

Thermolysis of Scrap Tire Using Supercritical Toluene

Seung Nam Joung, Sung Wook Park, Sun Young Kim, Ki-Pung Yoo[†] and Seong Youl Bae*

Laboratory of Thermodynamics & Supercritical Fluid Engineering,
Department of Chemical Engineering, Sogang University, C.P.O. Box 1142, Seoul, Korea

*Department of Chemical Engineering, Hanyang University, Ansan, Korea

(Received 19 June 1999 • accepted 10 August 1999)

Abstract—With toluene in the supercritical state, scrap tire was decomposed into low molecular weight hydrocarbon liquid and solid residual. The experiment was carried out at 523.15, 573.15 and 623.15 K and pressures of 5, 10, and 15 MPa. The liquid and solid residual products were further separated by a simple filtering method. The reaction time, tire weight and the amount of the solvent were determined for the optimal thermolysis. The decomposition percent and TGA were used to evaluate the decomposition characteristics in terms of temperature and pressure. The GC-MS was applied to the decomposed liquid products from the various conditions. The average molecular weight of the decomposed liquid products tended to become lower with the increasing temperature.

Key words : Supercritical Toluene, Thermolysis, Tire, TGA

INTRODUCTION

It is a major challenge to dispose of scrap tires without causing environmental pollution as tire consumption increases. The scrap tire disposal process can be broadly divided into physical and chemical methods [Crane and Kay, 1975; Crane et al., 1978].

One of physical methods is to use the scrap tire for landfill, although this method should not be employed any more due to intrinsic environmental limitations. Another physical method is to make the scrap tires into granules and recycle them for carpets, tiles and road pavement materials. However, this method may not be economical [Crane et al., 1978].

As to chemical methods, thermal decomposition has been widely used. Thermal decomposition without oxygen source at high temperature can transform the rubbery substance of the scrap tire into low molecular weight hydrocarbon products. These hydrocarbon products are filtered further to collect useful oil and solid residual, which can be reused as additive material to asphalt [Crane et al., 1978; Warner, 1994]. This method has been one of the most popular treatment techniques since the early 1980's.

In recent years, special attention has been given to thermolysis of scrap tires by using supercritical fluid. The tire in general cannot be dissolved by an organic solvent because of its physically and chemically strong properties. However, if one can find an appropriate supercritical solvent, it can dissolve and decompose rubbers in the tire into useful liquid products [McHugh and Krukonic, 1994]. Supercritical thermolysis has several advantages over conventional thermal decomposition, such as no discharge of toxic gas, low temperature operation and fast decomposition time.

In the early 1980's, Modell developed the thermolysis pro-

cess using supercritical water for the decomposition of organic wastes [Modell, 1982]. This supercritical water oxidation was widely tested for the treatment of the scrap tire. For example, Funazukuri et al. performed a comparative study for the supercritical decomposition of the scrap tire with water and n-pentane. They also proposed the decomposition percent as first-order kinetics (170 KJ/mol) [Funazukuri et al., 1987]. Park et al. proposed another decomposition process of the scrap tire into the low molecular hydrocarbon liquid for recovering oil, using water in the supercritical state [Park and Gloyna, 1997]. There was also the reported data of supercritical water oxidation of PVC [Lee et al., 1996].

Besides using supercritical water for decomposition of the scrap tire, Sako et al. attempted to decompose PET polymer, using supercritical methanol [Sako et al., 1997]. Dhawan et al. reported the decomposition characteristics of polyisoprene, SBR and the scrap tire, using supercritical toluene [Dhawan et al., 1991, 1993]. Lee and Hong reported their result of decomposing polyisoprene, using tetrahydrofuran [Lee and Hong, 1998].

Thus, in principle, toluene as well as water can be used to treat polymeric materials like the scrap tire. However, an extreme process condition must be employed when water is used due to its high critical point ($T_c=647.3$ K and $P_c=22.05$ MPa) and oxidation. At the same time, it is difficult to be free from serious corrosion problems of equipment. As to using toluene, it has lower critical values, such as $T_c=591.6$ K and $P_c=4.11$ MPa, and can be considered as a better solvent for decomposing the scrap tire. Dhawan's research reports the decomposition result of using toluene only at one fixed condition, 622.15 K and 13.18 MPa.

