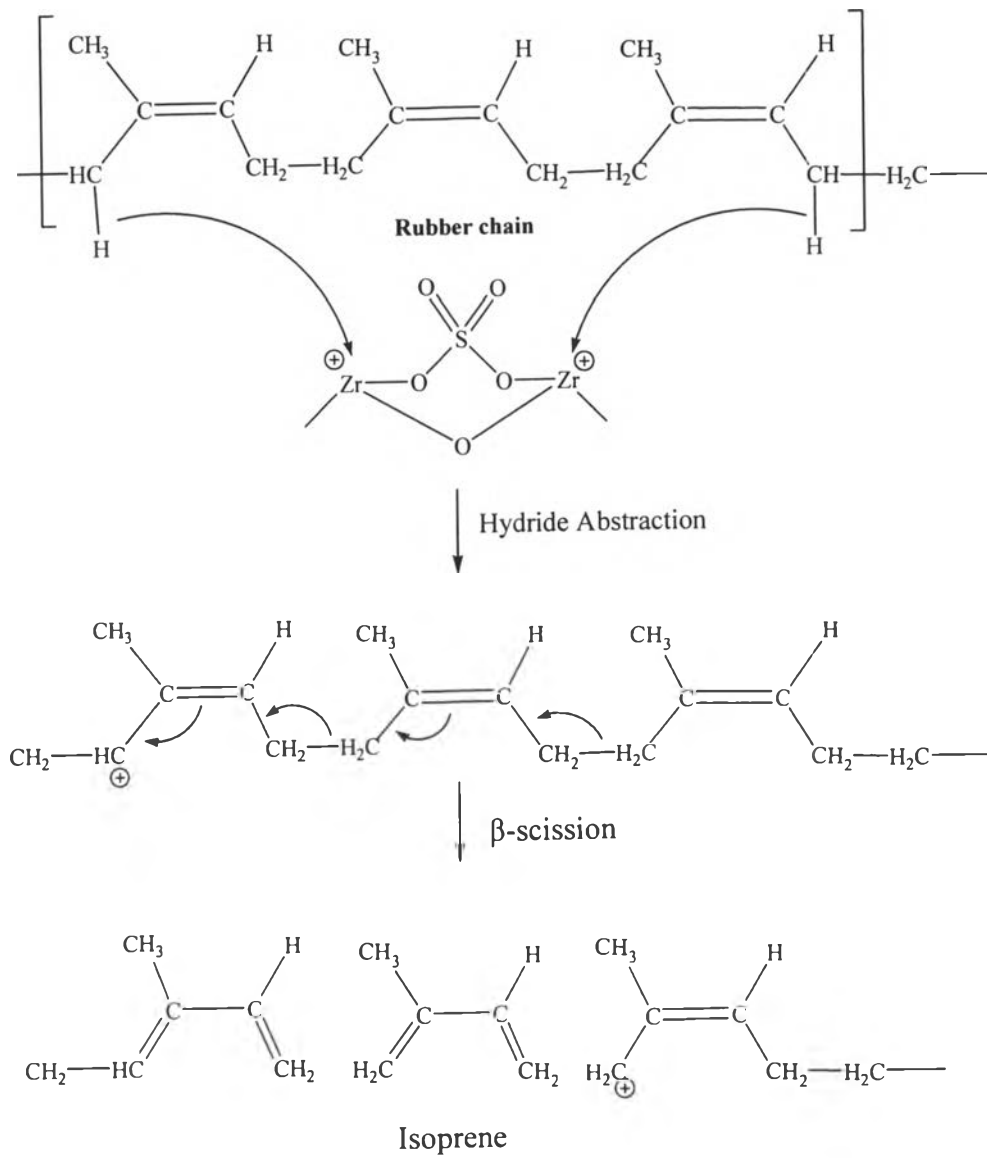


Figure 4.26 Catalytic cracking of rubber chain.

Thermal cracking on monomer may also occur to produce methane and ethane or hydrogen. The mechanism passes through free radical.

