Incineration of styrene–butadiene rubber: the influence of heating rate and oxygen content on gas products formation [1]

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Abstract

This study investigates thermal decomposition of styrene–butadiene rubber under various heating conditions in oxygen–nitrogen atmosphere. The experiments are performed to establish the effects of operating conditions and identify the gas products. The heating rate (2, 5, 10, 20 K/min) and oxygen contain (5%, 10%, 20%) are the main operating parameters. The gas products detected from the reaction tube are CO_2, CO and hydrocarbon. Experimental results indicate that the gas formation involves two stages of reaction when oxygen is presented: the initial reaction temperature decreases, but the reaction range and the reaction rate increase when the heating rate is raised. The presence of oxygen in carrier gas accelerates the decomposition slightly and the reaction rate becomes faster once reaction commences; and reduces the activation energy of volatile products. The hydrocarbon emissions such as styrene, benzene, toluene, propanone, xylene, butane and 4-ethenyl-cyclohexene are the major species. In addition, the formation of hydrocarbon products also involves the free radicals and monomer recombination processes. © 1998 Elsevier Science B.V.

Keywords: Styrene–butadiene rubber; Incineration; Volatile products

1. Introduction

Thermal treatment of solid wastes and materials by pyrolysis or incineration process has received extensive attention in recent years due to rapid by growing municipal and industrial waste centers regionally or worldwide. Waste tires produced in Taiwan

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annually amount to nearly 80 000 tons with this figure increasing every year. The heat values of tires range from about 29 400–33 600 KJ/kg (7000–8000 Kcal/kg). Styrene–butadiene rubber (SBR) is the main polymer in waste tires which can not easily be disposed or treated and contains what cannot be decomposed easily in long term [1]. Rubber materials are essentially non-biodegradable, thereby making them inappropriate either for decomposing or land-filling. Accordingly, thermal decomposition by pyrolysis or incineration of these materials are becoming promising alternative to conventional disposal methods.

SBR is the conventionally used type of synthetic rubber with its consumptions for all applications is being $4 \times$ that of polybutadiene, and $1.5 \times$ that of all other elastomers combined [2]. Thermal treating of tires and rubber has received extensive attention [1]. Waste tires could be decomposed and its final products are vapor, liquid oil and soot. By thermopyrolysis process at a constant heating rate, the main gas products were H_2, CO, CO_2, CH_4, C_2H_6, C_4H_6. The proportion of gas products were approximately 10% [3]. By thermal decomposition of tires with a fluidized bed, at 600°C, liquid oil proportion could reach 40%; moreover, H_2, CH_4 and other hydrocarbon increased when the temperature was raised [4]. At 800°C, vaporous products were 34.3%, whereas increasing detention time facilitates the formation of methane, hydrogen, benzene and toluene. There was a slightly increasing tendency of CO and CO_2 in longer retention [5]. Dellinger et al. [6] used differential scanning calorimeter and derivative thermogravimetric analysis to: (a) examine the peak temperature and product yields of nature rubber, polybutadiene rubber, and SBR in nitrogen at a heating rate of 10 K/min, and (b) obtain information on oil/plasticizer, carbon black, and inorganic content. Several previous studies examined the feasibility of thermally decomposing of commercial sample of butyl rubber [7] and epoxy resin [8] to determine the activation energy and kinetics in nitrogen. In addition, studies on the products and the effects during the thermal decomposition were made on the polystyrene [9] and acrylonitrile-butadiene–styrene, polyethylene and high density polyethylene [10]. All these informations are very important in determining the reaction rate of pyrolysis. Yet, no related data about the gas products of SBR under the atmosphere pressure condition in the previous studies has been reported. Therefore, the thermal decomposition of SBR under inert atmosphere, particularly when partial oxygen is presented, deserve further investigation.

