



CHAPTER IV

RESULTS AND DISCUSSION

This chapter is divided into two main parts: the effect of film reprocessing on pyrolyzed products and the effect of catalysts on pyrolyzed products. The particular results and discussion are presented in this chapter.

4.1 Effect of Film Reprocessing on Pyrolyzed Products

Polypropylene (PP) films from various number of reprocessing were employed in this part. Mechanical, rheological, and thermal properties of the films were investigated. Then, pyrolyzed product distribution and composition from pyrolysis of films were observed and compared to those from virgin PP pellets.

4.1.1 Mechanical and Rheological Properties of PP Films

4.1.1.1 *Tensile strength*

The investigation of properties of film samples using Instron Universal Testing Machine according to ASTM D638 test procedure is illustrated in Figure 4.1. It was found that there was no significant change in the tensile strength of virgin films upon four times of reprocessing.

4.1.1.2 *Viscosity*

Figure 4.2 shows the viscosity at a shear rate of 10^{-2}sec^{-1} of various numbers of reprocessed PP films. It could be seen that the viscosity tends to increase with increasing in the number of reprocessing. This figure shows an increase by 13% in viscosity of reprocessed films from virgin to the fourth generation. Two significant changes in viscosity occurred between

- (1) Virgin and 1st generation PP films, and
- (2) 3rd and 4th generation PP films.

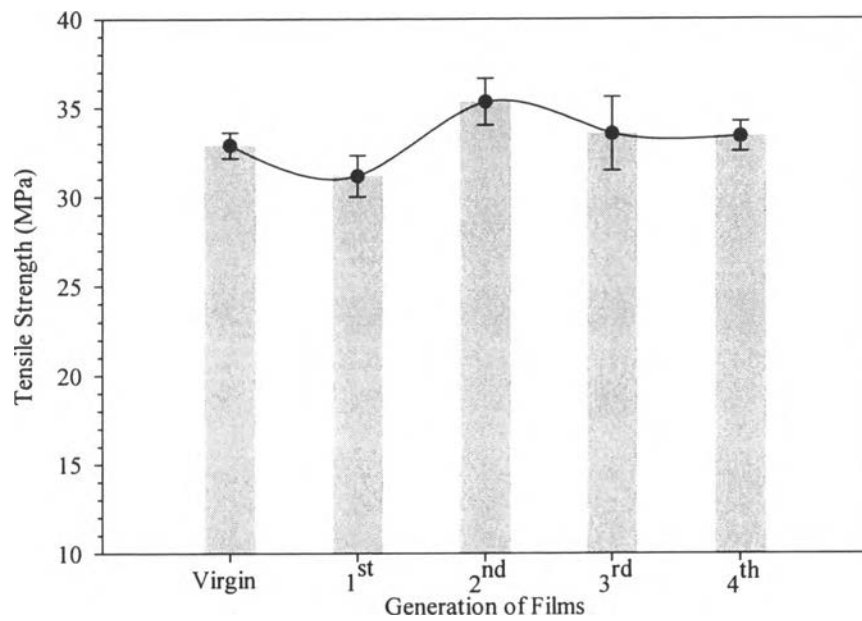


Figure 4.1 Tensile strength of polypropylene (PP) films upon the number of reprocessing.

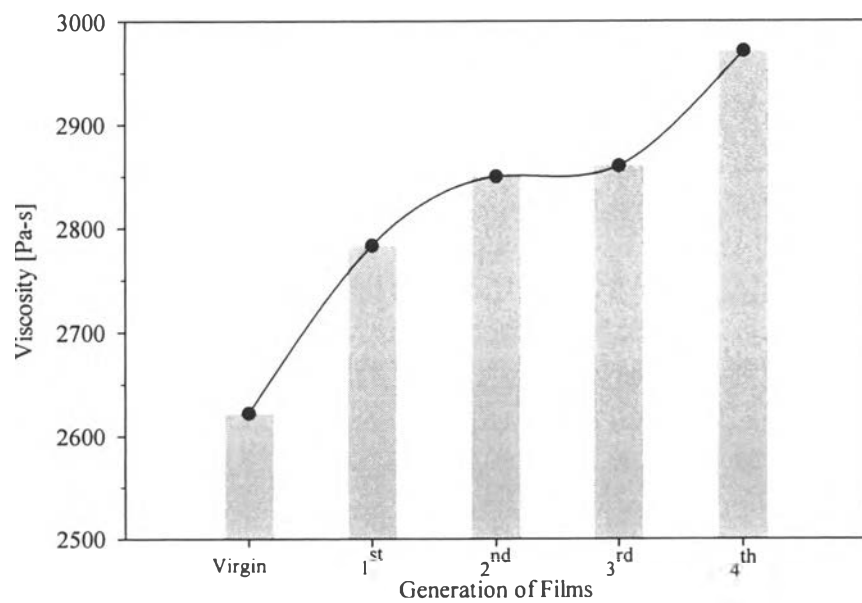


Figure 4.2 Viscosity of PP films as a function of number of reprocessing.

4.1.2 Thermal Properties of PP Films

4.1.2.1 *Melting temperature and percentage of crystallinity*

Figure 4.3 and 4.4 show melting temperature and percentage of crystallinity of original and reprocessed PP films, respectively. It was observed that virgin PP film exhibited some changes in the melting temperature (T_m) and the percentage of crystallinity during reprocessing. Up to three generations, T_m did not change significantly, however, a small decrease was observed on the fourth generation. On the other hand, crystallinity gradually increased upon reprocessing.

4.1.2.2 *Thermal stability*

The thermal stability of virgin and reprocessed films was investigated via TGA technique. Figure 4.5 shows that film samples can be completely decomposed at 500°C. Moreover, there are two regions of degradation. The first region is in the temperature range of 300-400°C. The second region falls in the temperature range of 400-500°C. The degradation temperature tends to increase with the increasing of number of reprocessing.

In conclusion, it was found that no significant change was observed in tensile strength and melting temperature during reprocessing of PP film. The most significant change was the increase in the viscosity along with the increase in the number of reprocessing, corresponding to the thermal stability of the films.

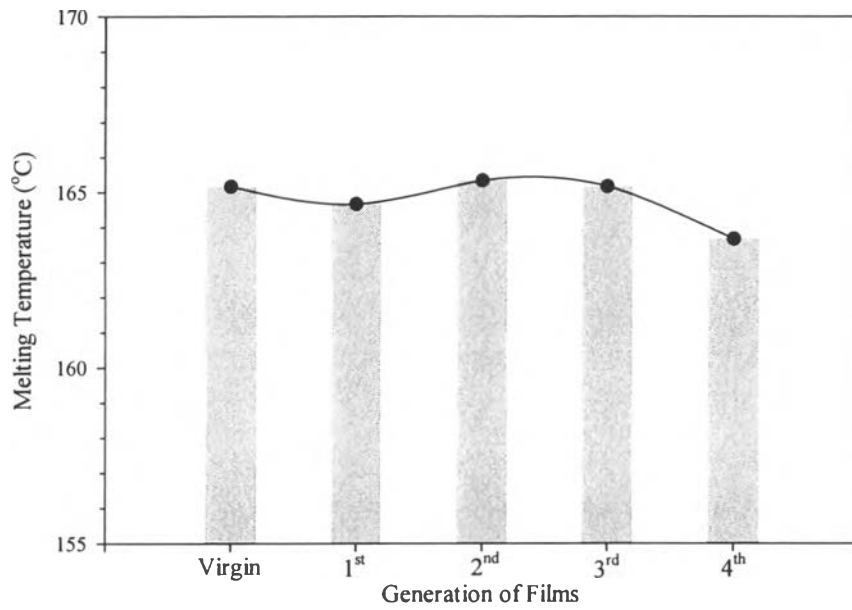


Figure 4.3 Melting temperatures of virgin and reprocessed PP films.

