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## APPENDICES

### Appendix A Raw Data

**Table A-1** The product distributions of aged rubber compounds

| Sample                          | % Yield |        |       |
|---------------------------------|---------|--------|-------|
|                                 | Gas     | Liquid | Solid |
| RCP <sup>a</sup> 0 <sup>b</sup> | 20.7    | 39.2   | 40.1  |
| RCP1                            | 20.3    | 39.8   | 39.9  |
| RCP2                            | 17.1    | 42.4   | 40.5  |
| RCP3                            | 16.1    | 44.4   | 39.5  |
| RCP4                            | 25.3    | 35.0   | 39.7  |

<sup>a</sup> rubber compound

<sup>b</sup> aging times

**Table A-2** The gas composition of aged rubber compounds showed in % volume from GC with FID

| Gases          | % Volume |      |      |      |      |
|----------------|----------|------|------|------|------|
|                | RCP0     | RCP1 | RCP2 | RCP3 | RCP4 |
| Methane        | 28.4     | 29.2 | 29.1 | 29.6 | 28.4 |
| Ethylene       | 5.42     | 5.51 | 5.50 | 5.62 | 5.55 |
| Ethane         | 13.3     | 13.7 | 13.4 | 13.6 | 13.2 |
| Propylene      | 5.22     | 5.25 | 5.34 | 5.35 | 5.18 |
| Propane        | 6.89     | 6.86 | 7.01 | 6.98 | 6.68 |
| C <sub>4</sub> | 14.8     | 15.5 | 15.0 | 15.8 | 14.2 |
| C <sub>5</sub> | 15.3     | 13.5 | 13.0 | 14.1 | 13.1 |
| C <sub>6</sub> | 7.23     | 6.66 | 6.71 | 6.78 | 8.40 |
| C <sub>7</sub> | 1.79     | 2.01 | 2.50 | 1.01 | 3.00 |
| C <sub>8</sub> | 1.64     | 1.81 | 2.44 | 0.98 | 2.28 |

<sup>a</sup> rubber compound

<sup>b</sup> aging times

**Table A-3** Amount of hydrocarbons in liquid products from pyrolysis of aged rubber compounds analyzed by DGC with FID

| Carbon number | Boiling Point | % Mass                          |      |      |      |      |
|---------------|---------------|---------------------------------|------|------|------|------|
|               |               | RCP <sup>a</sup> 0 <sup>b</sup> | RCP1 | RCP2 | RCP3 | RCP4 |
| 6             | 69.9          |                                 | 0.05 |      |      | 0.33 |
| 7             | 98.4          | 0.26                            | 0.79 |      |      | 0.92 |
| 8             | 125.1         | 1.18                            | 0.92 | 1.10 | 0.7  | 1.06 |
| 9             | 150.1         | 1.33                            | 1.07 | 1.47 | 1.0  | 1.20 |
| 10            | 173.6         | 1.47                            | 1.23 | 1.62 | 1.1  | 1.34 |
| 11            | 195.6         | 1.61                            | 1.39 | 1.77 | 1.3  | 1.48 |
| 12            | 216.3         | 1.76                            | 1.56 | 1.91 | 1.4  | 1.63 |
| 13            | 235.8         | 1.90                            | 1.73 | 2.05 | 1.6  | 1.77 |
| 14            | 254.0         | 2.03                            | 1.90 | 2.19 | 1.8  | 1.91 |
| 15            | 271.3         | 2.16                            | 2.07 | 2.32 | 1.9  | 2.05 |
| 16            | 287.5         | 2.29                            | 2.24 | 2.44 | 2.1  | 2.18 |
| 17            | 302.8         | 2.41                            | 2.41 | 2.56 | 2.3  | 2.31 |
| 18            | 317.4         | 2.52                            | 2.58 | 2.68 | 2.4  | 2.43 |
| 19            | 331.1         | 2.64                            | 2.74 | 2.79 | 2.6  | 2.56 |
| 20            | 344.2         | 2.75                            | 2.91 | 2.90 | 2.8  | 2.68 |
| 21            | 356.6         | 2.86                            | 3.07 | 3.00 | 3.0  | 2.80 |
| 22            | 368.5         | 2.96                            | 3.23 | 3.10 | 3.1  | 2.92 |
| 23            | 379.9         | 3.07                            | 3.38 | 3.20 | 3.3  | 3.04 |
| 24            | 390.8         | 3.17                            | 3.53 | 3.31 | 3.5  | 3.16 |
| 25            | 401.2         | 3.27                            | 3.67 | 3.41 | 3.7  | 3.28 |
| 26            | 411.3         | 3.37                            | 3.80 | 3.51 | 3.8  | 3.41 |
| 27            | 421.0         | 3.47                            | 3.91 | 3.61 | 4.0  | 3.53 |
| 28            | 430.5         | 3.55                            | 4.00 | 3.70 | 4.2  | 3.66 |
| 29            | 439.6         | 3.63                            | 4.06 | 3.79 | 4.3  | 3.79 |
| 30            | 448.4         | 3.69                            | 4.08 | 3.86 | 4.4  | 3.92 |
| 31            | 457.0         | 3.73                            | 4.05 | 3.91 | 4.4  | 4.03 |
| 32            | 465.4         | 3.74                            | 3.96 | 3.92 | 4.4  | 4.13 |
| 33            | 473.5         | 3.70                            | 3.81 | 3.88 | 4.3  | 4.20 |
| 34            | 481.3         | 3.62                            | 3.60 | 3.77 | 4.1  | 4.21 |
| 35            | 489.0         | 3.48                            | 3.34 | 3.58 | 3.8  | 4.13 |
| 36            | 496.4         | 3.28                            | 3.04 | 3.30 | 3.4  | 3.92 |
| 37            | 503.5         | 3.03                            | 2.70 | 2.94 | 3.0  | 3.54 |
| 38            | 510.4         | 2.73                            | 2.36 | 2.53 | 2.6  | 3.01 |
| 39            | 517.0         | 2.40                            | 2.03 | 2.09 | 2.1  | 2.40 |
| 40            | 523.2         | 2.07                            | 1.71 | 1.68 | 1.7  | 1.78 |
| 41            | 529.1         | 1.74                            | 1.42 | 1.31 | 1.4  | 1.25 |
| 42            | 534.7         | 1.44                            | 1.17 | 1.00 | 1.1  | 0.85 |
| 43            | 539.8         | 1.17                            | 0.95 | 0.75 | 0.8  | 0.56 |
| 44            | 544.5         | 0.94                            | 0.76 | 0.55 | 0.6  | 0.37 |
| 45            | 548.6         | 0.73                            | 0.60 | 0.40 | 0.5  | 0.24 |
| 46            | 552.2         | 0.57                            | 0.47 | 0.29 | 0.4  | 0.16 |
| 47            | 555.2         | 0.42                            | 0.35 | 0.21 | 0.3  | 0.10 |
| 48            | 557.5         | 0.30                            | 0.25 | 0.14 | 0.2  | 0.06 |
| 49            | 559.1         | 0.19                            | 0.16 | 0.09 | 0.1  | 0.04 |

<sup>a</sup> rubber compound

<sup>b</sup> aging times

**Table A-4** Oil fractions from pyrolysis of aged rubber compounds shown in %Mass

| Fraction             | Boiling Point (°C) | % Mass                          |      |      |      |      |
|----------------------|--------------------|---------------------------------|------|------|------|------|
|                      |                    | RCP <sup>a</sup> 0 <sup>b</sup> | RCP1 | RCP2 | RCP3 | RCP4 |
| Gasoline             | 69.6-149           | 2.71                            | 2.78 | 2.50 | 1.56 | 3.45 |
| Kerosine             | 149-232            | 6.41                            | 5.60 | 7.04 | 5.08 | 5.92 |
| Gas oil              | 232-343            | 16.9                            | 16.9 | 18.0 | 16.0 | 16.2 |
| Fuel Oil             | 343-371            | 6.73                            | 7.28 | 7.06 | 7.08 | 6.62 |
| Heavy vacuum gas oil | 371-559.1          | 65.8                            | 66.4 | 64.0 | 69.6 | 66.1 |