This paper investigates the thermal decomposition of SBR under non-isothermal conditions. Experiments were performed for various heating rates (2, 5, 10 and 20 K/min) with oxygen–nitrogen (5%, 10% and 20% O_2) as the carrier gas. Effects of heating rate, oxygen concentration rate in carrier gas on the gas-products formation were also examined. Gas variation explored in this experiment can not only establish the

Table 1
Properties of SBR sample

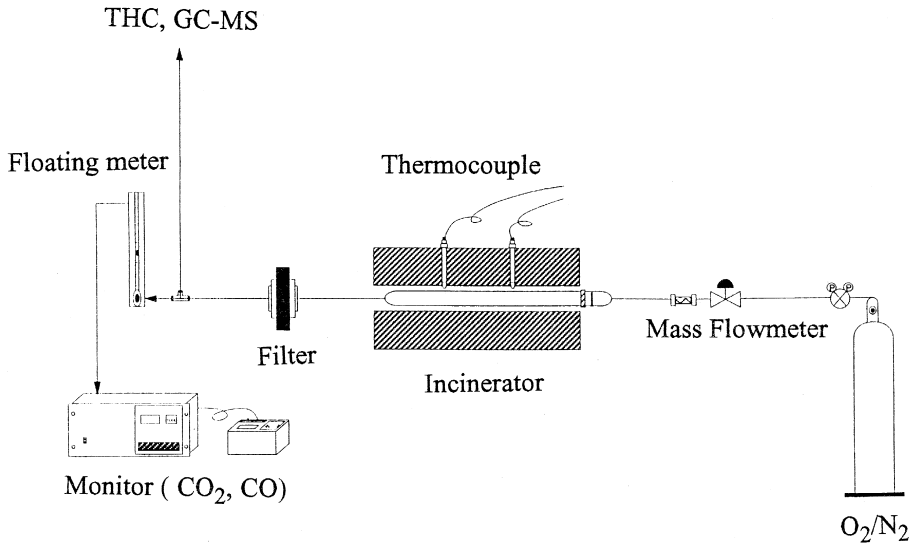| Proximate analysis	Low heating value	Elemental analysis
Water: 13.8%	10,091 (Cal/g)	C: 89.03%
Combustile: 98.58%		H: 10.92%
Ash: 0.04%		Others: 0.05%

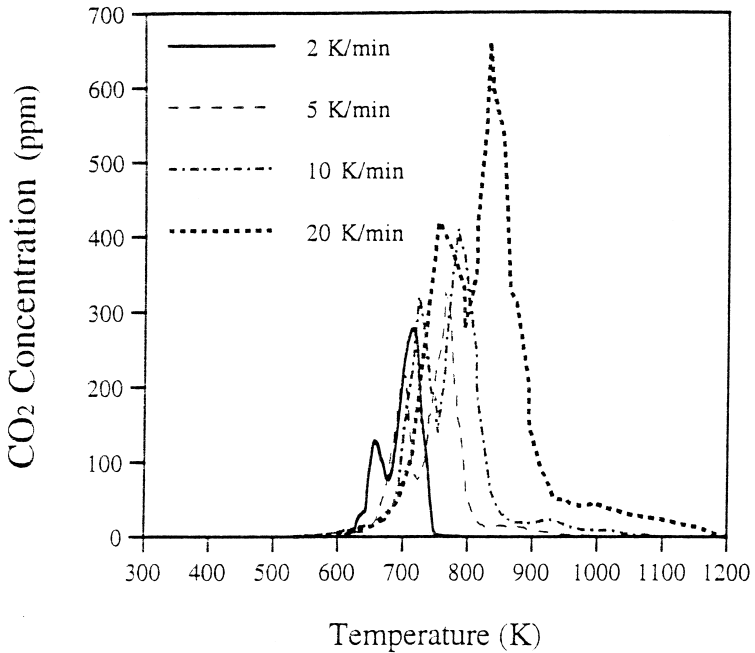Fig. 1. Schematic of the experimental apparatus.