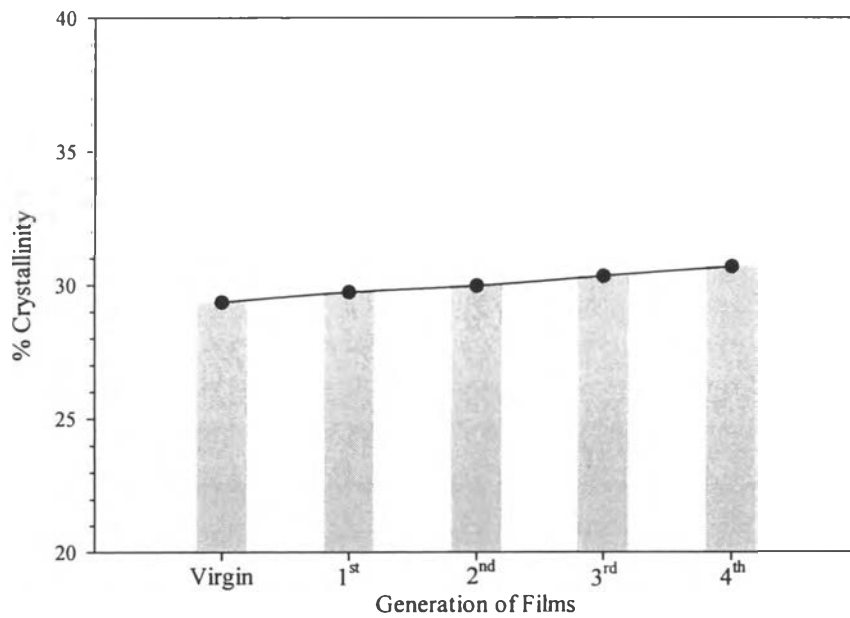


Figure 4.4 The degree of crystallinity of virgin and reprocessed PP films.

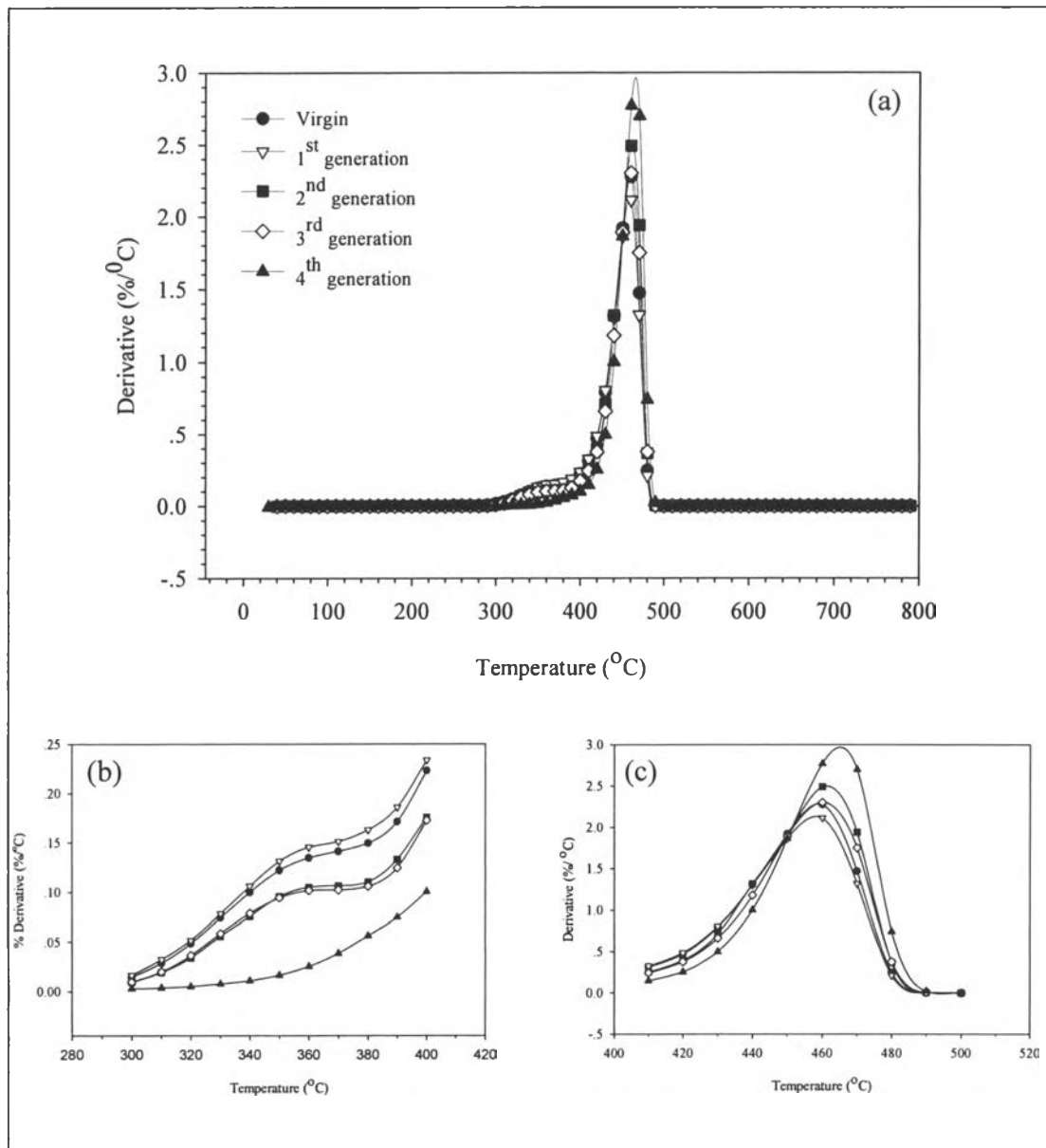


Figure 4.5 DTG curves of virgin and reprocessed PP films in the ranges of (a) 25-800°C, (b) 300-400°C, and (c) 400-500°C.

4.1.3 Pyrolyzed Products of PP Films

Pyrolysis of virgin and reprocessed films was performed to investigate the influence of number of reprocessing on pyrolyzed products. Pyrolysis of Virgin pellets was also conducted for comparison.

4.1.3.1 *Product yield*

Figure 4.6 shows product yield of virgin and reprocessed films as compared to that of virgin pellets. It can be clearly seen that for all samples liquid was highly produced as compared to gas and residue.

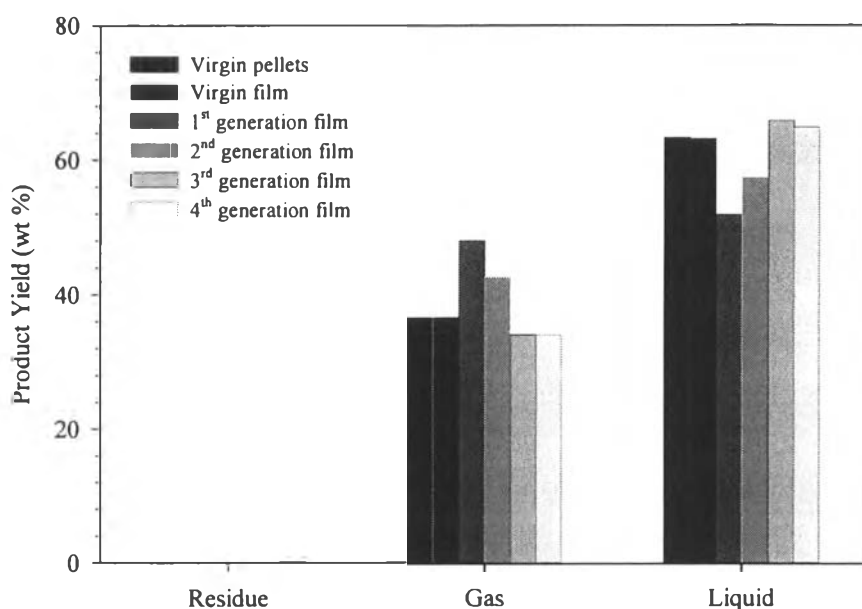


Figure 4.6 Product yield from pyrolysis of virgin PP pellets, virgin and reprocessed PP films.

Gas and liquid yields from virgin pellet and film were almost the same. After one time of reprocessing, gas yield was increased with the consequent decrease in liquid yield. This change might be the result of the jump of viscosity due to the polymer chain entanglement. But when increasing more times of reprocessing up to three times the gas yield tends to decrease and consequently liquid yield increases. At this point the viscosity, melting temperature, and crystallinity did not change so much, whereas, degradation temperature increased and might cause the increase in liquid product.

At the 4th generation of film the viscosity was very high and can not be further reprocessed. Hence, the pyrolyzed liquid product of the 4th generation was decreased with an increase in residue. It can be postulated that crosslinking or branching occurred.

4.1.3.2 Gas product composition

Gas product composition of PP samples is shown in Figure 4.7. It was observed that the highest amount of pyrolyzed gas was propylene, C₅ and C₆ hydrocarbons for all samples. Only a small amount of ethylene was produced. There were no significant changes in compositions of methane, ethylene, propane, and C₄ hydrocarbons upon four times of reprocessing. However, the compositions of the highest amount components varied in the similar way as appeared in Figure 4.6. Nevertheless, pyrolysis of virgin pellets gave significant change in gas composition, especially in C₆ components, as compared to that of virgin and reprocessed films. Consequently, pyrolysis of PP in form of films differs from that in the pellet form. Hence, forms of the PP-based materials must be considered in pyrolysis because they had an effect on pyrolyzed product distribution and composition.