<sup>a</sup>rubber compound<sup>b</sup> aging times

**Table A-5** The product distributions of tire co-pyrolysed with various %SO<sub>4</sub><sup>2-</sup> of ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>

| Sample                          | % Yield |        |       |
|---------------------------------|---------|--------|-------|
|                                 | Gas     | Liquid | Solid |
| Tire                            | 19.3    | 39.8   | 40.9  |
| WTZ <sup>a</sup> 0 <sup>b</sup> | 30.7    | 30.2   | 39.1  |
| WTZ2                            | 30.4    | 31.8   | 37.8  |
| WTZ4                            | 29.5    | 32.8   | 37.7  |
| WTZ6                            | 29.3    | 33.7   | 37.0  |
| WTZ8                            | 29.7    | 32.3   | 38.0  |

<sup>a</sup> Waste tire co-pyrolysed with ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>

<sup>b</sup> % SO<sub>4</sub><sup>2-</sup> of ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>

**Table A-6** The gas compositions of tire co-pyrolysed with ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> at various %SO<sub>4</sub><sup>2-</sup> shown in % volume from GC with FID

| Gases          | % Volume |                                 |      |      |      |      |
|----------------|----------|---------------------------------|------|------|------|------|
|                | Tire     | WTZ <sup>a</sup> 0 <sup>b</sup> | WTZ2 | WTZ4 | WTZ6 | WTZ8 |
| Methane        | 28.9     | 26.6                            | 25.7 | 25.7 | 24.7 | 24.9 |
| Ethylene       | 6.25     | 6.65                            | 6.22 | 6.22 | 6.16 | 6.63 |
| Ethane         | 14.5     | 13.3                            | 13.4 | 13.5 | 13.2 | 13.5 |
| Propylene      | 5.47     | 5.34                            | 5.15 | 5.23 | 5.15 | 5.40 |
| Propane        | 6.33     | 5.50                            | 5.67 | 5.85 | 5.68 | 5.72 |
| C <sub>4</sub> | 17.0     | 20.4                            | 18.8 | 18.8 | 19.5 | 20.4 |
| C <sub>5</sub> | 8.94     | 9.76                            | 11.4 | 11.5 | 12.6 | 10.3 |
| C <sub>6</sub> | 7.16     | 7.42                            | 7.19 | 7.43 | 7.55 | 7.52 |
| C <sub>7</sub> | 1.97     | 1.67                            | 2.03 | 2.09 | 1.84 | 2.03 |
| C <sub>8</sub> | 3.46     | 3.35                            | 4.44 | 3.68 | 3.62 | 3.60 |

<sup>a</sup> Waste tire co-pyrolysed with ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>

<sup>b</sup> % SO<sub>4</sub><sup>2-</sup> of ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>

**Table A-7** Amount of hydrocarbons in liquid products from pyrolysis of tire co-pyrolysed with  $ZrO_2/SO_4^{2-}$  at various % $SO_4^{2-}$  analyzed by DGC with FID

| Carbon number | Boiling Point (°C) | %Mass |                                 |      |      |      |      |
|---------------|--------------------|-------|---------------------------------|------|------|------|------|
|               |                    | Tire  | WTZ <sup>a</sup> 0 <sup>b</sup> | WTZ2 | WTZ4 | WTZ6 | WTZ8 |
| 6             | 69.9               |       |                                 |      | 0.22 |      | 0.20 |
| 7             | 98.4               |       |                                 | 0.41 | 0.50 |      | 0.61 |
| 8             | 125.1              | 0.88  | 0.90                            | 0.72 | 0.65 | 0.91 | 0.76 |
| 9             | 150.1              | 1.80  | 1.07                            | 0.90 | 0.83 | 1.32 | 0.94 |
| 10            | 173.6              | 1.95  | 1.23                            | 1.11 | 1.05 | 1.55 | 1.14 |
| 11            | 195.6              | 2.09  | 1.40                            | 1.34 | 1.29 | 1.79 | 1.36 |
| 12            | 216.3              | 2.23  | 1.58                            | 1.60 | 1.56 | 2.04 | 1.59 |
| 13            | 235.8              | 2.36  | 1.76                            | 1.88 | 1.85 | 2.29 | 1.84 |
| 14            | 254.0              | 2.48  | 1.95                            | 2.17 | 2.16 | 2.54 | 2.10 |
| 15            | 271.3              | 2.60  | 2.13                            | 2.47 | 2.49 | 2.78 | 2.36 |
| 16            | 287.5              | 2.71  | 2.32                            | 2.77 | 2.81 | 3.00 | 2.62 |
| 17            | 302.8              | 2.81  | 2.50                            | 3.07 | 3.13 | 3.21 | 2.87 |
| 18            | 317.4              | 2.90  | 2.68                            | 3.35 | 3.44 | 3.40 | 3.12 |
| 19            | 331.1              | 2.99  | 2.86                            | 3.62 | 3.71 | 3.55 | 3.34 |
| 20            | 344.2              | 3.08  | 3.03                            | 3.85 | 3.96 | 3.68 | 3.54 |
| 21            | 356.6              | 3.16  | 3.20                            | 4.05 | 4.15 | 3.78 | 3.72 |
| 22            | 368.5              | 3.23  | 3.37                            | 4.20 | 4.30 | 3.85 | 3.86 |
| 23            | 379.9              | 3.30  | 3.52                            | 4.31 | 4.40 | 3.88 | 3.97 |
| 24            | 390.8              | 3.37  | 3.67                            | 4.37 | 4.44 | 3.88 | 4.04 |
| 25            | 401.2              | 3.43  | 3.80                            | 4.38 | 4.42 | 3.86 | 4.07 |
| 26            | 411.3              | 3.49  | 3.91                            | 4.33 | 4.35 | 3.80 | 4.06 |
| 27            | 421.0              | 3.53  | 4.00                            | 4.24 | 4.23 | 3.73 | 4.02 |
| 28            | 430.5              | 3.57  | 4.06                            | 4.11 | 4.07 | 3.62 | 3.94 |
| 29            | 439.6              | 3.58  | 4.08                            | 3.94 | 3.87 | 3.50 | 3.82 |
| 30            | 448.4              | 3.58  | 4.06                            | 3.74 | 3.65 | 3.37 | 3.68 |
| 31            | 457.0              | 3.54  | 3.99                            | 3.51 | 3.41 | 3.21 | 3.51 |
| 32            | 465.4              | 3.47  | 3.87                            | 3.27 | 3.16 | 3.05 | 3.32 |
| 33            | 473.5              | 3.37  | 3.71                            | 3.02 | 2.90 | 2.88 | 3.12 |
| 34            | 481.3              | 3.22  | 3.50                            | 2.76 | 2.65 | 2.70 | 2.90 |
| 35            | 489.0              | 3.03  | 3.25                            | 2.51 | 2.40 | 2.51 | 2.68 |
| 36            | 496.4              | 2.81  | 2.97                            | 2.27 | 2.16 | 2.33 | 2.46 |
| 37            | 503.5              | 2.56  | 2.67                            | 2.03 | 1.93 | 2.15 | 2.24 |
| 38            | 510.4              | 2.28  | 2.37                            | 1.81 | 1.72 | 1.96 | 2.02 |
| 39            | 517.0              | 2.01  | 2.08                            | 1.60 | 1.52 | 1.79 | 1.82 |
| 40            | 523.2              | 1.73  | 1.79                            | 1.41 | 1.33 | 1.61 | 1.62 |
| 41            | 529.1              | 1.47  | 1.53                            | 1.23 | 1.16 | 1.45 | 1.43 |
| 42            | 534.7              | 1.23  | 1.29                            | 1.06 | 1.01 | 1.28 | 1.25 |
| 43            | 539.8              | 1.02  | 1.08                            | 0.91 | 0.86 | 1.13 | 1.09 |
| 44            | 544.5              | 0.83  | 0.89                            | 0.77 | 0.73 | 0.98 | 0.93 |
| 45            | 548.6              | 0.66  | 0.72                            | 0.65 | 0.61 | 0.83 | 0.78 |
| 46            | 552.2              | 0.52  | 0.57                            | 0.53 | 0.50 | 0.69 | 0.64 |
| 47            | 555.2              | 0.40  | 0.44                            | 0.42 | 0.39 | 0.56 | 0.51 |
| 48            | 557.5              | 0.29  | 0.32                            | 0.31 | 0.29 | 0.42 | 0.38 |
| 49            | 559.1              | 0.18  | 0.21                            | 0.20 | 0.19 | 0.28 | 0.25 |