Fig. 2. Profiles of concentrations of CO_2 monitored at the outlet of the incinerator, as a function of temperature for various heating rates. Oxygen content: 10% O_2–90% N_2 atmosphere, flow rate: 0.9 l/min.

characteristics of gas products, but also allow the influences of conditions to be more thoroughly understood. Other by-products of thermal decomposition of SBR were also identified by gas chromatography/mass spectrometer.

2. Experimental

2.1. Test materials

The SBR samples used in this experiment, SBR 1502, were produced from Taiwan Synthesis Rubber, which was copolymerized from 23.5% styrene $(C_6H_5CH:CH)$ and 76.5% butadiene $(H_2C:CHHC:CH_2)$ monomers. No special sample preparation procedures were adopted, the sample simply being cut from the center of the batch. Table 1 lists the basic properties of the sample obtained by the elemental analysis and heating value test. The main elements are C (89.03%) and H (10.92%).

2.2. Incineration apparatus and procedures

Fig. 1 depicts the system used herein, which is composed of a reaction tube, gas inlet and outlet analyzer. A glass quartz tube is used to simulate the post flame region with
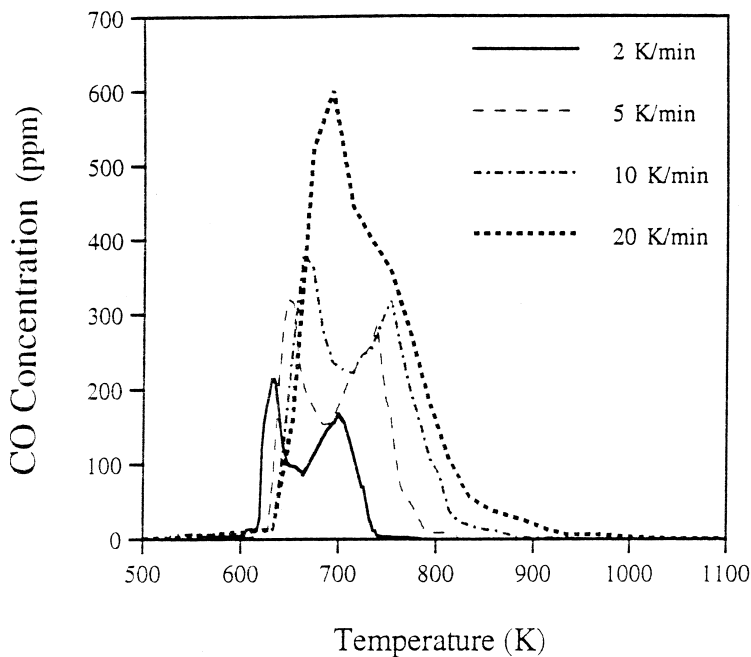

Fig. 3. Profiles of concentrations of CO monitored at the outlet of the incinerator, as a function of temperature for various heating rates. Oxygen content: 10% O_2 –90% N_2 atmosphere, flow rate: 0.9 l/min.

screwy top for loading in the tube's end. It is 90-cm long, 40-cm as main reaction region, 3-cm i.d. and reaction volume is 282.7 ml. Heating style adopted a heating coil in which temperature rising rate can be manually pre-set in the range of 0–20 K/min. Temperature was controlled by 9 PID (Tobishikosan) auto calculator. Temperature control was in the reaction tube's center with 2 R-Type thermocouple showing temperature and protecting surpass in both side 5 cm from the center. The stove, lay-down style, is made of stainless steel. The axial temperature profile was isothermally controlled (± 10 K error between 700 K-1280 K). Pipeline connecting was 2-m long, composed a stainless steel pipe (SS304), which included a flow meter (SIERRA Instrument, 0–10 l/min) and a floating meter (TOKYO KEISO, 0–2.0 l/min). The carrier gas was high purity (99.99%) of nitrogen–oxygen mixing gas (O_2: 5%, 10%, 20%). The test SBR was flattened to be a flake (1 mm in thickness and 0.8 cm in diameter) and filled in a quartz dish. In this study, the constant heating rates (2 K/min, 5 K/min, 10 K/min, 20 K/min) were set to elevate the temperature to 1000°C continuously.