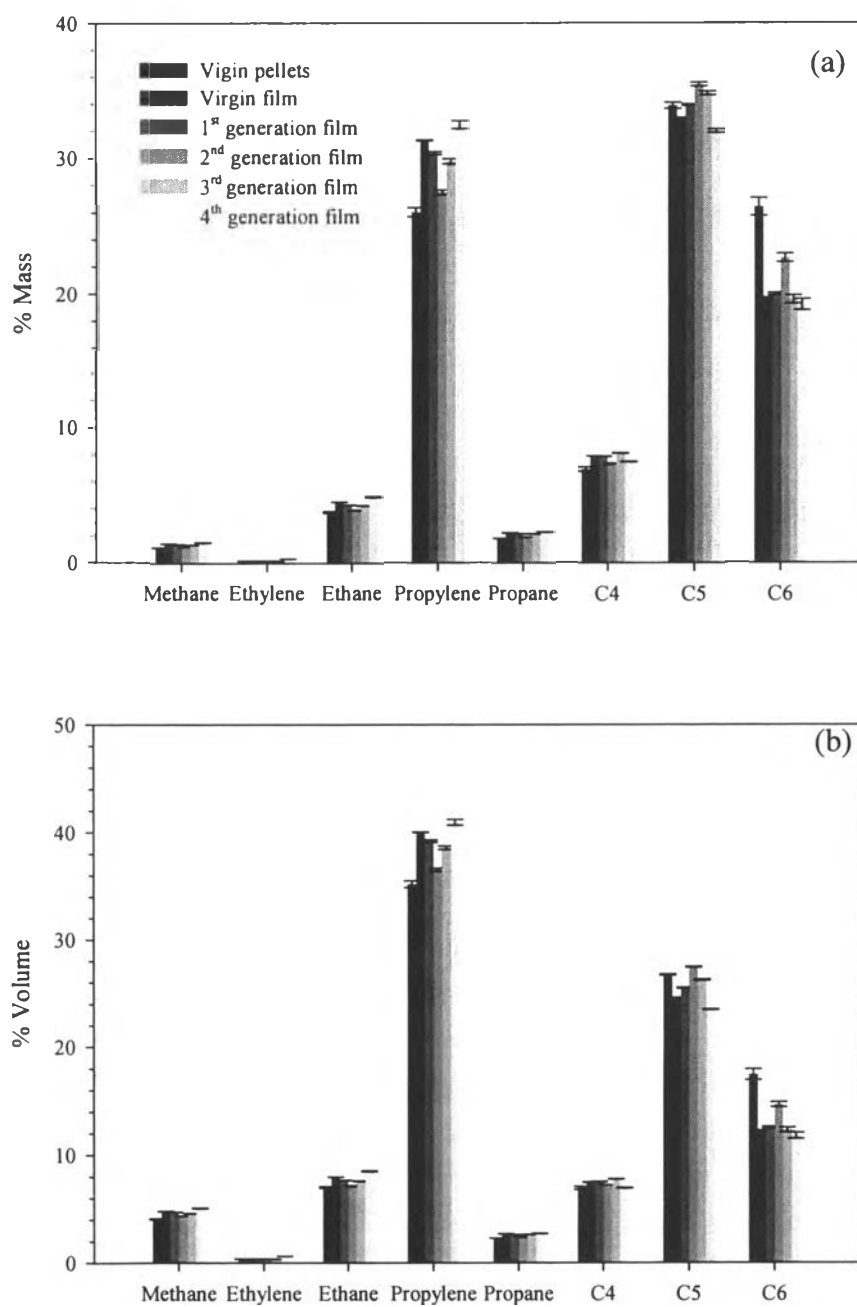


Figure 4.7 Gas composition from pyrolysis of virgin PP pellets, virgin and reprocessed PP films based on: (a) mass and (b) volume.

4.1.3.3 Liquid product composition

Figure 4.8 shows thermal degradation liquid components distributed in a wide range of number of carbon atoms. From Figures 4.6 and 4.8, the weight percent at C_{20}^- varies in the similar trend as appeared in gas yield, whereas, $C_{20} - C_{49}$ varies in the similar trend as appeared in liquid yield. (The weight percent at C_{20}^- means the sum of weight percentage for all the liquid products which have carbon numbers of below C_{20} .)

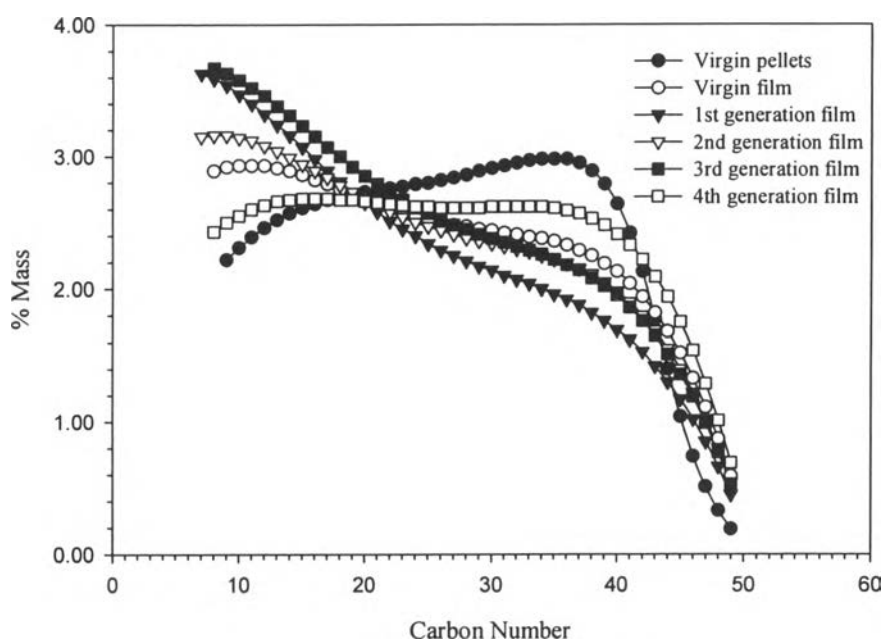


Figure 4.8 Carbon number distribution of liquid products from thermal degradation of virgin PP pellets, reprocessed and virgin PP films.

Furthermore, there was a clear difference between the products from pyrolysis of virgin pellets and reprocessed films. The distribution of liquid product shifted to lower number of carbon atoms as compared to that from virgin pellets.

4.1.3.4 Oil fractions of liquid product

The liquid product derived from a thermal degradation of PP film sample was classified into five fractions according to its boiling range (Speight, 2002). There were gasoline (boiling range: 15.5-149°C), kerosene (149-232°C), gas oil (232-343°C), fuel oil (343-371°C), and heavy vacuum gas oil (371-566°C). In Figure 4.9, gasoline or petrol, used as fuel for internal combustion engines, can be highly produced at the first generation of film. The maximum amount of kerosene, gas oil, and fuel oil represents in the third generation. Virgin pellets produced the highest amount of heavy fractions as compared to the films. The minimum amount of heavy vacuum gas oil was generated from the first generation since it was converted into lighter fractions. Moreover, no significant change in fuel oil fraction of all samples.

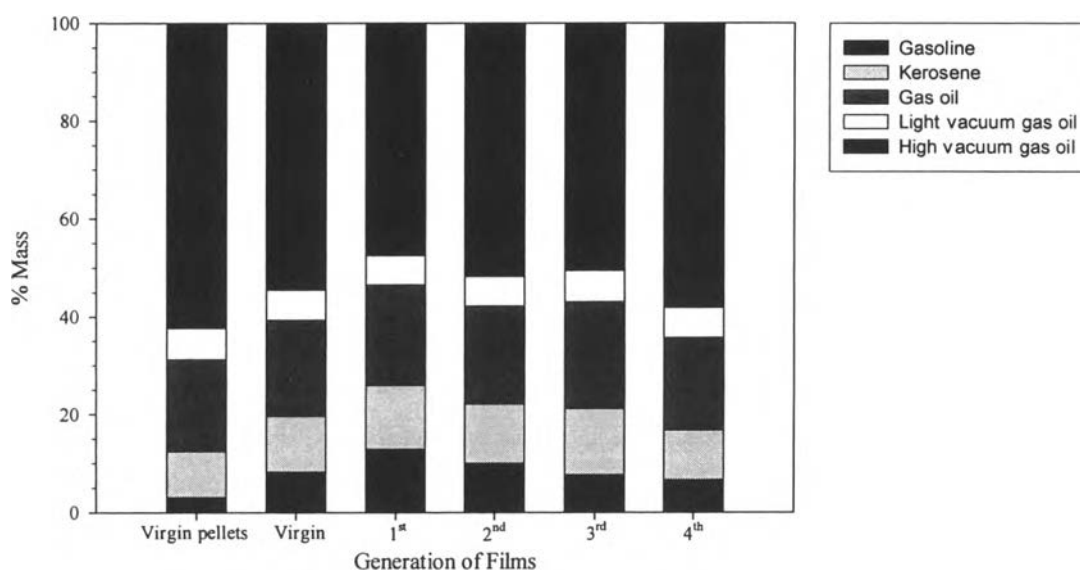


Figure 4.9 Liquid fractions from pyrolysis of virgin PP pellets, virgin and reprocessed PP films.