Our research team examined the quantitative data, such as the reaction time, tire and solvent amount that were used for the complete decomposition of the scrap tire using toluene as a supercritical solvent. We used various combinations of temperatures and pressures, 523.15, 573.15, 623.15 K and 5, 10, 15

[†]To whom correspondence should be addressed.

E-mail : kpyoo@ccs.sogang.ac.kr

MPa for this supercritical thermolysis of the scrap tire. The TGA and GC/MS were used to find out how the thermolysis result and the molecular weight of the product liquid change as temperature and pressure vary.

EXPERIMENTAL

1. Materials

The sample tire that was used in the research was produced by the Kumho Tire Co. in Seoul, Korea. A piece of the tread portion was used for this experiment. The steel wires and cords were removed from the tire. The toluene (>99% purity) was used as a supercritical solvent without further purification.

2. Apparatus and Procedure

A specially designed high-pressure autoclave was used as a reactor since the decomposition was performed in the supercritical state. This equipment worked safely up to 723.15 K and 35.0 MPa. The internal volume of the reactor was 1,000 mL. It had a cooling coil for controlling temperature and rapidly cooling; and a magnetically driven stirrer (mixer) for agitating the solid-liquid mixture in the reactor, which was operable up to 1,000 rpm. The electric heater surrounding the reactor and the PID were used to control the temperature inside the reactor. The temperature was measured at within the range of ± 1.0 K accuracy, using the Pt-100 Ω thermocouple. The reactor pressure was measured within ± 0.1 MPa accuracy. The reactor, valves, and tubes were made by the HIP Co. in the USA with stainless steel 316 material. The liquid pump used in the experiment was made by the Thermo-Separation Product Inc. in USA. A schematic diagram of the apparatus is shown in Fig. 1.

The experiment was performed at 523.15, 573.15, and 623.15 K and pressures of 5, 10, and 15 MPa. The agitator speed was set to 500 rpm until the decomposition was completed. First, about 25 grams of the sample tire was charged into the reactor. Next, the reactor was sealed and then a measured solvent was fed

into the reactor, using the liquid pump. To minimize the existence of air and other gaseous agents in the reactor, nitrogen gas was purged for 30 minutes. With these preparations, the reactor was heated to the specified temperature in the 5 K/min rate. The internal pressure of the reactor would increase as the temperature increased. To control this excess of pressure during the heating period, some solvent was released using the back-pressure regulator. Once the reactor condition reached the designated pressure and temperature, these conditions were maintained for the duration of the predetermined reaction time. The reactor then was quickly cooled to the ambient temperature without discharging any content in the reactor. Then, the reactor was opened. The content was separated into the liquid product and the residual solid such as carbon black. The components of the liquid product and their composition were analyzed by the Gas Chromatography Mass Spectrometer (GC-MS), HP 6890 series, manufactured by the Hewlett Packard in USA. The residual solid was dried and measured for the weight to calculate the degree of decomposition. In our research, the decomposition percent was defined in the Eq. (1).

$$\text{Decomposition (\%)} = \left[1 - \frac{W_R}{W_T} \right] \times 100 + W_C \quad (\%) \quad (1)$$

Where W_R denotes the weight of the dried residual solid in gram after reaction,

W_T denotes the weight of the sample tire in gram used initially,

W_C denotes the weight percent of carbon black in the sample tire.

Also, the Thermogravimetric Analyzer (TGA, Du Pont, USA) was used to examine the reduction rate of weight as the residual solid was heated up to 873.15 K and to evaluate the degree of decomposition of the rubber compound.

RESULTS AND DISCUSSION

1. TGA Analysis of Synthetic Rubbers and Automotive Tire Sample

The automotive tire, in general, consists of various com-

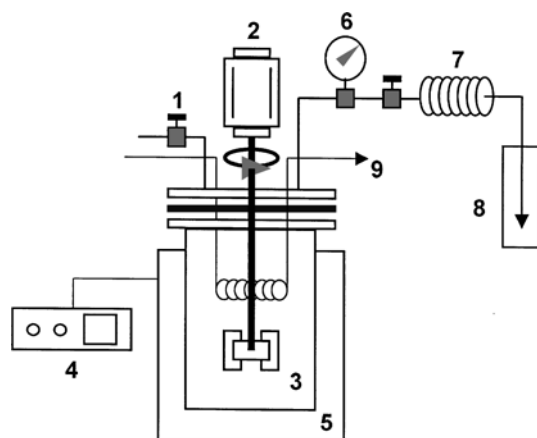


Fig. 1. Schematic diagram of supercritical fluid thermolysis system.