2.3. Analysis of gas products

The concentrations of gas products in the effluent from the reactor were measured by two sampling ports: one was two monitors in a series for CO_2 and CO determination and the other was an outlet into a gas chromatography (Shimadzu 14B) equipped with a flame-ionization detector for total hydrocarbon (THC) determination. CO and CO_2 was
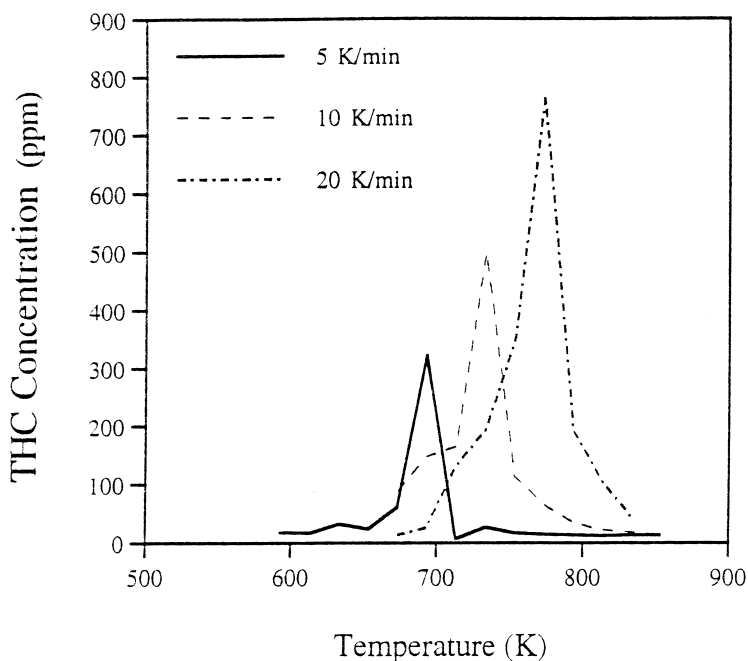

Fig. 4. Profiles of concentrations of THC measured at the outlet of the incinerator, as a function of temperature for various heating rates. Oxygen content: 10% O_2 –90% N_2 atmosphere, flow rate: 0.9 l/min.

measured by continuous emission monitors (CEMs) identified by EPA. CO detector was Model 300 made by American API of 0.5 ppm limited. CO_2 monitor was ZRF infrared gas analyzer made by Fuji Electric of 0.05 ppm limited. THC was calibrated by CH_4 standard gas. To identify the components of organic products, in the same manner, we injected the exhaust sample 15 ml to a gas chromatography/mass spectrometer (GC-MS) system (Shimadzu QP 2000A). The GC was equipped with a capillary column (0.22 mm × 25 m, 25 QC2/BP624), which was directly interfaced to a quadruple mass spectrometer. Standard procedures of gas analysis using GC and MS were employed throughout the experiments.