Conclusively, the number of reprocessing of PP film is a very important parameter controlling physical properties of the film and pyrolyzed products. It was found that the weight percent of propylene and C_{20} hydrocarbons were changed in the same trend as the gas yield, and the weight percent of $C_{20} - C_{49}$ was varied in the same trend as liquid yield.

4.2 Effect of Catalysts on Pyrolyzed Products

Sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) was employed as a catalyst in this study. Physico-chemical properties such as catalyst crystal structure, surface area, and pore size distribution, as well as thermal stability of the catalyst at various amounts of sulfate loaded on zirconia were characterized. After that pyrolyzed product distribution and composition were investigated with an increase of catalyst to polymer ratio and amount of sulfate loading, consecutively.

4.2.1 Physico-Chemical Properties of Catalysts

4.2.1.1 *Crystal structure of catalysts*

XRD patterns of the $\text{SO}_4^{2-}/\text{ZrO}_2$ at various amounts of sulfate loaded on zirconia were recorded and are shown in Figures 4.10 after calcination at the same condition. The addition of sulfate did not affect the crystal structure of catalysts which was identified as a monoclinic structure.

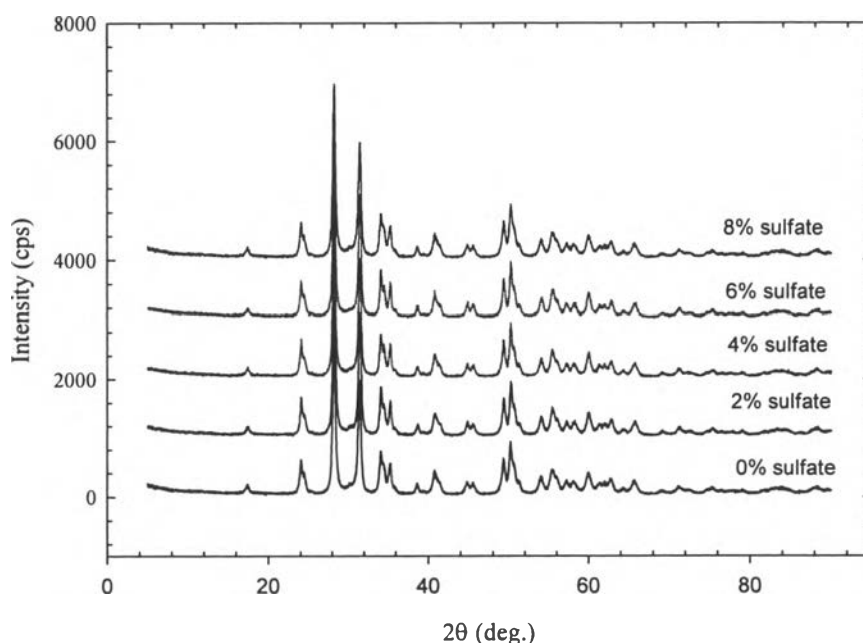


Figure 4.10 XRD patterns of sulfated zirconia at different percentages of sulfate loading.

4.2.1.2 Surface area, average pore volume and pore size of catalysts

The BET surface area, average pore size and crystal structure of catalysts calcined at 550°C for 2 hours were determined and are listed in Table 4.1. It was found that surface area of the catalysts was about the same, however, a slightly decrease was observed as the amount of sulfate loaded on zirconia increased.

Table 4.1 Physico-chemical properties of catalysts

Sample	% SO ₄ ²⁻	Colour	S _{BET} (m ² /g)	Pore volume (cc/g)	Pore size (nm)	Crystal Structure
ZrO ₂	0	White	6.680	1.182×10 ⁻²	7.077	Monoclinic
SO ₄ ²⁻ /ZrO ₂	2	White	3.588	4.196×10 ⁻³	4.678	Monoclinic
SO ₄ ²⁻ /ZrO ₂	4	White	3.784	2.880×10 ⁻³	3.054	Monoclinic
SO ₄ ²⁻ /ZrO ₂	6	White	1.028	1.480×10 ⁻³	5.762	Monoclinic
SO ₄ ²⁻ /ZrO ₂	8	White	1.963	3.178×10 ⁻³	6.476	Monoclinic

4.2.2 Thermal Stability of Catalysts

Figures 4.11 shows the weight loss of sulfated zirconia containing various percentages of sulfate loading (up to 8 wt.% sulfate). There are two regions of weight loss; the first is in the temperature region of 30 to about 500°C and the second is in the temperature region of 550 to 800°C. In the first region the weight loss is similar for all samples, except 6% and 8% loading. The small derivative peaks from 6% and 8% loading are believed to be excess water on the catalyst surface due to high amount of sulfate loading. In the second region, the weight loss increases linearly with increasing initial sulfate concentration. These results agree with previous work (Davis et al., 1994). The second region occurred from the desorptions of sulfate ions. Area under the curves in this region relates to the concentration of sulfate ion previously impregnated on the surface of ZrO₂.

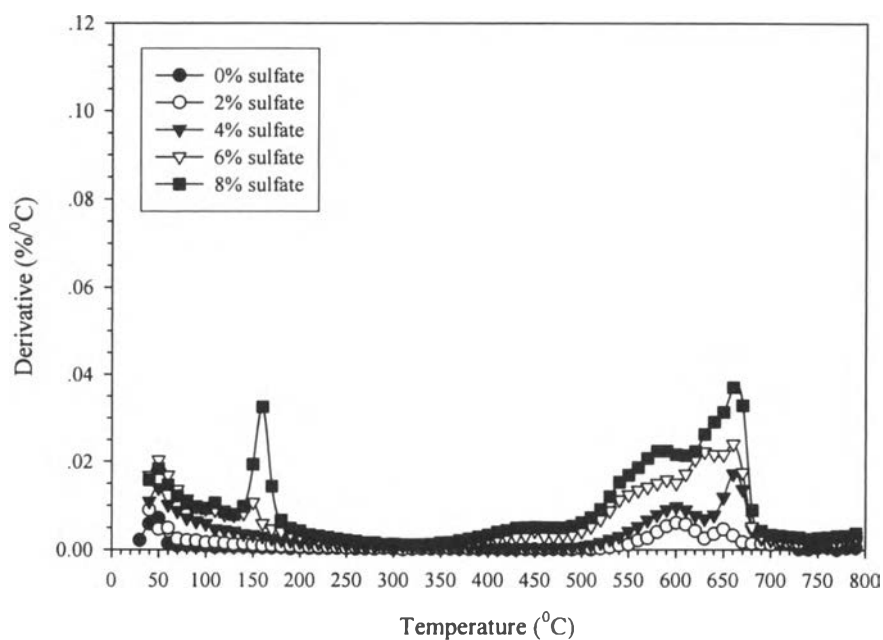


Figure 4.11 DTG curves of $\text{SO}_4^{2-}/\text{ZrO}_2$.

4.2.3 Preliminary Test for Dependence of Catalysts on Pyrolysis

Virgin PP film was selected for this test. Sulfated zirconia was mixed with the film and introduced to characterize via TGA to investigate the influence of the catalyst to the sample.

Figure 4.12 shows ability of catalysts to reduce pyrolysis temperature as compared to the case when no catalyst was added. As shown in the figure, the peaks of adding sulfated zirconia shift to lower decomposition temperature, indicating that catalyst acidity might help pyrolyzing the plastic.