- | | |
|---------------------------|-------------------|
| 1. High-pressure valve | 6. Pressure gauge |
| 2. Mixing device | 7. Heat exchanger |
| 3. Reactor | 8. Sampling |
| 4. Temperature controller | 9. Cooling line |
| 5. Electric furnace | |

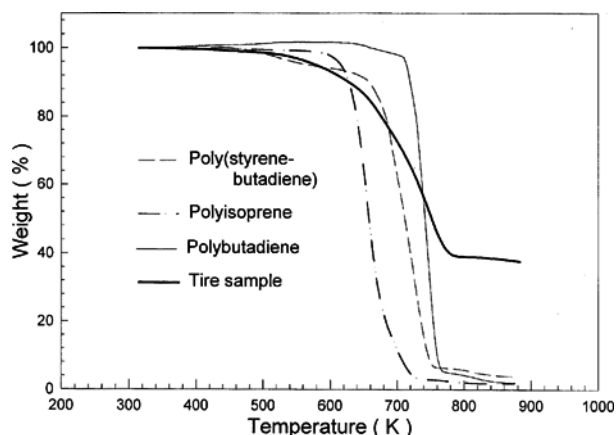


Fig. 2. TGA analysis of main rubbers in scrap tire and tire sample.

pounds, such as 50% of rubber, 30% of carbon black and reinforcing compound, and 20% of steel wire, cord and glue. The rubber in the typical (automotive) tire consists of poly(styrene-butadiene), polyisoprene and polybutadiene. The TGA results of these typical rubber components and the decomposed sample tire are summarized in Fig. 2.

According to Fig. 2, the decomposition of polyisoprene, poly(styrene-butadiene) and polybutadiene started from 623.15 K, 673.15 K and 723.15 K, respectively. As mentioned before, the steel wire, cord and glue components were removed from the scrap tire and the sample piece was mainly rubber. This sample rubber piece was decomposed in the temperature range of 623.15 to 723.15 K. Based on the TGA data, it was necessary to adopt a temperature above 673.15 K for the traditional pyrolysis process, and the weight ratio of the rubber content to the carbon black was 0.64 to 0.36 in the sample tire. Based on these data, the value of W_c (%) in Eq. (1) was determined to be 36.

2. Determination of Reaction Time

To obtain the quantitative data in thermolysis, the reaction time should be determined first for a fixed amount of sample tire to be decomposed completely. The condition used for this thermolysis was at the supercritical state, 623.15 K and 10 MPa. The sample tire amount was 25 g, and 620 mL of toluene were used. Every 30 minute intervals, 30, 60, 90, and 120 minutes, the decomposition percent was examined to see if it reached 100% and determine the reaction time.

The reaction time referred to in this work was measured from the point that the reactor reached the designated temperature and pressure, to the point that the reaction was completed. Thus, the reaction time did not include the times spent on heating and cooling the reactor. The reactor temperature was

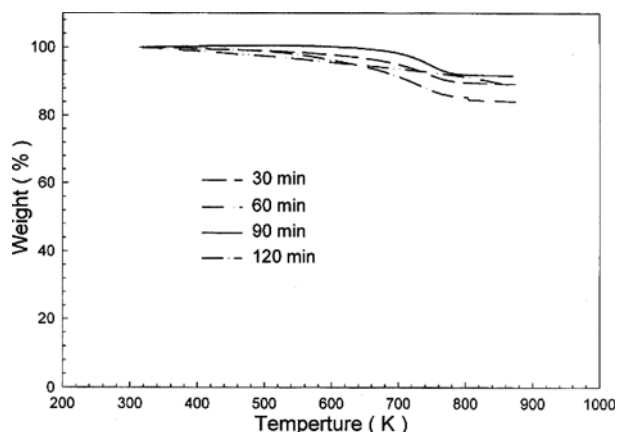


Fig. 3. TGA analysis of residues according to reaction time.