3. Results and discussion

The complicated processes occur [11] when polymer are subjected to heating conditions or burning conditions. Anderson and Freeman [12] explained the volatile formation mechanism of polystyrene and polyethylene by means of rate curves. They found that the predominant processes in the formation of volatile appeared to be the intermolecular transfer of radicals. However, the above results did not provide a simple method to evaluate the volatile formation practically, in order to study the influence of
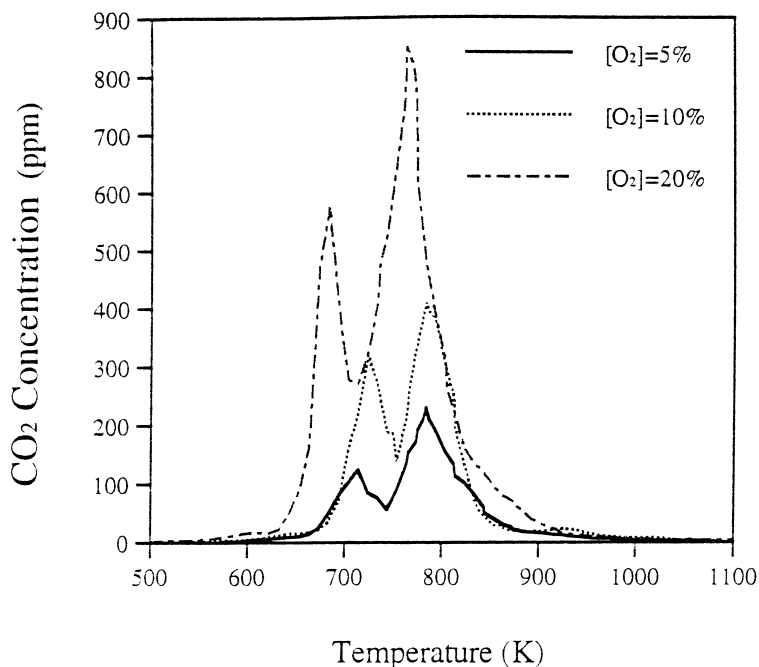
Fig. 5. Profiles of concentrations of CO_2 monitored at the outlet of the incinerator, as a function of temperature for various oxygen contents. Heating rate: 10 K/min, flow rate: 0.9 l/min.

operating conditions and the behaviors of volatile of SBR incineration. Therefore, the global and simple reaction is assumed:

$$SBR + O_2 \xrightarrow{k} CO_2, CO, THC \tag{1}$$

and k is the rate constant. According to the simple reaction, dominant volatiles are CO_2, CO and THC.

3.1. Effect of heating rate on gas-products formation

To find the behaviors of the gas products of the incineration of SBR, a constant heating rate method was used [13]. The furnace was heated at various heating rates (β) of 2, 5, 10 and 20 K/min in this experiments, respectively. Besides, the effects of the resistance caused by heat and mass transfer should be eliminated. The common way is to employ thin diskshape or fine powder samples, and high carrier gas velocities [14]. For this, several carrier gas flow rates were carried out. Experimental results show that the flow rate at 0.9 l/min were appropriate. The effects of sample weight on the reaction extent were also investigated. The results indicated the sample weights between 10 to 30 mg were observed to be negligible. Thus, the sample weight of SBR of 24 mg was performed for all experimental runs.
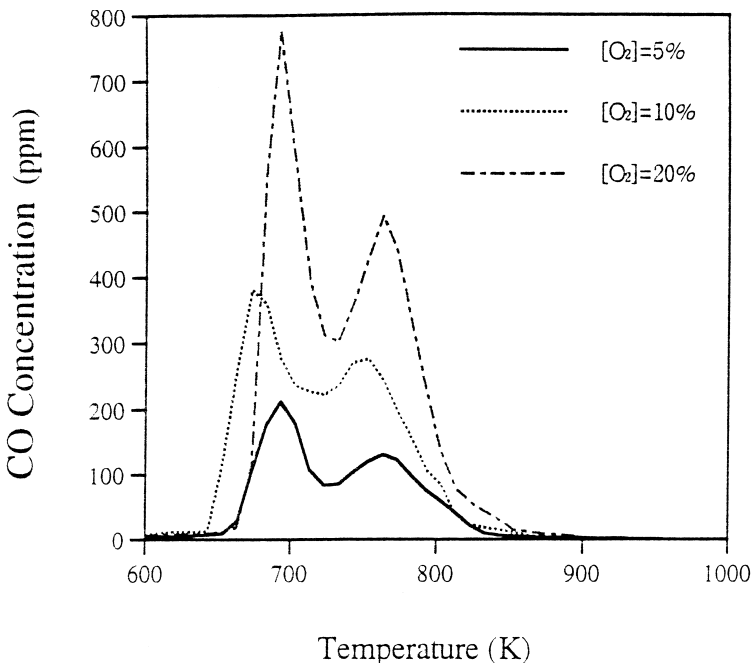

Fig. 6. Profiles of concentrations of CO monitored at the outlet of the incinerator, as a function of temperature for various oxygen contents. Heating rate: 10 K/min, flow rate: 0.9 l/min.