<sup>a</sup> Waste tire co-pyrolysed with  $ZrO_2/SO_4^{2-}$

<sup>b</sup> %  $SO_4^{2-}$  of  $ZrO_2/SO_4^{2-}$

**Table A-8** Oil fraction of tire co-pyrolysed with  $\text{ZrO}_2/\text{SO}_4^{2-}$  at various  $\% \text{SO}_4^{2-}$  shown in %Mass by model

| Fraction             | Boiling Point ( $^{\circ}\text{C}$ ) | % Mass |                                 |      |      |      |      |
|----------------------|--------------------------------------|--------|---------------------------------|------|------|------|------|
|                      |                                      | Tire   | WTZ <sup>a</sup> 0 <sup>b</sup> | WTZ2 | WTZ4 | WTZ6 | WTZ8 |
| Gasoline             | 69.6-149                             | 2.59   | 1.90                            | 1.98 | 2.16 | 2.17 | 2.46 |
| Kerosine             | 149-232                              | 8.24   | 5.70                            | 5.58 | 5.40 | 7.26 | 5.59 |
| Gas oil              | 232-343                              | 19.8   | 17.5                            | 21.3 | 21.7 | 22.3 | 20.0 |
| Fuel Oil             | 343-371                              | 7.39   | 7.60                            | 9.54 | 9.78 | 8.81 | 8.77 |
| Heavy vacuum gas oil | 371-559                              | 61.7   | 67.6                            | 62.7 | 61.4 | 60.6 | 63.7 |

<sup>a</sup> Waste tire co-pyrolysed with  $\text{ZrO}_2/\text{SO}_4^{2-}$

<sup>b</sup>  $\% \text{SO}_4^{2-}$  of  $\text{ZrO}_2/\text{SO}_4^{2-}$

**Table A-9** The product distributions of tire co-pyrolysed with various catalyst : tire ratios

| Sample              | % Yield |        |       |
|---------------------|---------|--------|-------|
|                     | Gas     | Liquid | Solid |
| R 0.00 <sup>a</sup> | 19.2    | 39.8   | 40.8  |
| R 0.11              | 20.3    | 40.2   | 39.5  |
| R 0.25              | 18.5    | 40.6   | 40.9  |
| R 0.50              | 29.5    | 32.8   | 37.7  |
| R 1.00              | 28.3    | 35.8   | 35.9  |

<sup>a</sup> ratio of catalyst to tire

**Table A-10** The gas composition of tire co-pyrolysed with various catalyst: tire ratio shown in %volume from GC with FID

| Gases          | % Volume            |        |        |        |        |
|----------------|---------------------|--------|--------|--------|--------|
|                | R 0.00 <sup>a</sup> | R 0.11 | R 0.25 | R 0.50 | R 1.00 |
| Methane        | 10.5                | 11.12  | 12.2   | 8.88   | 7.57   |
| Ethylene       | 3.98                | 4.12   | 4.32   | 3.75   | 3.62   |
| Ethane         | 9.86                | 10.4   | 10.7   | 8.79   | 7.49   |
| Propylene      | 5.22                | 5.41   | 5.70   | 4.74   | 4.27   |
| Propane        | 6.33                | 6.65   | 6.66   | 5.55   | 4.60   |
| C <sub>4</sub> | 22.0                | 23.5   | 25.4   | 23.1   | 23.1   |
| C <sub>5</sub> | 14.6                | 14.7   | 14.6   | 17.9   | 14.2   |
| C <sub>6</sub> | 14.0                | 13.1   | 12.8   | 13.8   | 14.5   |
| C <sub>7</sub> | 4.48                | 4.19   | 2.89   | 4.48   | 5.21   |
| C <sub>8</sub> | 8.95                | 6.78   | 4.74   | 9.00   | 15.4   |

<sup>a</sup> ratio of catalyst to tire

**Table A-11** Amount of hydrocarbons in liquid products from pyrolysis of tire co-pyrolysed with various catalyst : tire ratio analyzed by DGC with FID

| Carbon number | Boiling Point | % Mass              |        |        |        |        |
|---------------|---------------|---------------------|--------|--------|--------|--------|
|               |               | R 0.00 <sup>a</sup> | R 0.11 | R 0.25 | R 0.50 | R 1.00 |
| 6             | 69.9          |                     |        | 1.03   | 0.22   |        |
| 7             | 98.4          |                     | 0.35   | 0.38   | 0.50   |        |
| 8             | 125.1         | 0.88                | 1.28   | 0.53   | 0.65   |        |
| 9             | 150.1         | 1.80                | 1.46   | 0.74   | 0.83   |        |
| 10            | 173.6         | 1.95                | 1.65   | 1.00   | 1.05   | 0.50   |
| 11            | 195.6         | 2.09                | 1.84   | 1.31   | 1.29   | 1.17   |
| 12            | 216.3         | 2.23                | 2.03   | 1.68   | 1.56   | 1.35   |
| 13            | 235.8         | 2.36                | 2.21   | 2.10   | 1.85   | 1.53   |
| 14            | 254.0         | 2.48                | 2.40   | 2.56   | 2.16   | 1.72   |
| 15            | 271.3         | 2.60                | 2.57   | 3.05   | 2.49   | 1.91   |
| 16            | 287.5         | 2.71                | 2.74   | 3.54   | 2.81   | 2.11   |
| 17            | 302.8         | 2.81                | 2.90   | 4.02   | 3.13   | 2.31   |
| 18            | 317.4         | 2.90                | 3.05   | 4.45   | 3.44   | 2.51   |
| 19            | 331.1         | 2.99                | 3.19   | 4.80   | 3.71   | 2.71   |
| 20            | 344.2         | 3.08                | 3.32   | 5.06   | 3.96   | 2.91   |
| 21            | 356.6         | 3.16                | 3.42   | 5.21   | 4.15   | 3.11   |
| 22            | 368.5         | 3.23                | 3.52   | 5.24   | 4.30   | 3.30   |
| 23            | 379.9         | 3.30                | 3.59   | 5.17   | 4.40   | 3.49   |
| 24            | 390.8         | 3.37                | 3.65   | 5.00   | 4.44   | 3.67   |
| 25            | 401.2         | 3.43                | 3.68   | 4.75   | 4.42   | 3.84   |
| 26            | 411.3         | 3.49                | 3.69   | 4.44   | 4.35   | 3.99   |
| 27            | 421.0         | 3.53                | 3.68   | 4.10   | 4.23   | 4.12   |
| 28            | 430.5         | 3.57                | 3.64   | 3.73   | 4.07   | 4.22   |
| 29            | 439.6         | 3.58                | 3.57   | 3.37   | 3.87   | 4.28   |
| 30            | 448.4         | 3.58                | 3.48   | 3.01   | 3.65   | 4.29   |
| 31            | 457.0         | 3.54                | 3.37   | 2.67   | 3.41   | 4.26   |
| 32            | 465.4         | 3.47                | 3.23   | 2.36   | 3.16   | 4.17   |
| 33            | 473.5         | 3.37                | 3.07   | 2.07   | 2.90   | 4.03   |
| 34            | 481.3         | 3.22                | 2.89   | 1.81   | 2.65   | 3.84   |
| 35            | 489.0         | 3.03                | 2.70   | 1.57   | 2.40   | 3.59   |
| 36            | 496.4         | 2.81                | 2.50   | 1.37   | 2.16   | 3.32   |
| 37            | 503.5         | 2.56                | 2.29   | 1.18   | 1.93   | 3.01   |
| 38            | 510.4         | 2.28                | 2.08   | 1.02   | 1.72   | 2.69   |
| 39            | 517.0         | 2.01                | 1.87   | 0.87   | 1.52   | 2.37   |
| 40            | 523.2         | 1.73                | 1.67   | 0.75   | 1.33   | 2.06   |
| 41            | 529.1         | 1.47                | 1.48   | 0.64   | 1.16   | 1.77   |
| 42            | 534.7         | 1.23                | 1.29   | 0.54   | 1.01   | 1.50   |
| 43            | 539.8         | 1.02                | 1.12   | 0.46   | 0.86   | 1.26   |
| 44            | 544.5         | 0.83                | 0.95   | 0.38   | 0.73   | 1.04   |
| 45            | 548.6         | 0.66                | 0.80   | 0.31   | 0.61   | 0.85   |
| 46            | 552.2         | 0.52                | 0.66   | 0.25   | 0.50   | 0.68   |
| 47            | 555.2         | 0.40                | 0.52   | 0.20   | 0.39   | 0.52   |
| 48            | 557.5         | 0.29                | 0.39   | 0.15   | 0.29   | 0.38   |
| 49            | 559.1         | 0.18                | 0.26   | 0.10   | 0.19   | 0.25   |