Table 1. Decomposition according to amount of tire

Tire (g)	Amount of solvent (mL)	Decomposition (%)
5.1	620	100
12.6	620	100
25.0	620	100
35.0	620	95
50.2	620	94
100.3	590	93

increased at the rate of 5 K/min till it reached equilibrium. Although this was not negligible, any effect that might occur was excluded in the determination of the reaction time. The reactor was cooled down below 373.15 K within 15 minutes to minimize any significant effect to the outcome of the experiment.

For each run of the reaction timeframe, the amount of residual solid was measured and the decomposition percent was calculated based on Eq. (1). However, the calculated decomposition percent by Eq. (1) had mostly high values in the close range, and it was difficult to evaluate the reliable decomposition percent. Therefore, the decomposition percent was confirmed by using the TGA data for residues as shown in Fig. 3.

From Fig. 3, the reaction time between 30 and 120 minutes produced the weight reduction of 15% and there was virtually no rubber content. Thus, we concluded that the reaction time should be at least 60 minutes for 25 g of the sample tire at 623.15 K and 10 MPa.

3. Determination of Decomposed Tire Amount in Gram for Toluene

To examine how efficient toluene is for the decomposition of tire, the supercritical thermolysis was carried out with various weights, 5, 12.5, 25, 35, 50 and 100 g of the sample tire. The experimental condition was at the 623.15 K and 10 MPa, and the reaction time was set for 60 minutes. For each run, 620 mL of toluene were used. The residual solid weight was measured and the decomposition percent was calculated by the Eq. (1). Also, the complete decomposition was confirmed by TGA. These results were summarized in Table 1.

As noted in Table 1, the decomposition percent was 100% for the sample weight up to 25 g, and below 95% for the sample weight above 35 g. The TGA data for the degree of weight reduction for different weight samples was shown in Fig. 4. Also, as shown in the TGA data from Fig. 4, the weight reduction rate was about 10% for the sample amount of 5 to 35 g, and a complete decomposition of the rubber component was confirmed. However, the weight reduction rate was about 30% for the sample weight of 50 and 100 g, which indicated incomplete decomposition.

Thus, we concluded that a sample weight of 5 to 35 g of tire could be completely decomposed by using toluene for the re-

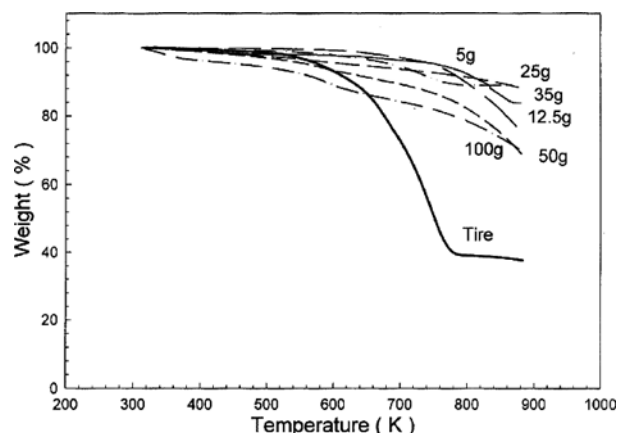


Fig. 4. TGA analysis of residues generated from SC-toluene thermolysis.

action time of 60 minutes and using 620 mL of toluene at the supercritical state, 623.15 K and 10 MPa.

4. Thermolysis of Tire Sample

Based on the works mentioned in the previous section, a series of thermolysis with toluene was carried out for 25 g of the sample tire over a wide range of temperatures (523.15, 573.15 and 623.15 K) and pressures (5, 10, and 15 MPa) with the 60 minutes reaction time. The liquid product and residuals were used to calculate the decomposition percent and analyze the components as temperature and pressure changed.

The solid residue after each run was filtered from the decomposed liquid, dried at vacuum oven and weighed. This weight was used for W_R and the degree of decomposition for each run was calculated by Eq. (1). All experimental results were summarized in Table 2. For the same samples, TGA was also performed as shown in Fig. 5. From Table 2, the degree of decomposition at 523.15 K was between 60 and 84% for all experimented pressures. It was 100% in the range of critical temperature at 573.15 K and above the critical temperature at 623.15 K for all experimented pressures. The relative degree of decomposition at a constant temperature was not obvious with increasing pressure. However, the degree of decomposition with respect to the variation of temperature at an isobaric state was substantial.