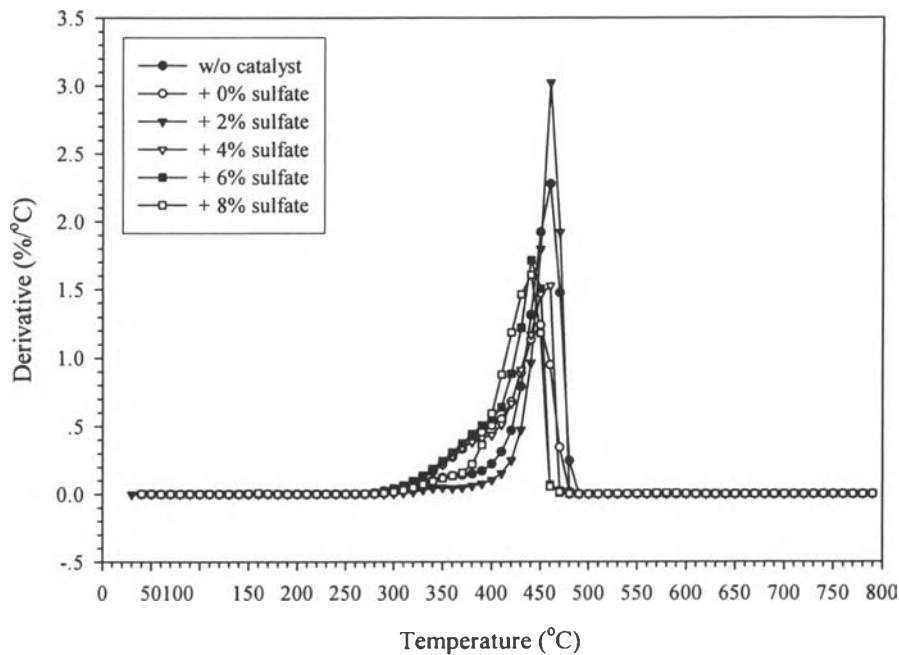


Figure 4.12 DTG curves from pyrolysis of virgin PP film using $\text{SO}_4^{2-}/\text{ZrO}_2$ at various amounts of sulfate loading.

4.2.4 Effect of Catalyst to Polymer Ratio on Pyrolyzed Products

The catalyst employed in this section was 4% $\text{SO}_4^{2-}/\text{ZrO}_2$. A total of 0.5 gram of polypropylene (PP) film sample and catalyst were mixed together and loaded at the bottom of the reactor. The ratio of catalyst to polymer (C/P) was varied from 0.0-1.0.

4.2.4.1 Product yield

Product yield from pyrolysis of commercial PP film with 4% $\text{SO}_4^{2-}/\text{ZrO}_2$ at various catalyst to polymer (C/P) ratios are shown in Figure 4.13. No residue production was observed. The liquid fraction was the most dominant degradation products. Moreover, it was found that the gas yield decreased and the liquid yield increased as the C/P ratio increased from approximately 50 wt.% (C/P = 0.0) to 71 wt.% (C/P = 1.0).

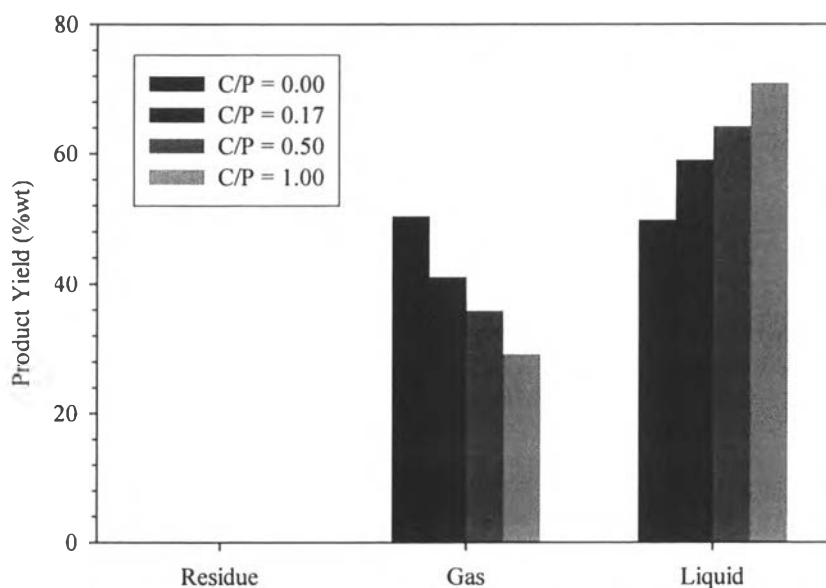


Figure 4.13 Product yield from catalytic pyrolysis of commercial PP film with 4% $\text{SO}_4^{2-}/\text{ZrO}_2$ at various catalyst to polymer ratios.

4.2.4.2 Gas product composition

Gaseous products were identified as methane, ethylene, ethane, propylene, propane, C_4 , C_5 and C_6 hydrocarbons as shown in Figure 4.14. Propylene, C_4 , C_5 and C_6 hydrocarbons were mainly produced from pyrolysis of commercial PP film at various catalyst to polymer (C/P) ratios. As the C/P ratio increased, propylene decreased from 23 wt.% to 11 wt.%, C_4 hydrocarbons increased from 7 wt.% to 24 wt.%, whereas, other gas components remained fairly constant.

In 1999, from using silica-alumina and zeolite ZSM-5 Sakata *et al.* reported that the decrease of C_3 components with the consequent increase of C_4 components in the gaseous products was a special feature of the solid acid catalyst on degradation of polypropylene.

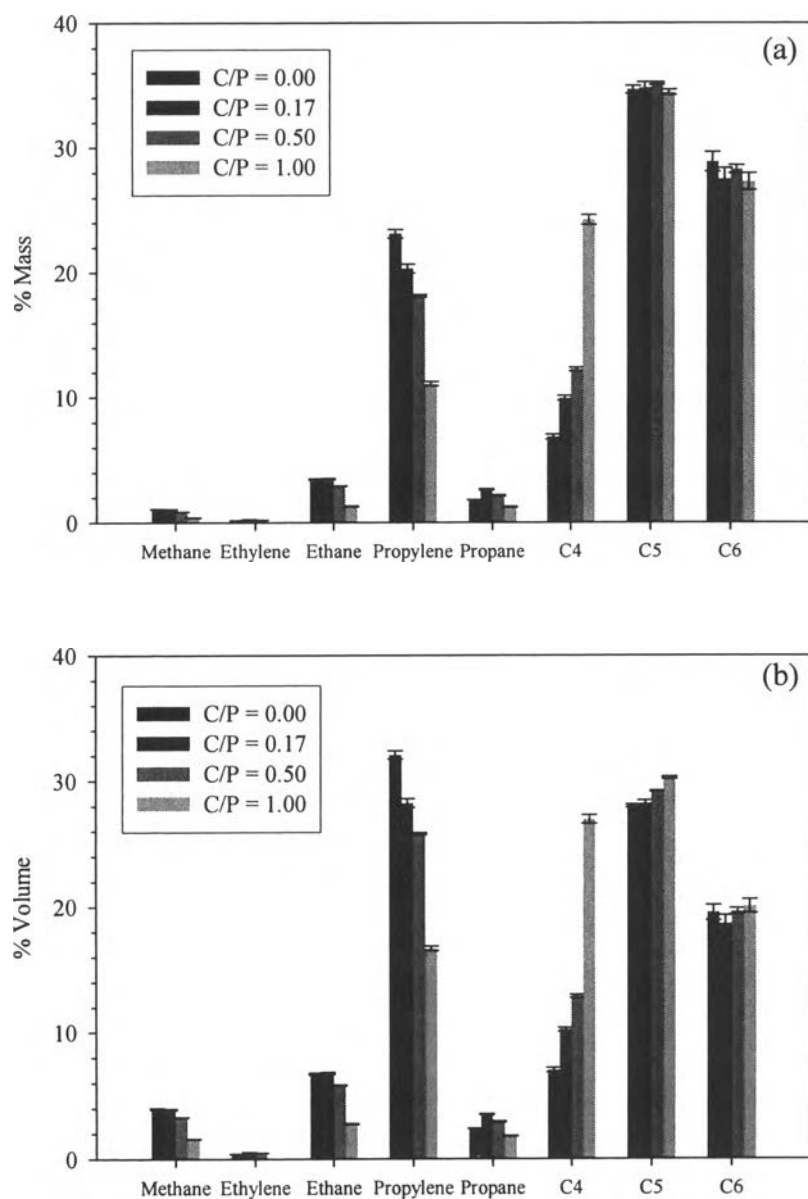


Figure 4.14 Gas composition from catalytic pyrolysis of commercial PP film with 4% sulfated zirconia at various catalyst to polymer ratios on the basis of (a) mass and (b) volume.

Ishihara *et al.*, (1993) have been proposed the mechanism of gas formation in catalytic decomposition of polypropylene in the presence of silica-alumina catalyst with 13% alumina content. They suggested that gases were produced from the chain-ends of the liquid fraction as shown in Figure 4.15.