<sup>a</sup> ratio of catalyst to tire

**Table A-12** Oil fraction of tire co-pyrolysed with various catalyst: tire ratio shown in %Mass by model

| Fraction             | Boiling Point<br>(°C) | % Mass              |        |        |        |        |
|----------------------|-----------------------|---------------------|--------|--------|--------|--------|
|                      |                       | R 0.00 <sup>a</sup> | R 0.11 | R 0.25 | R 0.50 | R 1.00 |
| Gasoline             | 69.6-149              | 2.59                | 3.00   | 2.64   | 2.16   | -      |
| Kerosine             | 149-232               | 8.24                | 7.34   | 5.67   | 5.40   | 4.23   |
| Gas oil              | 232-343               | 19.8                | 20.3   | 27.5   | 21.7   | 16.2   |
| Fuel Oil             | 343-371               | 7.39                | 8.02   | 12.1   | 9.78   | 7.43   |
| Heavy vacuum gas oil | 371-559               | 61.7                | 61.3   | 51.1   | 61.4   | 72.8   |

<sup>a</sup> ratio of catalyst to tire

**Table A-13** The organic carbon in solid residues of aged rubber compounds, tire co-pyrolysed with  $\text{ZrO}_2/\text{SO}_4^{2-}$  at various  $\% \text{SO}_4^{2-}$ , tire co-pyrolysed with various catalyst: tire ratios shown in % weight

| Sample                          | % Weight          |                |
|---------------------------------|-------------------|----------------|
|                                 | Inorganic Residue | Organic Carbon |
| RCP <sup>a</sup> 0 <sup>b</sup> | 7.85              | 92.2           |
| RCP1                            | 8.33              | 91.7           |
| RCP2                            | 8.10              | 91.9           |
| RCP3                            | 8.30              | 91.7           |
| RCP4                            | 8.30              | 91.7           |
| Tire                            | 16.5              | 83.5           |
| WTZ <sup>c</sup> 0 <sup>d</sup> | 16.2              | 83.8           |
| WTZ2                            | 18.3              | 81.7           |
| WTZ4                            | 16.1              | 83.9           |
| WTZ6                            | 17.2              | 82.8           |
| WTZ8                            | 21.3              | 78.7           |
| R 0.00 <sup>e</sup>             | 16.5              | 83.5           |
| R 0.11                          | 15.2              | 84.8           |
| R 0.25                          | 16.9              | 83.1           |
| R 0.50                          | 16.1              | 83.9           |
| R 1.00                          | 17.8              | 82.2           |

<sup>a</sup> rubber compound

<sup>b</sup> aging times

<sup>c</sup> Waste tire co-pyrolysed with  $\text{ZrO}_2/\text{SO}_4^{2-}$

<sup>d</sup> %  $\text{SO}_4^{2-}$  of  $\text{ZrO}_2/\text{SO}_4$

<sup>e</sup> ratio of catalyst to tire

**Table A-14** The curve fitting and equation of % OFF of aged rubber compounds

| $y = y_o + \frac{a}{\left[1 + e^{-\left(\frac{x-x_o}{b}\right)}\right]}^c$ | Parameter | Coefficient | $R^2$      |
|--|-----------|-------------|------------|
| RCP <sup>a</sup> <sup>b</sup>  | a         | 107.393     | 0.99972174 |
|  | b         | 24.0125     |            |
|  | c         | 0.1656      |            |
|  | $x_o$     | 520.173     |            |
|  | $y_o$     | -5.5975     |            |
| RCP1   | a         | 105.0765    | 0.99985130 |
|  | b         | 28.5676     |            |
|  | c         | 0.2358      |            |
|  | $x_o$     | 502.1591    |            |
|  | $y_o$     | -2.9175     |            |
| RCP2   | a         | 106.7039    | 0.99976428 |
|  | b         | 18.5555     |            |
|  | c         | 0.1231      |            |
|  | $x_o$     | 512.8172    |            |
|  | $y_o$     | -7.0524     |            |
| RCP3   | a         | 104.1937    | 0.99988707 |
|  | b         | 22.4441     |            |
|  | c         | 0.1941      |            |
|  | $x_o$     | 503.9794    |            |
|  | $y_o$     | -3.282      |            |
| RCP4   | a         | 102.3127    | 0.99934792 |
|  | b         | 12.7777     |            |
|  | c         | 0.093       |            |
|  | $x_o$     | 514.9334    |            |
|  | $y_o$     | -3.6839     |            |

<sup>a</sup> rubber compound<sup>b</sup> aging times

**Table A-15** The curve fitting and equation of % OFF of tire co-pyrolysed with  $\text{ZrO}_2/\text{SO}_4^{2-}$

| $y = y_o + \frac{a}{\left[1 + e^{-\left(\frac{x-x_o}{b}\right)}\right]^c}$ | Parameter | Coefficient | $R^2$      |
|--|-----------|-------------|------------|
| Tire   | a         | 113.6842    | 0.99982224 |
|  | b         | 28.6036     |            |
|  | c         | 0.1704      |            |
|  | $x_o$     | 514.6187    |            |
|  | $y_o$     | -10.2836    |            |
| WTZ <sup>a</sup> 0 <sup>b</sup>  | a         | 108.8422    | 0.99979960 |
|  | b         | 34.2582     |            |
|  | c         | 0.2924      |            |
|  | $x_o$     | 498.7826    |            |
|  | $y_o$     | -3.5788     |            |
| WTZ2   | a         | 110.1107    | 0.99965825 |
|  | b         | 52.404      |            |
|  | c         | 0.5982      |            |
|  | $x_o$     | 448.9839    |            |
|  | $y_o$     | -1.6004     |            |
| WTZ4   | a         | 108.5783    | 0.99976101 |
|  | b         | 53.9779     |            |
|  | c         | 0.6577      |            |
|  | $x_o$     | 439.5238    |            |
|  | $y_o$     | -0.9782     |            |
| WTZ6   | a         | 118.3624    | 0.99965237 |
|  | b         | 64.3649     |            |
|  | c         | 0.609       |            |
|  | $x_o$     | 459.7268    |            |
|  | $y_o$     | -4.0596     |            |
| WTZ8   | a         | 111.9381    | 0.99969754 |
|  | b         | 55.0624     |            |
|  | c         | 0.5873      |            |
|  | $x_o$     | 461.7913    |            |
|  | $y_o$     | -1.5148     |            |