TGA results for the residues with various temperatures at 10 MPa were shown in Fig. 5. The change of weight reduction rate of the residues was not noticeable even another pressure range with increasing pressure at a constant temperature. This

Table 2. The results of tire decomposition (%)

Temperature (K)	Pressure (MPa)	Amount of solvent (mL)	Decomposition (%)
523.15	5	827	60
	10	835	65
	15	845	84
573.15	5	660	100
	10	727	100
	15	775	100
623.15	5	360	100
	10	620	100
	15	700	100

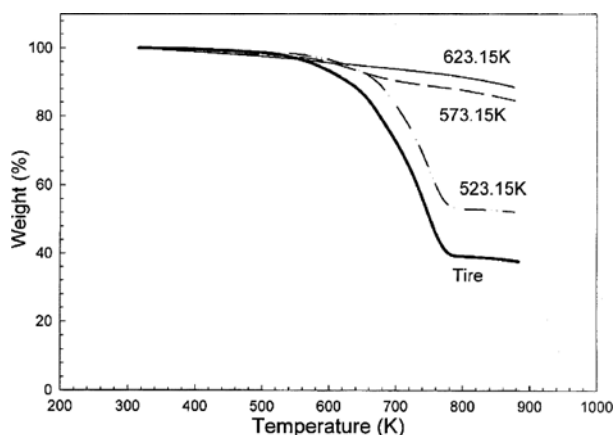


Fig. 5. TGA analysis of residues at 10 MPa.

result was consistent with the result of the decomposition percent shown in Table 2.

At the subcritical temperature, 523.15 K, the rate of weight reduction based on TGA analysis was significant. Thus, we concluded that a significant amount of rubber was not decomposed and remained in the solid residue when the thermolysis was carried out at the subcritical temperature. However, at the supercritical temperatures of 573.15 K and 623.15 K, the weight reduction rate was 15% and 10%, respectively. It indicated that almost complete decomposition could be realized when the thermolysis was performed in the supercritical state, using toluene. Also, at the other pressures (5 and 15 MPa), the general trend of decomposition percents was similar to the case of 10 MPa as shown in Fig. 5.

5. GC-MS Analysis of Liquid Product

GC-MS analysis was performed for the decomposed liquid products that were obtained by the supercritical thermolysis, using toluene. The result was shown in Tables 3 to 5, where pressure set to 10 MPa with varying temperatures of 523.15, 573.15, and 623.15 K. The A in the table denoted the composi-

Table 3. Results of GC-MS analysis at 523.15 K and 15 MPa

No.	Compound	Mol. weight	Composition (%)	
			A	B
1	Pentane	72	0.481	-
2	Hexane	86	0.009	-
3	Cyclohexane	84	0.395	0.027
4	Toluene	92	91.898	98.837
5	Benzaldehyde	106	0.005	0.026
6	Benzenamine	93	0.022	-
7	Limonene	136	0.083	-
8	1,2-Diphenylcyclopropene	180	0.011	-
9	Benzothiazole	135	0.037	-
10	1,2-dihydro-2,2,4-trimethyl-Quinoline	173	0.280	-
11	2,6-bis(1,1-dimethylethyl)-4-methyl-Phenol	220	0.062	-
12	N-phenyl-Benzenamine	169	0.007	-
13	2-methyl-tetramer-1-Propene	224	0.015	-
14	4-(1-methylethyl)-N-phenyl benzenamine	211	0.063	-
15	9,10-dihydro-9,9-dimethyl-Acridine	209	0.016	-
16	2-(2-benzoxazolyl)-Phenol	211	0.032	-
17	Tricosane	324	0.111	-
18	Diisooctyl-1,2-Benzenedicarboxylic acid	390	0.036	-
19	Nonacosane	408	0.035	-
20	Hexacosane	366	0.330	-
21	3 β -Acetoxy-17-methyl-5 α -18(13-17)abeoandrost-13-ene	330	0.118	-
22	Tetradecane	198	0.337	-
23	5 α -cholestane-2 α , 19-diol	404	0.038	-
24	Pentacosane	352	0.040	-
25	2,4-dimethyl-heptane	-	-	1.110
(Mn)		222		

- : undetected compound

A : composition (%) of tire thermolysis using toluene

B : composition (%) of toluene thermolysis

tion of components collected from the thermolysis of the sample tire and toluene, while the **B** collected from the thermolysis of pure toluene. We chose only the components identifiable over 90% in quality.