Figs. 2–4 display the concentrations of CO_2, CO and THC with respect to reaction temperature T under various heating rates in oxygen–nitrogen atmosphere (10% O_2). Obviously, all these curves have the same trends. According to Figs. 2–4, the first peak of CO_2 curve is lower than the second one but CO curve is completely opposite to that; the first peak is not obviously in THC curve. It is seen that the reaction zone shifts to the high temperature region and peak height increases with an increasing heating rate. That is, an increasing heating rate causes the starting temperature to increase and gas formation curve to move toward a high-temperature region. This effect is caused by the kinetic control and not by the heat transfer control for any heating rate when the reactions were finished. The gas formation rate is also of increasing tendency, that might be due to the higher energy and quicker reaction caused by a higher heating rate.

3.2. Effect of oxygen content on gas-products formation

The decomposition behaviors of SBR may also be compared by examining the profiles variations of concentration of gas-products formation with T at the same heating rate (10 K/min) and a fixed flow rate (0.9 l/min). It is found from Fig. 5 that the decomposition temperatures of SBR is observed to begin at about 650 K (at $[O_2] = 5$–20%). The CO_2 formation peaks become very rapid at 660 K when oxygen content increases. The reactions are nearly completed at about 950 K.
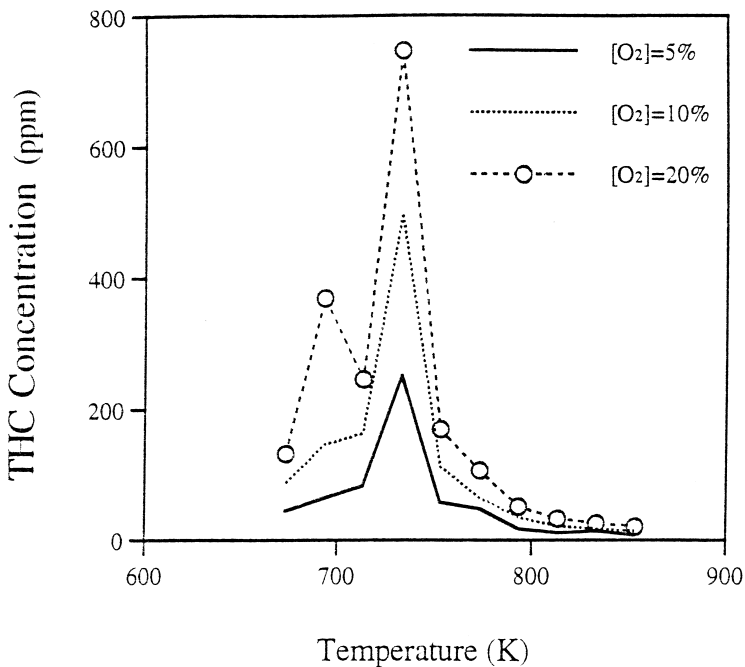

Fig. 7. Profiles of concentrations of THC measured at the outlet of the incinerator, as a function of temperature for various oxygen contents. Heating rate: 10 K/min, flow rate: 0.9 l/min.