<sup>a</sup> Waste tire co-pyrolysed with  $\text{ZrO}_2/\text{SO}_4^{2-}$

<sup>b</sup> %  $\text{SO}_4^{2-}$  of  $\text{ZrO}_2/\text{SO}_4^{2-}$

**Table A-16** The curve fitting and equation of % OFF of tire co-pyrolysed with various catalysts to tire ratios

| $y = y_o + \frac{a}{\left[1 + e^{-\left(\frac{x-x_o}{b}\right)}\right]} - c$ | Parameter      | Coefficient | $R^2$      |
|--|----------------|-------------|------------|
| R 0.00 <sup>a</sup>  | a              | 113.6842    | 0.99982224 |
|  | b              | 28.6036     |            |
|  | c              | 0.1704      |            |
|  | x <sub>o</sub> | 514.6187    |            |
|  | y <sub>o</sub> | -10.2836    |            |
| R 0.11   | a              | 114.3135    | 0.99989275 |
|  | b              | 47.974      |            |
|  | c              | 0.3653      |            |
|  | x <sub>o</sub> | 492.6158    |            |
|  | y <sub>o</sub> | -5.3311     |            |
| R 0.25   | a              | 101.797     | 0.99959161 |
|  | b              | 50.9986     |            |
|  | c              | 0.7776      |            |
|  | x <sub>o</sub> | 397.0371    |            |
|  | y <sub>o</sub> | 0.3322      |            |
| R 0.50   | a              | 108.5783    | 0.99976101 |
|  | b              | 53.9779     |            |
|  | c              | 0.6577      |            |
|  | x <sub>o</sub> | 439.5238    |            |
|  | y <sub>o</sub> | -0.9782     |            |
| R 1.00   | a              | 111.2513    | 0.99960512 |
|  | b              | 34.6044     |            |
|  | c              | 0.3263      |            |
|  | x <sub>o</sub> | 500.8223    |            |
|  | y <sub>o</sub> | -4.5886     |            |

<sup>a</sup> ratio of catalyst to tire

## Appendix B Physical Properties

**Table B-1** The hardness of aged rubber compounds

| Sample                          | Hardness (shore A) |      |      |      |      |      |       |
|---------------------------------|--------------------|------|------|------|------|------|-------|
|                                 | 1                  | 2    | 3    | 4    | 5    | AVG. | STD.  |
| RCP <sup>a</sup> 0 <sup>b</sup> | 58.0               | 58.0 | 58.5 | 58.0 | 58.0 | 58.1 | 0.204 |
| RCP1                            | 62.0               | 62.0 | 62.0 | 62.0 | 62.0 | 62.0 | 0     |
| RCP2                            | 66.0               | 66.5 | 66.5 | 66.0 | 66.0 | 66.2 | 0.258 |
| RCP3                            | 68.0               | 68.0 | 68.0 | 68.0 | 68.0 | 68.0 | 0     |
| RCP4                            | 70.0               | 70.0 | 70.0 | 70.0 | 70.0 | 70.0 | 0     |

<sup>a</sup> Rubber compound

<sup>b</sup> aging times

**Table B-2** The density of aged rubber compounds

| Sample                          | Density (g/cc) |             |             |             |             |
|---------------------------------|----------------|-------------|-------------|-------------|-------------|
|                                 | 1              | 2           | 3           | AVG.        | STD.        |
| RCP <sup>a</sup> 0 <sup>b</sup> | 1.239834393    | 1.24534461  | 1.245049321 | 1.243409442 | 0.002530814 |
| RCP1                            | 1.237459796    | 1.241800467 | 1.242757106 | 1.240672456 | 0.00230502  |
| RCP2                            | 1.251036116    | 1.240566038 | 1.235078457 | 1.24222687  | 0.006619692 |
| RCP3                            | 1.244422027    | 1.239434955 | 1.239396628 | 1.241084537 | 0.002360014 |
| RCP4                            | 1.242640792    | 1.244173068 | 1.241659566 | 1.242824475 | 0.00103432  |

<sup>a</sup> Rubber compound

<sup>b</sup> aging times

**Table B-3** The density of swollen rubber compounds

| Sample                          | Density (g/cc) |             |             |             |             |             |
|---------------------------------|----------------|-------------|-------------|-------------|-------------|-------------|
|                                 | 1              | 2           | 3           | 4           | AGV.        | STD         |
| RCP <sup>a</sup> 0 <sup>b</sup> | 1.008584196    | 1.007169306 | 1.004974351 | 1.004119581 | 1.006211858 | 0.002037461 |
| RCP1                            | 1.035743241    | 1.035366267 | 1.029147216 | 1.034911069 | 1.033791948 | 0.003115124 |
| RCP2                            | 1.033267483    | 1.033441252 | 1.037319296 | 1.041489628 | 1.036379415 | 0.003886497 |
| RCP3                            | 1.036946658    | 1.044645918 | 1.042548775 | 1.048187445 | 1.043082199 | 0.004705959 |
| RCP4                            | 1.050863684    | 1.052344822 | 1.061418902 | 1.067201518 | 1.057957231 | 0.007729975 |

<sup>a</sup> Rubber compound<sup>b</sup> aging times**Table B-4** The measured volume fraction of rubbers in the swollen vulcanizate samples

| Sample                          | Volume Fraction |             |             |             |             |
|---------------------------------|-----------------|-------------|-------------|-------------|-------------|
|                                 | 1               | 2           | 3           | AVG.        | STD.        |
| RCP <sup>a</sup> 0 <sup>b</sup> | 0.21751766      | 0.214568292 | 0.225971065 | 0.217421739 | 0.006185663 |
| RCP1                            | 0.23861812      | 0.234085349 | 0.2375742   | 0.242550156 | 0.011742915 |
| RCP2                            | 0.238899118     | 0.239254006 | 0.243600826 | 0.242456918 | 0.004311751 |
| RCP3                            | 0.241365059     | 0.243064589 | 0.246494374 | 0.245245132 | 0.003852256 |
| RCP4                            | 0.253084582     | 0.252952635 | 0.252491639 | 0.252062162 | 0.001582133 |

<sup>a</sup> Rubber compound<sup>b</sup> aging times

**Table B-5** The C<sub>1</sub> value of aged rubber compounds

| Sample                          | C <sub>1</sub> Value |             |             |             |             |
|---------------------------------|----------------------|-------------|-------------|-------------|-------------|
|                                 | 1                    | 2           | 3           | AVG.        | STD.        |
| RCP <sup>a</sup> 0 <sup>b</sup> | 0.648618943          | 0.634072258 | 0.691375067 | 0.65802209  | 0.029786194 |
| RCP1                            | 0.758352834          | 0.733926052 | 0.75268501  | 0.748321299 | 0.012784694 |
| RCP2                            | 0.759882817          | 0.761817743 | 0.785757113 | 0.769152558 | 0.014412475 |
| RCP3                            | 0.773388548          | 0.78277983  | 0.801940236 | 0.786036205 | 0.014551725 |
| RCP4                            | 0.839546295          | 0.838783062 | 0.836119812 | 0.838149723 | 0.001798898 |