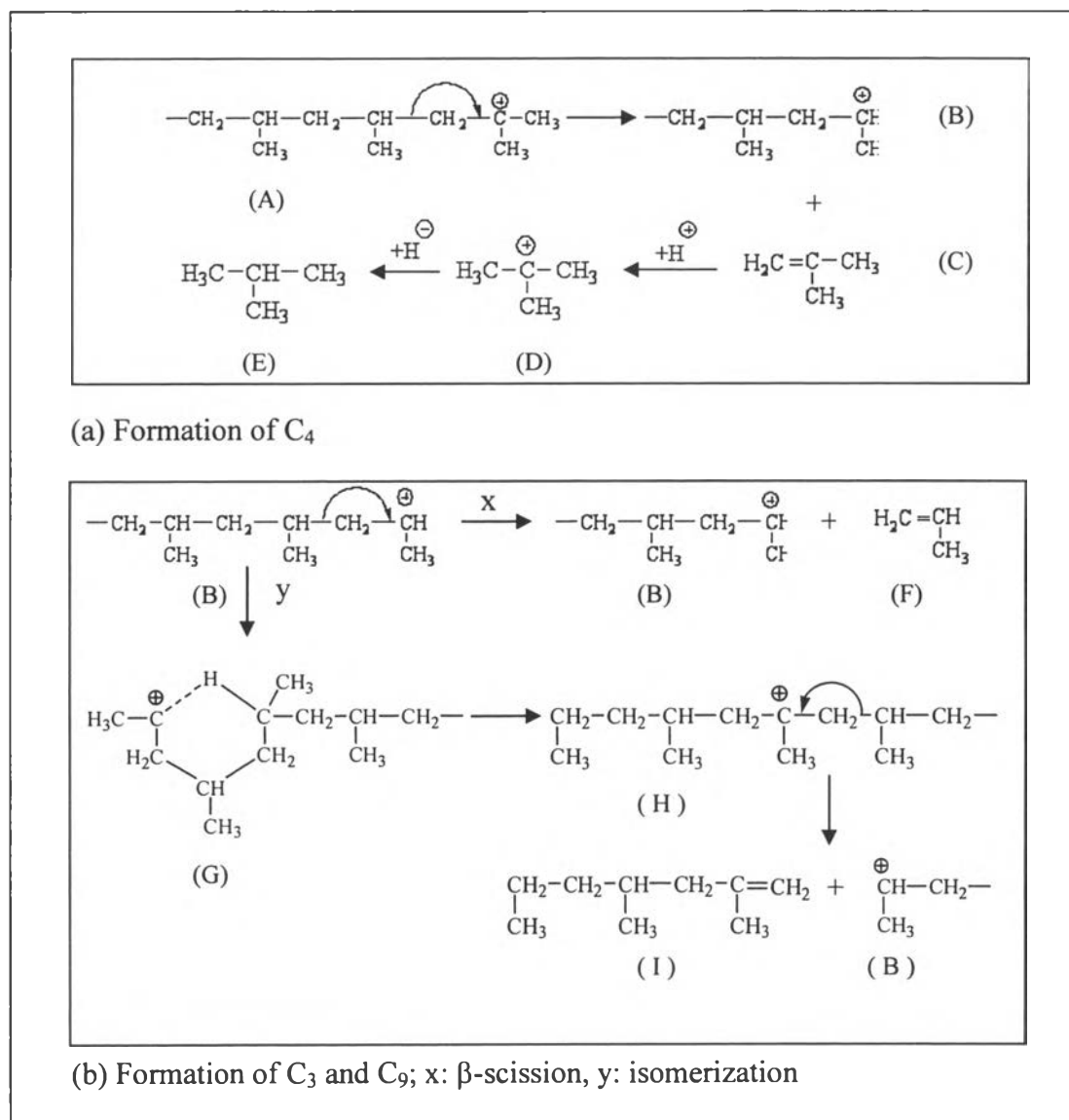


Figure 4.15 Gas formation mechanisms in catalytic pyrolysis of polypropylene (Ishihara, Y. *et al.*, 1993).

They indicated the components of liquid fraction by using FID-MS and ¹³C NMR technique. Carbenium ions (A) and (B) were the main components. Gases may be produced by decomposition of ions (A) and (B).

Chain-ends (B) and isobutene (C) were produced via β -scission of ion (A). Then, isobutene (C) produced isobutane (E) by hydrogenation according to Equation (a). Carbenium ions (D) also attacked the on-chain tertiary hydrogen atoms of the oligomer and liquid fractions, leading again to the production of on-chain tertiary carbenium ions.

According to Equation (B), C_3 fraction (F) may be produced via β -scission of ion (B). Nevertheless, β -scission of ion (B) requires a higher activation energy (190 kJ/mol) than isomerization (63 kJ/mol) and thus isomerization of ion (B) is more easily stabilized by isomerization, and small amount of propylene can be produced. The isomerization proceeded by intramolecular rearrangement via six-membered transition state to inner tertiary carbon atoms (back-biting reaction). C_9 components were produced as the main product in liquid fraction via β -scission of ion (H).

The influence of catalyst to polymer ratio on pyrolyzed products was considered compared to the previous work (Ishihara, Y. *et al.*, 1993). The selectivity ratio in gas formation of C_3/C_4 is shown in Figure 4.16.

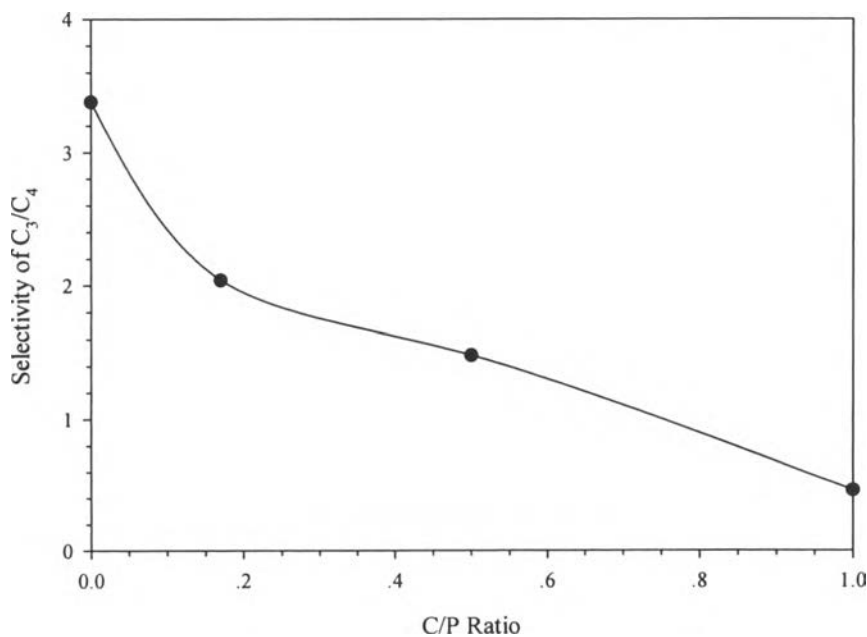


Figure 4.16 Selectivity ratio of C_3/C_4 from catalytic pyrolysis of commercial PP film with 4% sulfated zirconia at various catalyst to polymer ratios.

As shown in the figure, the selectivity of C₃ (propylene) over C₄ components decreased with increasing C/P ratio.

Ishihara, Y. *et al.* studied the effect of catalyst to polymer ratio on gas composition. Reaction was carried out at 220°C. Nitrogen was passed through the reactor at 120 ml/min for 1 hour. The polymer and catalyst were mixed together at different C/P ratios of 0.5-6.0 before introduced into the reactor. They found that the main component was isobutane (C₄), and the yields of all components were essentially the same at all C/P ratios.

Compared to this work, reaction was carried out at 500°C for 1 hour with nitrogen gas flow rate of 30 ml/min. using solid superacid catalyst, SO₄²⁻/ZrO₂, in the catalytic degradation. C₄ hydrocarbons were the most dominant product in the case of C/P of 1.00. In addition, the yield of C₃ reduced with a consequent increase in C₄ components as the C/P ratio increased.

It is known that thermal degradation occurs by radical mechanism. However, catalytic degradation of PP is known to proceed by carbenium ion mechanism (Audisio, *et al.*, 1984). At C/P ratio of 0.0, propylene can be highly produced as compared to other ratios through radical mechanism since no catalyst was used. But when increase the amount of catalyst propylene tends to decrease with a consequent increase in C₄ components due to more catalytic degradation of polymer in the presence of a catalyst according to the gas formation mechanism proposed by Ishihara, Y. *et al.* Therefore, it may be concluded that the presence of SO₄²⁻/ZrO₂ exhibited the catalytic degradation in the pyrolysis of polypropylene with a maximum amount of the degradation at C/P of 1.0.