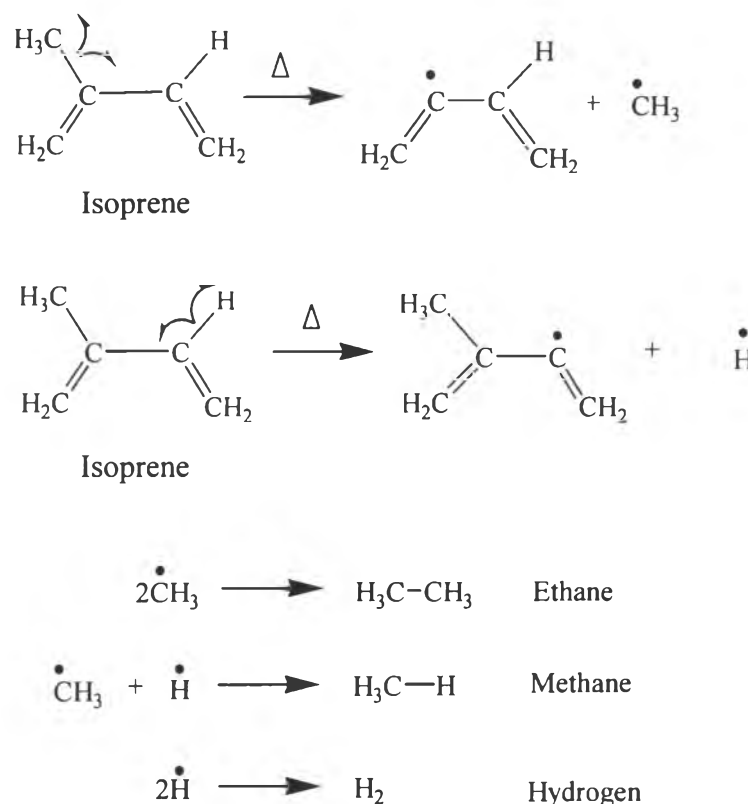
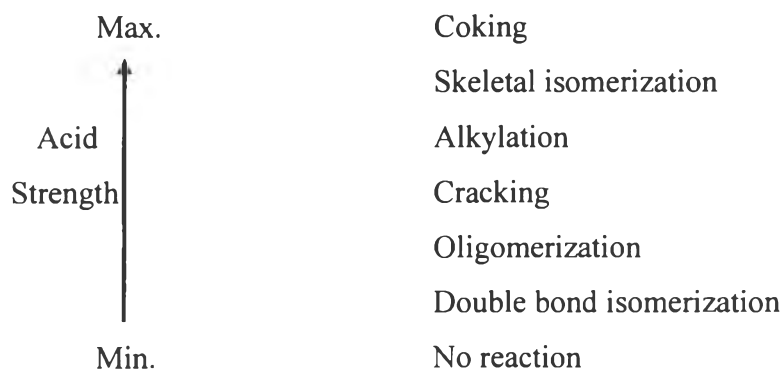


Figure 4.27 Thermal cracking of isoprene.

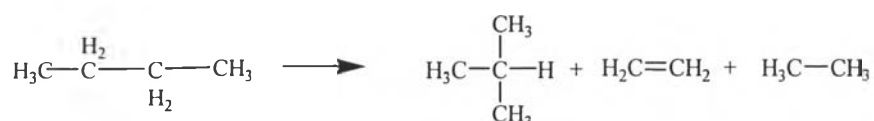
Furthermore, the effect of loaded sulfate and of catalyst to tire ratio can be explained with similar reasons. When the sulfate loaded amount increases, the yield of gas slightly decreased but the liquid yield slightly increased and little fell at 8% sulfate. It seems that various reactions trend to occur. With increasing acid strength or sulfate loaded, higher ability of catalyst produced the smaller carbenium ions. They will further undergo rapidly isomerization to a more stable structure. As followings, each reaction requires different acid strength.



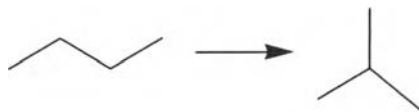
At 8% loaded sulfate, the liquid yield dropped while solid residue increased. This was possibly enhanced by the coking reaction. Furthermore, the quality of oil fraction indicates higher heavy vacuum gas oil due to the products of polymerization and condensation reaction of olefin and by forming polyaromatics.

In the case of catalyst to tire ratio, the quality of liquid was not stable. Initially, it was added at ratio 0.11, double bond isomerization displayed. The acid strength of ratio 0.25 can optimally produce appropriate carbenium ions and their amounts to form a volatility range suitable for producing light hydrocarbons. As a result, it indicates narrow distribution of carbon number range and produces the less heavy fraction. Cracking at this point was dominant reaction. Moreover, when the amount of catalyst was added to ratio of 0.5 and 1.00, carbon number range shifted to wider carbon number distribution and higher vacuum gas oil. They may produce many primary products and undergo secondary reaction in skeletal isomerization and coking, respectively. The consequences are in accord with reducing gas yield and increasing liquid yield at 8% sulfate. Carbenium ions merge into huge molecules. In addition, sulfated zirconia can be used in a variety of synthetically useful reactions. Examples, of the other types of reactions that can be catalysed by sulfated zirconia and can be useful in fine chemical products as follows.

i) Isomerisation and cracking of n-butane



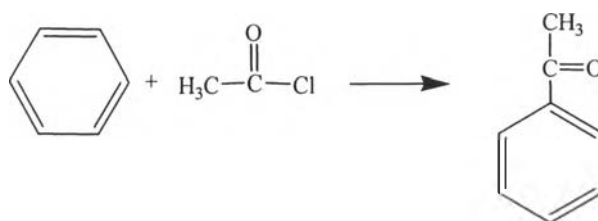
ii) Butane isomerization



iii) Cyclopropane isomerisation



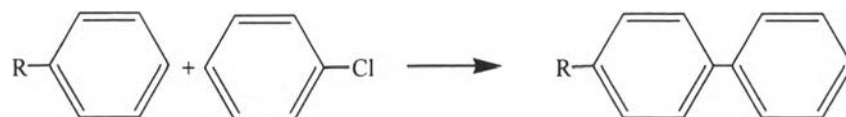
iv) Acetylation of toluene and benzene with acylchloride



v) Esterification of alcohol with acetic acid



vi) Acylation of aromatics by chlorobenzene



vii) Dehydration of alcohols



viii) Methyl isomerisation



Figure 4.28 Reactions catalyzed by sulfated zirconia (MEL CHEMICAL).