<sup>a</sup> Rubber compound<sup>b</sup> aging times**Table B-6** Crosslink density value of rubber compounds

| Sample                          | Crosslink Density (x10 <sup>4</sup> mol/cm <sup>3</sup> ) |          |          |             |          |
|---------------------------------|---|----------|----------|-------------|----------|
|                                 | 1   | 2        | 3        | AVG.        | STD.     |
| RCP <sup>a</sup> 0 <sup>b</sup> | 1.957781  | 1.927572 | 2.052238 | 1.979196665 | 0.065034 |
| RCP1                            | 2.219735  | 2.155632 | 2.204529 | 2.193298815 | 0.033495 |
| RCP2                            | 2.223853  | 2.22911  | 2.296238 | 2.249733478 | 0.040359 |
| RCP3                            | 2.261084  | 2.287692 | 2.343931 | 2.297569108 | 0.042297 |
| RCP4                            | 2.462549  | 2.460024 | 2.451253 | 2.457941788 | 0.005929 |

<sup>a</sup> Rubber compound<sup>b</sup> aging times

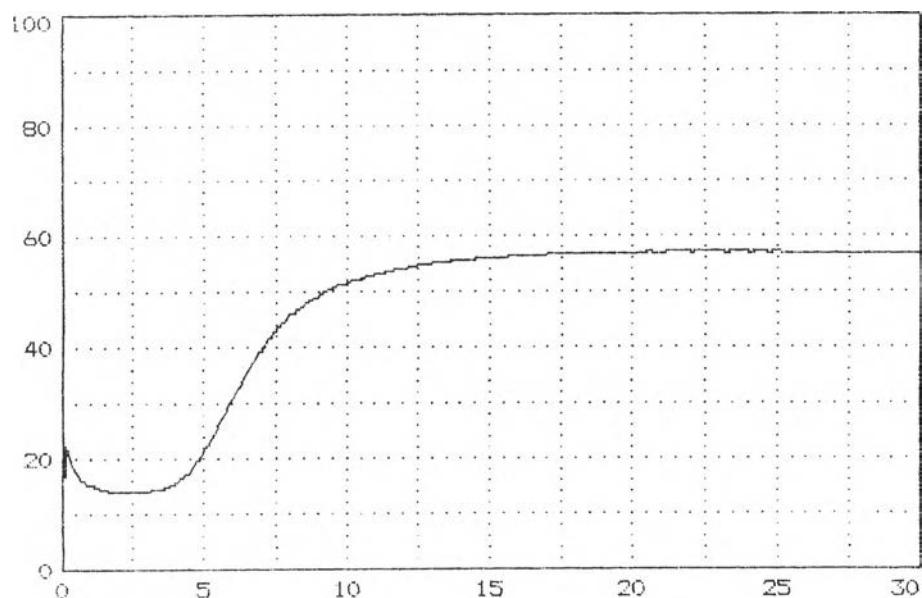
**Table B-7** The molecular weight per crosslink

| Sample                          | Molecular weight per crosslink ( $\times 10^{-4}$ g/mol) |            |            |            |            |
|---------------------------------|--|------------|------------|------------|------------|
|                                 | 1  | 2          | 3          | AVG.       | STD.       |
| RCP <sup>a</sup> 0 <sup>b</sup> | 0.2553912  | 0.25939374 | 0.24363651 | 0.25280715 | 0.00819027 |
| RCPI                            | 0.22525211   | 0.23195051 | 0.2268058  | 0.22800281 | 0.00350596 |
| RCP2                            | 0.22483503   | 0.22430475 | 0.21774751 | 0.22229576 | 0.00394782 |
| RCP3                            | 0.22113283   | 0.21856089 | 0.21331687 | 0.2176702  | 0.00398338 |
| RCP4                            | 0.20304167   | 0.20325007 | 0.20397732 | 0.20342302 | 0.00049122 |

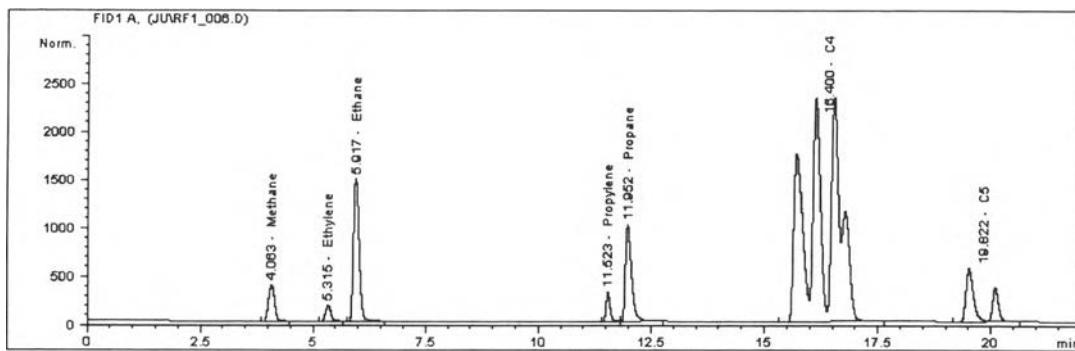
<sup>a</sup> Rubber compound<sup>b</sup> aging times

## Appendix C Chromatograms

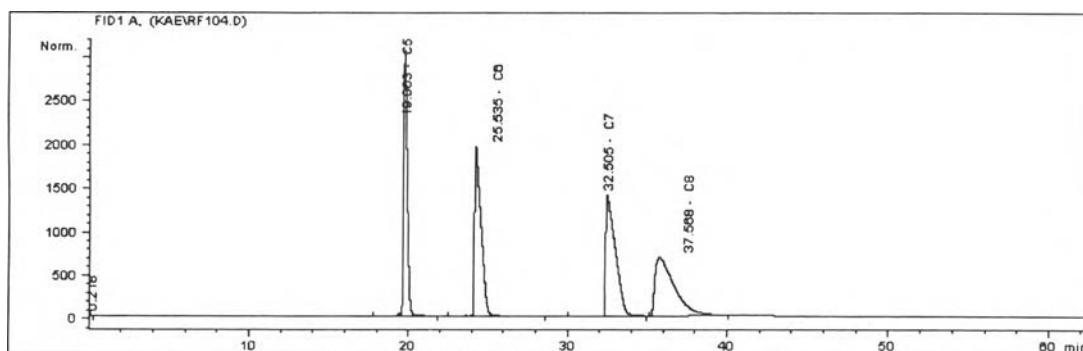
| Max. Torque | Min. Torque | TC10 | TC50 | TC90  |
|-------------|-------------|------|------|-------|
| 57.00       | 13.97       | 4.71 | 6.58 | 10.96 |



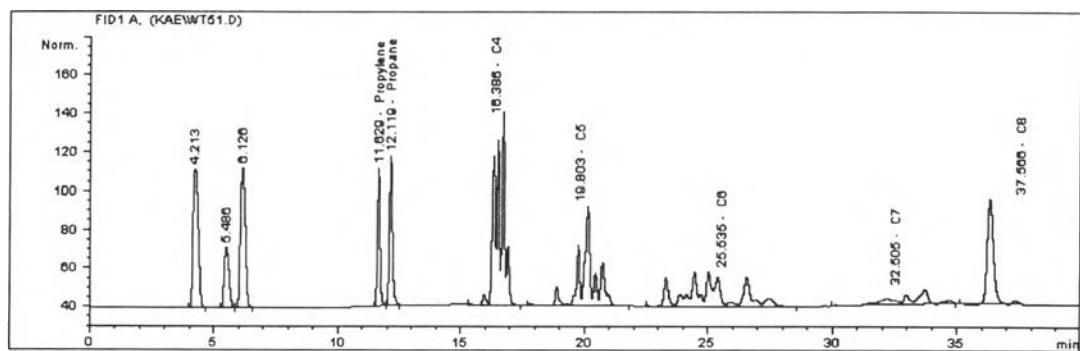
**Figure C-1** Chromatogram of cure time of non-aged rubber compound.