4.2.4.3 Liquid product composition

Composition of the liquid products from pyrolysis of commercial PP film with 4% sulfated zirconia at various catalyst to polymer (C/P) ratios as compared to thermal degradation is shown in Figure 4.17. For thermal degradation, the liquid products were distributed over a wide range of carbon numbers (C_9 to C_{49}) equivalent to boiling point ranges of 170 to 600°C. In the case of using sulfated zirconia at the catalyst to polymer ratio of 0.17, the distribution of carbon number shifted to heavier hydrocarbons. The increase of catalyst to polymer ratio from 0.17 to 0.50 and 1.00 resulted in an increase of lighter hydrocarbons.

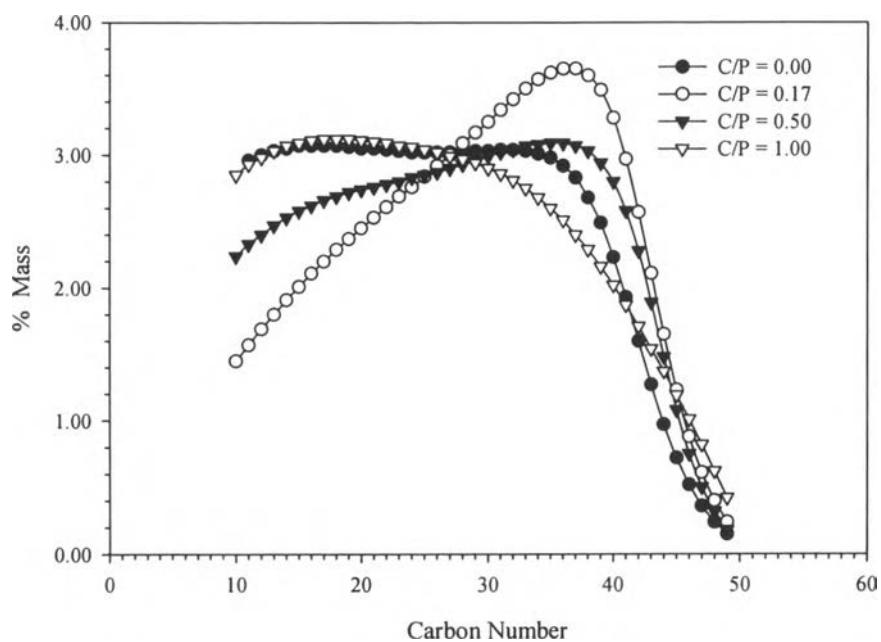


Figure 4.17 Carbon number distribution of liquid products from thermal and catalytic degradation of commercial PP film with 4% sulfated zirconia at various catalyst to polymer ratios.

4.2.4.4 Oil fractions of liquid product

Figure 4.18 shows the distribution of liquid product at various C/P ratios. Many petrochemical products can be produced from the pyrolysis of polypropylene film. In the thermal degradation ($C/P = 0.00$), there was no gasoline production. On the other hand, gasoline can be produced when the catalyst was introduced. It indicates that using catalyst has a positive effect on gasoline production. At C/P ratio of 0.50, it gave the maximum amount of gasoline as compare to other ratios. As the ratios increased, from 0.17 to 1.00, kerosene, gas oil, and fuel oil were dramatically increased with a consequent decrease in heavy vacuum gas oil.

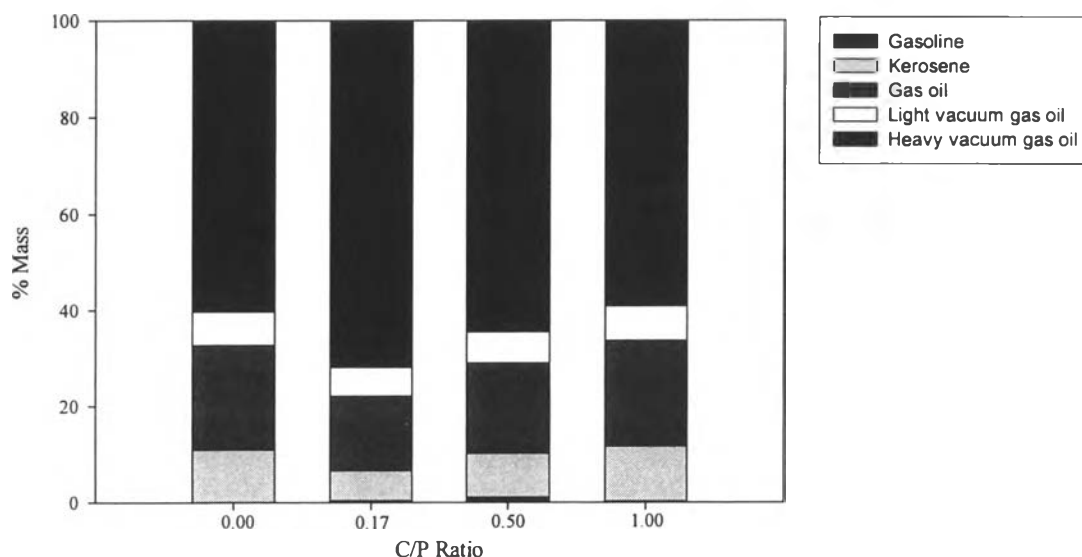


Figure 4.18 Liquid fractions from catalytic pyrolysis of commercial PP film with 4% sulfated zirconia at various catalyst to polymer ratios.

4.2.5 Effect of Amount of Sulfate Loaded on Zirconia on Pyrolyzed Products

Catalyst to polymer ratio at 0.17 was selected to study the effect of amount of sulfate loaded on zirconia on the catalytic pyrolysis of commercial PP film. The amount of sulfate was varied from 0-8 %.

4.2.5.1 *Product yield*

Figure 4.19 shows the product yield obtained from the catalytic pyrolysis of commercial PP film using various amounts of sulfate loaded on zirconia. Pyrolysis in the absence of catalyst produced negligible residue, a yield of 50.3 wt. % gas and 49.7 wt. % liquid. As the amount of sulfate loaded on zirconia increased, the liquid yield increased with a consequent decrease in gas yield.

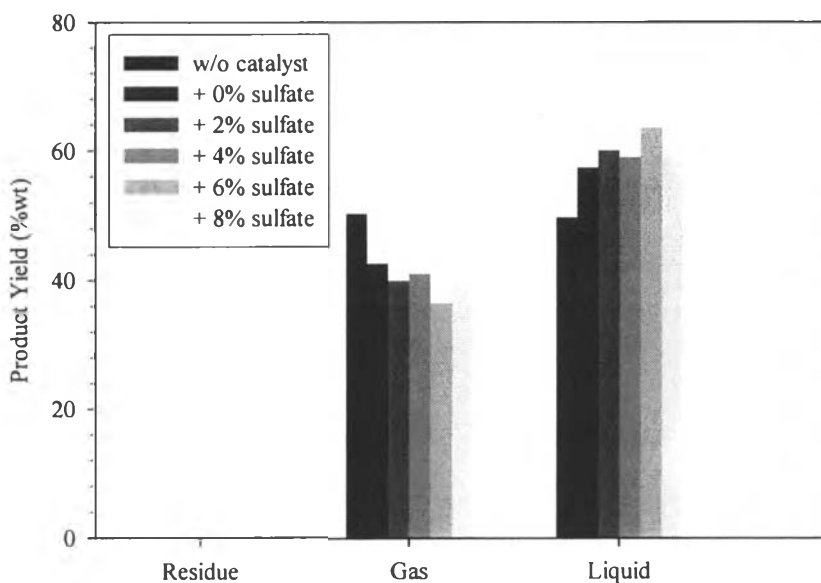


Figure 4.19 Product yield from catalytic pyrolysis of commercial PP film using sulfated zirconia at various amounts of sulfate loading.

4.2.5.2 Gas product composition

Figure 4.20 shows the gas composition obtained from the catalytic pyrolysis of commercial PP film using various amounts of sulfate loaded on zirconia. On the basis of volume, it was found that propylene and C₅ hydrocarbons were dominating gases. Moreover, it was evidenced that propylene yield obtained from thermal degradation was higher than catalytic degradation, whereas C₄ components were lower, and other gas components remained fairly constant. Ethylene was in low concentration. Furthermore, propylene decreased with increasing amount of sulfate loaded on catalyst while C₄ hydrocarbons increased. This trend was consistent with that of gas composition when increasing catalyst to polymer ratio.