Similarly, Figs. 6 and 7 present the CO and THC formation curves with various oxygen compositions. Figs. 6 and 7 illustrate that oxygen is beneficial to the formation of each species particularly at a high heating rate. When the oxygen content increases, the formation reaction is impelled and the starting temperature is reduced and shifts to a low temperature region. Moreover, as Figs. 6 and 7 reveal, two peaks appear (thus, two reaction stages) in CO_2 and CO curves, indicating that around 40% of the total mass of CO_2 and 60% of the total mass of CO are formed at the end of the first reaction, respectively. Moreover, the width of the first peak becomes narrower (i.e., the reaction time is shorter), but the peak height becomes bigger when the oxygen concentration increases.

3.3. Apparent activation energy

The methods for calculating the apparent activation energy from the experimental data have been developed by several investigators (Friedman [15], Westbrook and Dryer [16]). The overall rate equation for the gas product is expressed in Arrhenius form as:

$$\frac{dC}{dt} = A \cdot \exp\left\{ - \frac{E}{RT} \right\} \cdot (1 - \alpha)^n \cdot [O_2]^m \tag{2}$$

where

$$\alpha = \frac{W_o - W}{W_o - W_f}$$

and C is the concentration of gas product (ppmv), t is time (min), A is a pre-exponential factor l/min), E is the activated energy (Kcal/mol), T is the temperature of reaction (K), R is the universal gas constant, $[O_2]$ is the oxygen concentration (by volume) in carrier gas, W is the mass of the sample at time t, and W_o and W_f are the initial and final masses of the sample, respectively. The variation of the sample mass was measured by a photoelectric element and weight-measuring circuits [17]. α is the fractional conversion factor.

Then, taking natural logarithms of Eq. (2) yields:

$$\ln\left[\frac{dC}{dt} \right] = - \frac{E}{RT} + \ln\left\{ A \cdot (1 - \alpha)^n \cdot [O_2]^m \right\}. \tag{3}$$

For a fixed $[O_2]$ and α the second term on the right-hand side of Eq. (3) is a constant. Thus, a plot of $\ln\left(\frac{dC}{dt}\right)$ vs. $1/T$ for various heating conditions should yield a straight line, whose slope is $-\frac{E}{R}$. Hence, the apparent activation energy can be obtained from the average value of the activation energy for different α. All the values of α are normalized between 0 and 1.

The apparent activation energy of gas products under different conversions are illustrated in Figs. 8–10. Fig. 8 plots the apparent activation energy of CO_2 vs. conversion (α) for the overall reaction for various oxygen concentrations. The results indicate that the average activation energy of CO2 formation is about 17.1 Kcal/mol (for 5% O_2) and is 15.1 Kcal/mol (for 20% O_2) for $0 \leq \alpha \leq$. It is seen that when
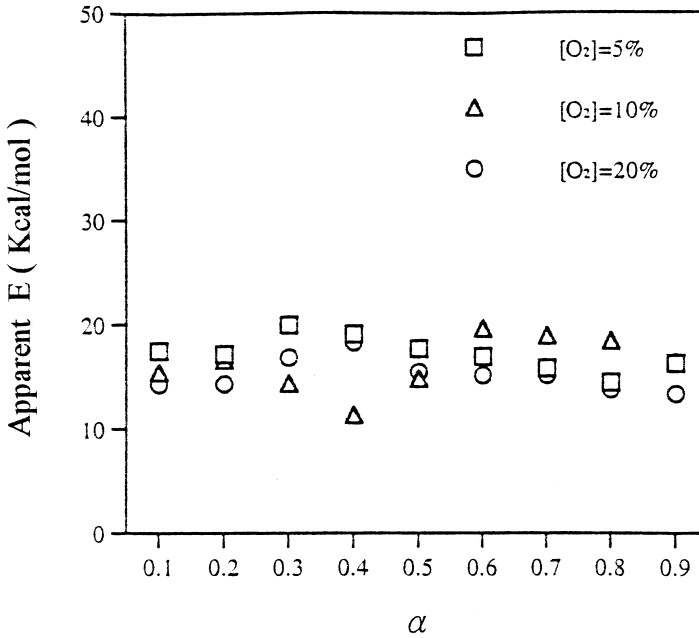
Fig. 8. Apparent activation energy of CO formation vs. conversion factor for various oxygen concentrations.
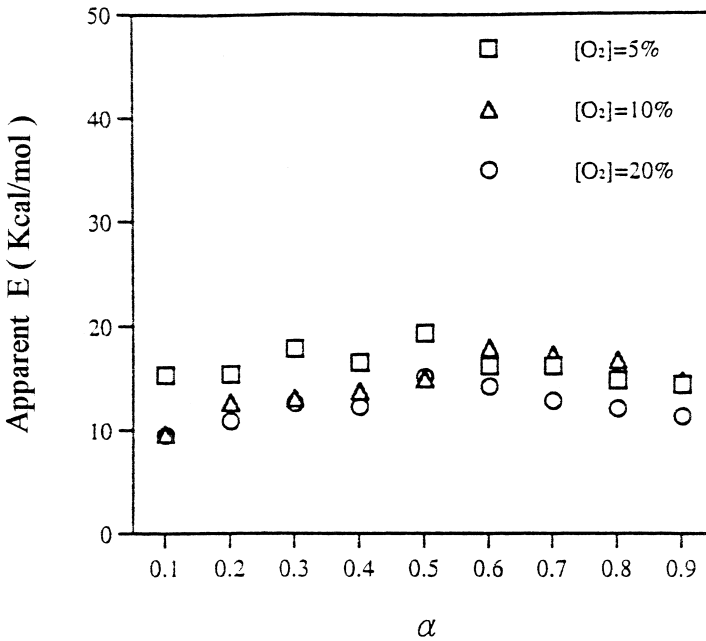