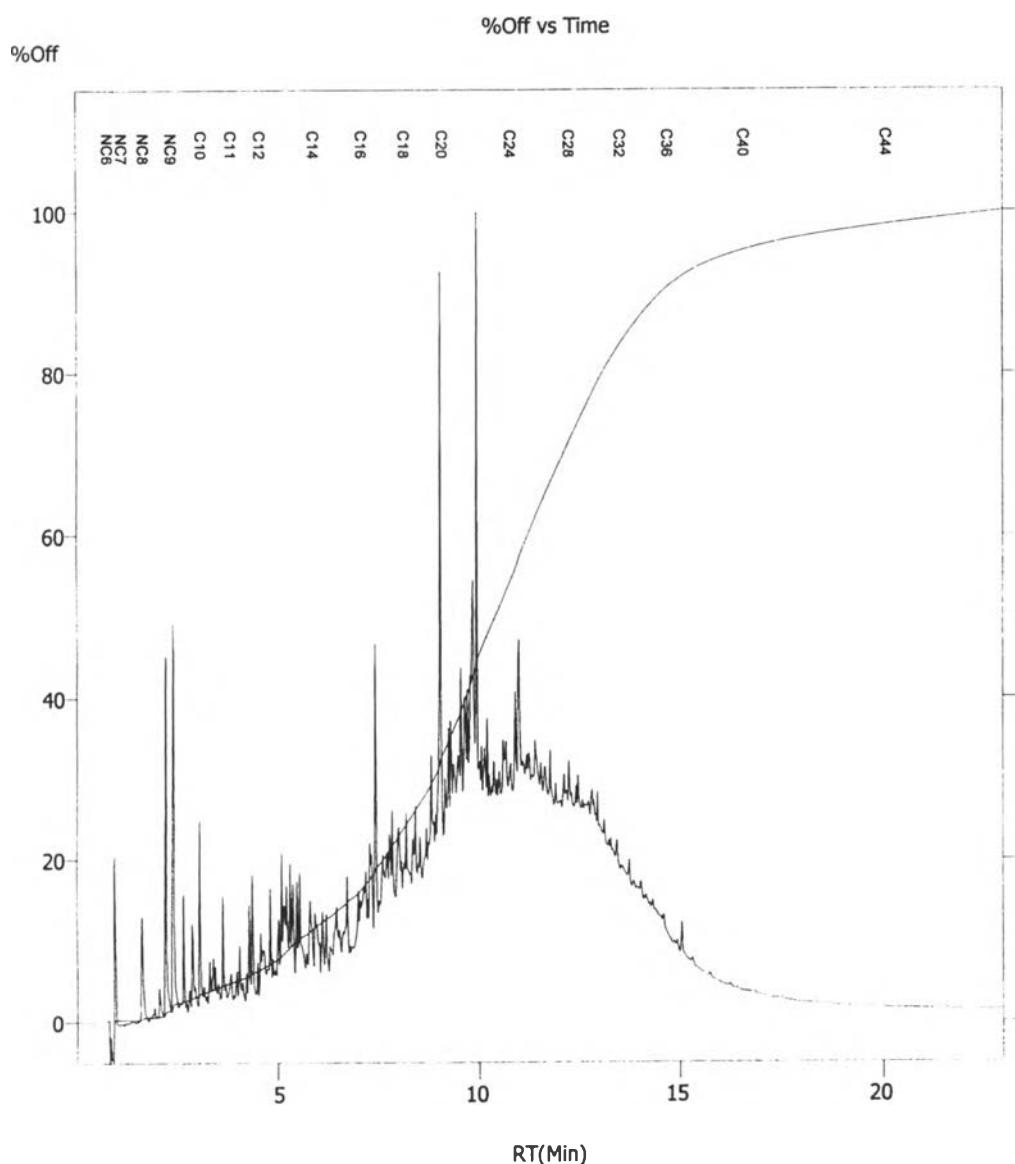
**Figure C-2** Chromatogram of standard gas for GC calibration.



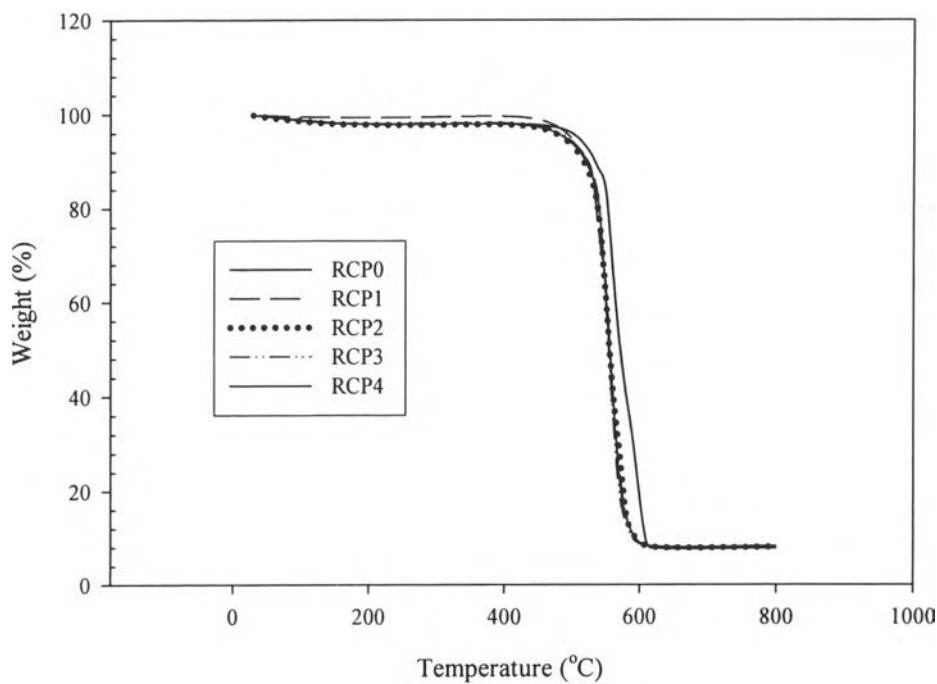
**Figure C-3** Chromatogram of liquid standard for calibration GC.



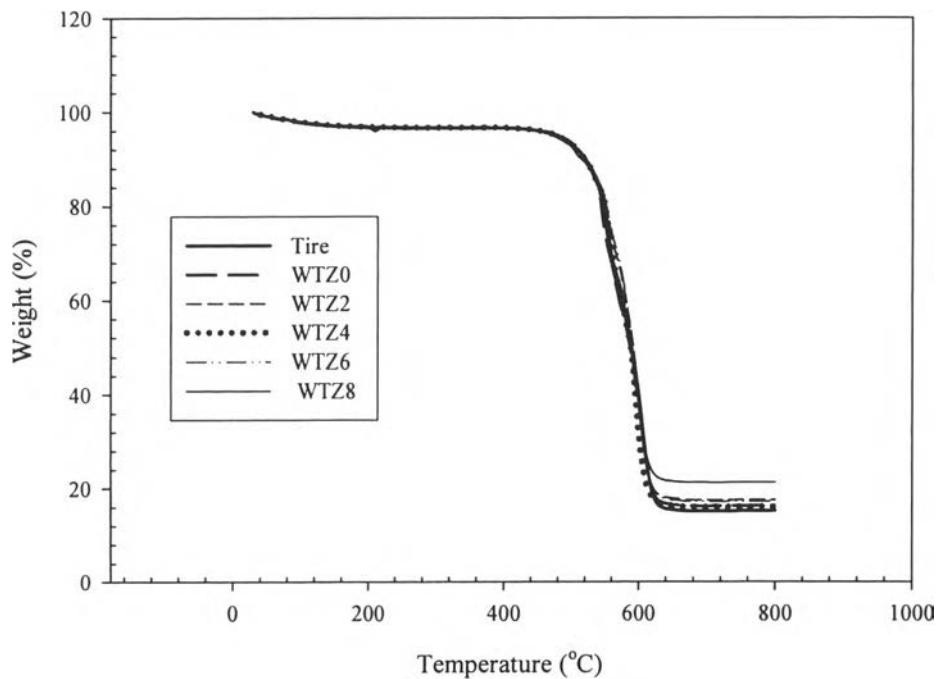
**Figure C-4** Chromatogram of gas product from pyrolysis of waste tire analyzed by GC.