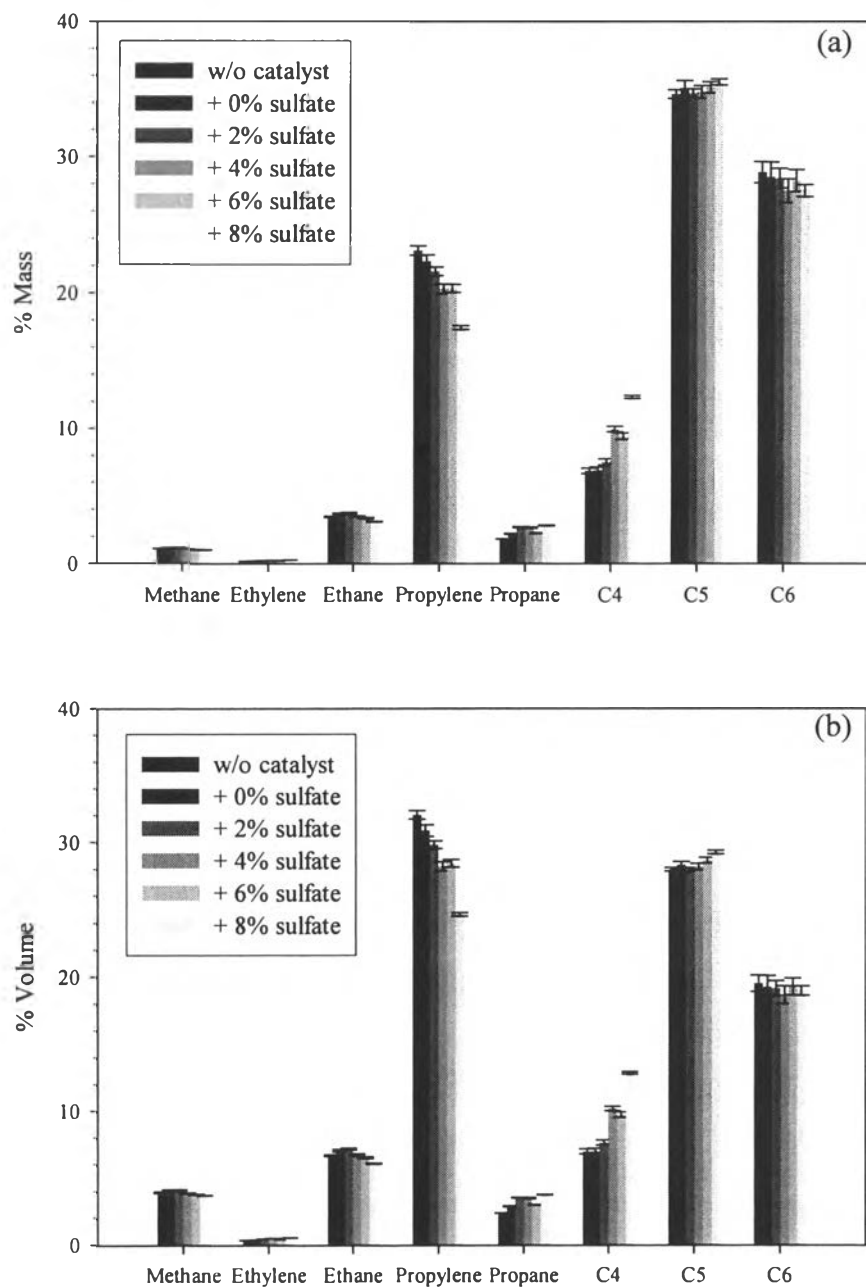


Figure 4.20 Gas composition from catalytic pyrolysis of commercial PP film using sulfated zirconia at various amounts of sulfate loading on the basis of (a) mass and (b) volume.

4.2.5.3 Liquid product composition

In order to study the effect of amount of sulfate loaded on zirconia on pyrolyzed liquid product, the distribution of liquid components from loading with different amounts of sulfate are compared in Figure 4.21. The distribution of liquid products shifted to lower number of carbon atoms when higher amount of sulfate was loaded. This result implied that sulfate loading enhanced the degradation of heavier liquid hydrocarbons into lighter liquid hydrocarbons.

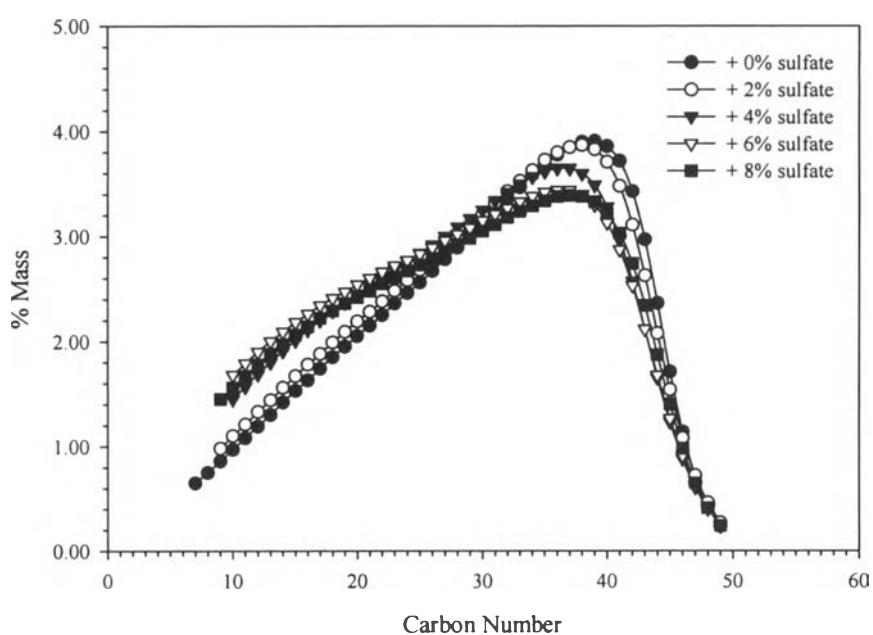


Figure 4.21 Carbon number distribution of liquid products from catalytic pyrolysis of commercial PP film using sulfated zirconia at various amounts of sulfate loading.

4.2.5.4 Oil fractions of liquid product

The fractions of oils yielded from samples at various amount of sulfate loaded on zirconia are shown in Figure 4.22. Heavy vacuum gas oil was the most dominant degradation product. Gasoline was observed for all samples, especially at 0% and 8% sulfate. However, the highest amount of heavy vacuum gas oil was generated at 0% sulfate. The increase in the amount of sulfate loading showed a higher amount of kerosene and caused a decrease in heavy fractions. Kerosene is suitable for use as an illuminant when burned in a wide lamp. Therefore, adding of sulfate enhanced the catalytic degradation of polypropylene film into high valuable products.

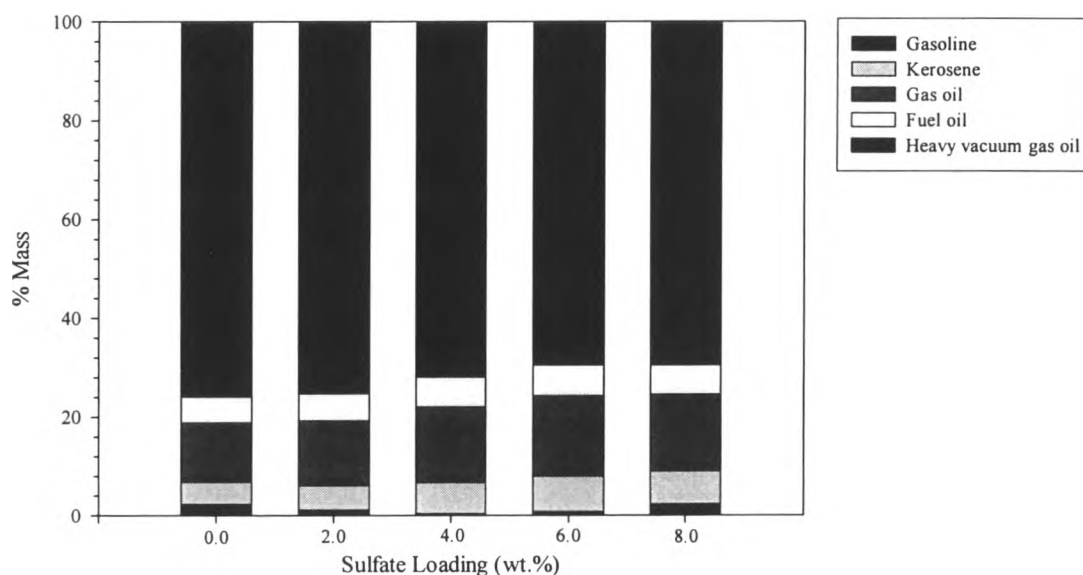


Figure 4.22 Liquid fractions from catalytic pyrolysis of commercial PP film using sulfated zirconia at various amounts of sulfate loading.