After the thermolysis, 98% of pure toluene were collected in the same quality as the original while the other 2% became non toluene substance. Dhawan reported the similar results. In their work, 2% of toluene at the supercritical state, 616.15 K and 13.8 MPa were decomposed into diphenyl, diphenylmethane and diphenylethane [Dhawan et al., 1993]. It was easy to compare the decomposed components between the sample tire and the pure toluene because the thermolysis of the sample tire produced more various components. The major components in the decomposed liquids were produced by the chemical reaction between toluene and decomposed hydrocarbons from the sam-

Table 4. Results of GC-MS analysis at 573.15 K and 15 MPa

No. Compound	Mol. weight	Composition (%)	
		A	B
1 Pentane	72	0.018	-
2 Cyclohexane	84	0.368	0.056
3 Toluene	92	89.294	98.684
4 Styrene	104	0.099	-
5 Benzaldehyde	106	0.076	-
6 Benzenamine	93	0.070	-
7 Limonene	136	0.752	-
8 Terpinolene	136	0.053	-
9 (4-methyl-4-pentenyl)-Benzene	160	0.235	-
10 (2R*,1'S*)-2-(2'-(Benzyloxy)-1'-methyl-1-methylethyl)	260	0.074	-
11 2-methyl-Benzothiazole	149	0.038	-
12 2,2,4-Trimethyl-1,2,3,4-tetrahydroquinol	175	0.045	-
13 2,4-dimethyl-Quinoline	157	0.449	-
14 2,6-bis(1,1-dimethylethyl)-4-methyl-Phenol	220	0.020	-
15 N-phenyl-Benzenamine	169	0.019	-
16 6-Phenyl-1,2-hexadiene	158	0.126	-
17 1,1'-(1,3-propanediyl)bis-Benzene	196	0.050	-
18 4-(1-methylethyl)-N-phenyl benzenamine	211	0.072	-
19 2,5-dimethyl-3-vinyl-hexa-1,4-diene	136	0.011	-
20 9,10-dihydro-9,9-dimethyl-Acridine	209	0.111	-
21 δ -Guaiene	204	0.018	-
22 2-(2-benzoxazolyl)-Phenol	211	0.030	-
23 Diisooctyl-1,2-Benzenedicarboxylic acid	390	0.049	-
24 Hexacosane	366	0.334	-
25 3 β -Acetoxy-17-methyl-5 α -18(13-17)abeoandrost-13-ene	330	0.525	-
26 Tetradecane	198	0.302	-
27 Nonacosane	408	0.424	-
28 Tricosane	324	0.242	-
29 Pentacosane	352	0.052	-
30 Octane	-	-	1.241
31 Cyclohexanone	-	-	0.019
(Mn)	192		

Table 5. Results of GC-MS analysis at 623.15 K and 15 MPa

No. Compound	Mol. weight	Composition (%)	
		A	B
1 Pentane	72	0.028	-
2 Cyclohexane	84	0.668	0.408
3 Toluene	92	73.495	98.523
4 Ethyl benzene	106	0.229	-
5 Styrene	104	0.164	-
6 1-methyl-4-(1-methylethyl diene)-cyclohexane	94	0.221	-
7 α -terpipene	136	0.052	-
8 1-methyl-4-(1-methylethyl)-benzene	134	1.842	-
9 α -terpinene	136	0.259	-
10 4-pentenyl-Benzene	146	0.116	-
11 (2-methyl-3-butenyl)-Benzene	146	0.679	-
12 Benzothiazole	135	0.064	-
13 (2R*,1'S*)-2-(2'-(Benzyloxy)-1'-methyl-1-methylethyl)	260	1.043	-
14 6-ethyl-1,2,3,4-tetrahydro-naphthalene	160	0.699	-
15 3-cyclohexen-1-yl-Benzene	158	0.243	-
16 2,4-dimethyl-Quinoline	157	0.481	-
17 1,1'-(1,2-ethanediy)bis-benzene	182	0.231	-
18 6-Phenyl-1,2-hexadiene	158	0.068	-
19 Benzenbutanal	148	0.358	-
20 1,1'-(1,3-propanediyl)bis-Benzene	196	0.392	-
21 2-(2-benzoxazolyl)-Phenol	211	0.618	-
22 3 β -Acetoxy-17-methyl-5 α -18(13-17)abeoandrost-13-ene	330	0.686	-
23 Octane	-	-	0.776
24 Bicyclo[5.1.0]octane	-	-	0.146
25 Cyclohexanone	-	-	0.021
(Mn)	152		

ple tire. They were alkane, benzene and phenol.