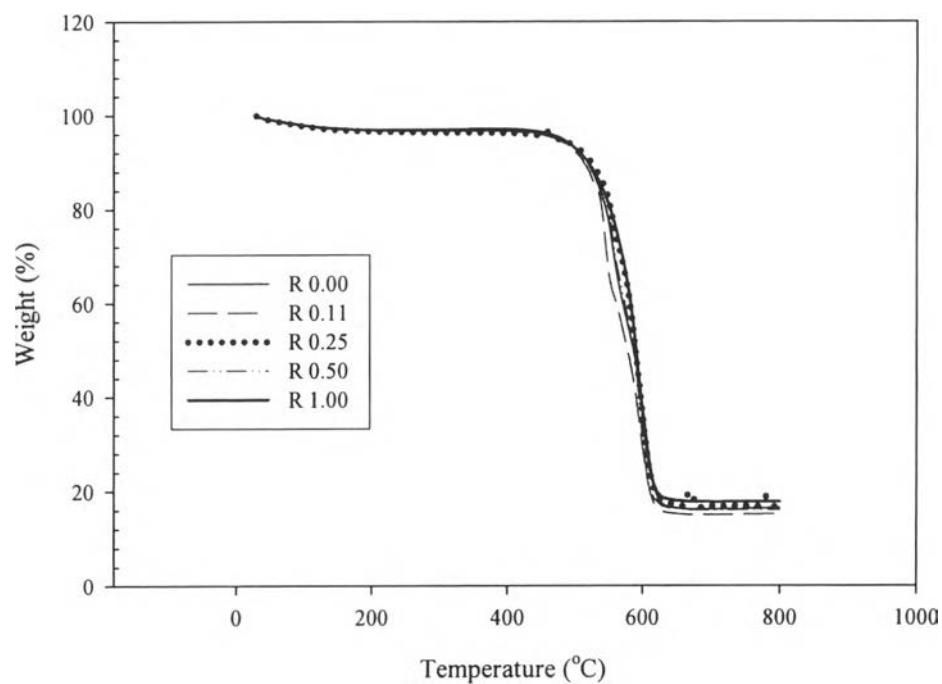
**Figure C-5** Chromatogram of liquid sample from pyrolysis of waste tire with catalyst to tire ratio at 0.25.



**Figure C-6** TGA curves of solid residues of aged rubber compound.



**Figure C-7** TGA curves of solid residues of tire co-pyrolysed with various  $\text{ZrO}_2/\text{SO}_4^{2-}$ .



**Figure C-8** TGA curves of solid residues of tire co-pyrolysed with various catalyst to tire ratio.

## **Appendix D Standard for gas chromatography**

**Table D-1** Standard Refinery Gas Compositions for gas chromatography calibration

Approximate concentration % volume/volume

| Compositions    | % volume/volume |
|-----------------|-----------------|
| Hydrogen        | 15              |
| Nitrogen        | 15              |
| Carbon dioxide  | 5               |
| Carbon monoxide | 5               |
| Methane         | 5               |
| Ethane          | 1               |
| Ethylene        | 10              |
| Propane         | 1               |
| Propylene       | 5               |
| Iso-butane      | 10              |
| N-butane        | 5               |
| Butane          | 10              |
| Trans-2-butene  | 5               |
| Cis-2-butene    | 5               |
| N-pentane       | 1               |
| Iso-pentane     | 2               |

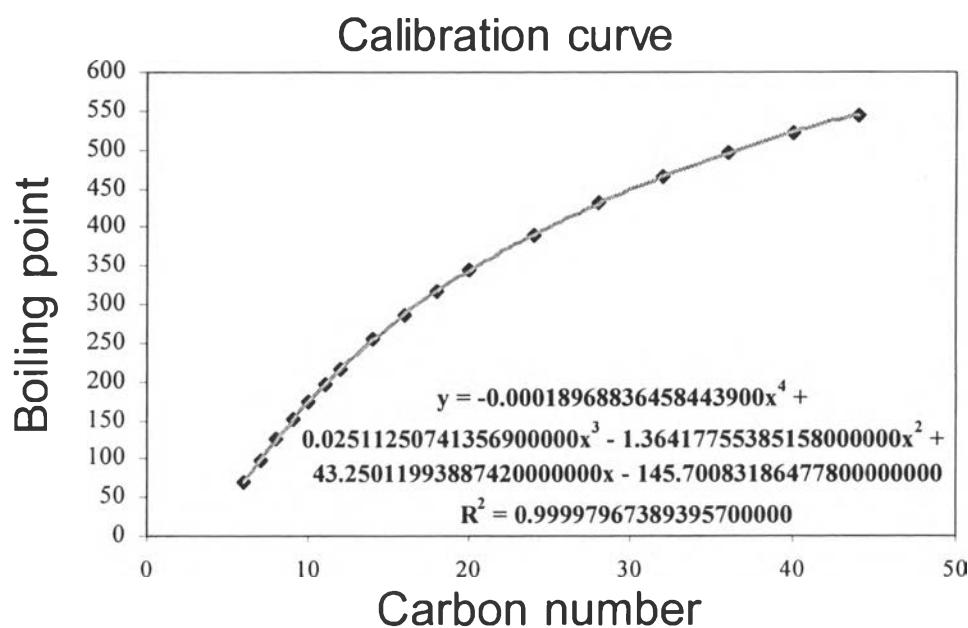
**Table D-2** Liquid for gas chromatography calibration

| Liquid standard | Density @ 20°C |
|-----------------|----------------|
| N-pentane       | 0.626          |
| N-hexane        | 0.659          |
| N-heptane       | 0.684          |
| Iso-octane      | 0.6919         |

**Table D-3** ASTM Method D2887 Column Test Mixture

This ULTRA standard (TM) solution was gravimetrically prepared, and the analyte concentrations were verified using high resolution gas chromatography.

| Components          | Carbon number | % By weight |
|---------------------|---------------|-------------|
| N-hexane            | 6             | 6.0         |
| N-heptane           | 7             | 6.0         |
| N-octane            | 8             | 8.0         |
| N-nonane            | 9             | 8.0         |
| N-decane            | 10            | 12.0        |
| N-undecane          | 11            | 12.0        |
| N-dodecane          | 12            | 12.0        |
| N-tetradecane       | 14            | 12.0        |
| N-hexadecane        | 16            | 10.0        |
| N-octadecane        | 18            | 5.0         |
| N-eicosane          | 20            | 2.0         |
| N-tetracosane       | 24            | 2.0         |
| N-octacosane        | 28            | 1.0         |
| N-dotriacontane     | 32            | 1.0         |
| N-hexatriacontane   | 36            | 1.0         |
| N-tetracontane      | 40            | 1.0         |
| N-tetratetracontane | 44            | 1.0         |



**Figure D-1** GC calibration curve of ASTM D2887 Column Test Mixture with the equation of fitted curve.

## CURRICURUM VITAE

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