At 523.15 K (Table 3), the molecular weight distribution of the decomposed liquid products was over 300. About 92% of toluene were not decomposed. In Table 4, there were more of low molecular components as their weight reduced to 192. When it came to the supercritical state (Table 5), the average molecular weight significantly reduced to 152, and the toluene composition in **A** was about 73%, which indicated the increased decomposition percent of the sample tire.

CONCLUSIONS

Using toluene at the supercritical state, the scrap tire can be decomposed into low molecular weight liquid hydrocarbons, such as oil. It is confirmed that 40 g of tire can be completely decomposed by using 1,000 mL of toluene, at 623.15 K and 10 MPa, in 60 minutes of reaction time. It shows only 60 to 80% of decomposition percent and higher average molecular weight at 523.15 K in the subcritical state. At 573.15 K in the critical area, the average molecular weight is similar to that of 523.15 K although the decomposition percent reaches 100%. However, at the supercritical temperature, 623.15 K, the decomposi-

tion percent become 100% with low average molecular weight. It is also confirmed that the temperature is a more important factor than pressure in the thermolysis based on the decomposition percent, TGA and GC-MS analysis.

ACKNOWLEDGEMENT

The authors thank the R&D Management Center for Energy and Resources for the financial support.

REFERENCES

- Crane, G. and Kay, E. L., "Scrap Tire Disposal Process," *Rubber Chem. Technol.*, **48**, 50 (1975).
- Crane, G., Elefritz, R. A., Kay, E. L. and Laman, J. R., "Scrap Tire Disposal Procedures," *Rubber Chem. Technol.*, **51**, 577 (1978).
- Dhawan, J. C., Bencsath, A. F. and Legendre, R. C., "Depolymerization Reactions of Cis-polyisoprene and Scrap Rubber in Supercritical Toluene," *Supercritical Fluid Science and Technology*, American Chemical Society, Washington, DC, 380 (1993).
- Dhawan, J. C., Legendre, R. C., Bencsath, A. F. and Davis, R. M., "Reaction Products of Styrene-Butadiene ABA Block Copolymer in Supercritical Toluene and Tetralin," *J. Supercrit. Fluids*, **4**, 160 (1991).
- Funazukuri, T., Takanashi, T. and Wakao, N., "Supercritical Extraction of Used Automotive Tire with Water," *J. Chem. Eng. Jpn.*, **20**, 23 (1987).
- Lee, S. B. and Hong, I. K., "Depolymerization Behavior for cis-Polyisoprene Rubber in Supercritical Tetrahydrofuran," *J. Ind. Eng. Chem.*, **4**, 26 (1998).
- Lee, S., Azzam, F. O. and Kocher, B. S., US patent, 5516952, 1996.
- McHugh, M. A. and Krukoni, V. J., "Supercritical Fluid Extraction Principles and Practice," Butterworth-Heinemann, Stoneham, MA, 311 (1994).
- Modell, M., US patent, 4338199, 1982.
- Park, S. and Gloyna, E. F., "Statistical Study of the Liquefaction of Used Rubber Tire in Supercritical Water," *Fuel*, **76**, 999 (1997).
- Sako, T., Sugeta, T., Otake, K., Nakazawa, N., Namiki, K., Tsugumi, M. and Sato, M., "Depolymerization of Polyethylene Terephthalate to Monomers with Supercritical Methanol," *The 4th International Symposium on Supercritical Fluids*, **Vol. A**, 107 (1997).
- Sahouli, B., Blacher, S., Brouers, F., Darmstadt, H., Roy, C. and Kaliaguine, S., "Surface Morphology and Chemistry of Commercial Carbon Black and Carbon Black from Vacuum Pyrolysis of Used Tyres," *Fuel*, **75**, 1244 (1996).
- Warner, W. C., "Methods of Devulcanization," *Rubber Chem. Technol.*, **67**, 559 (1994).