Fig. 9. Apparent activation energy of CO formation vs. conversion factor for various oxygen concentrations.
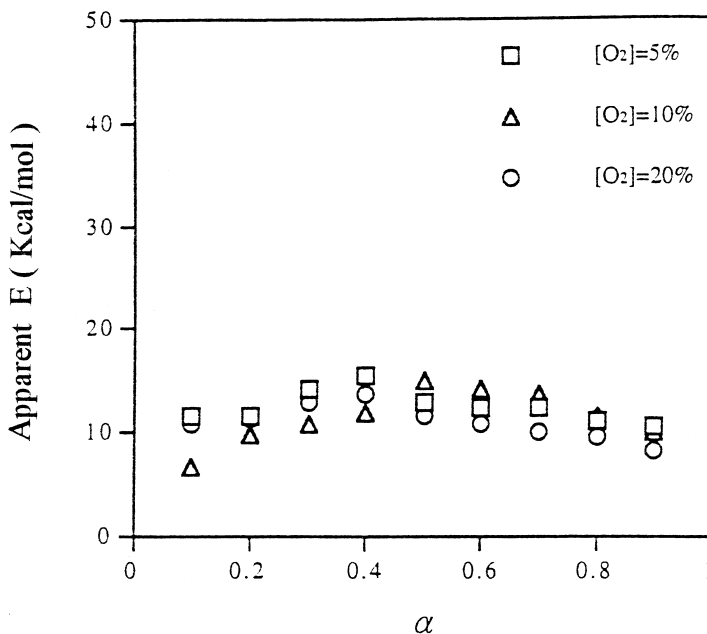
Fig. 10. Apparent activation energy of THC formation vs. conversion factor for various oxygen concentrations.

oxygen is present, the activation energy is lowered. Figs. 9 and 10 plots the apparent activation energy of CO and THC vs. conversion (α) for various oxygen concentrations, respectively. Similar behavior is also found in Figs. 9 and 10. The measured average activation energy are in the range of 12.2 to 16.1 Kcal/mol for the reaction of CO formation; and are 11.0–12.5 Kcal/mol for the reaction of THC formation.

3.4. Organic products identification

The volatile formation mechanisms of polymer pyrolysis have been studied by several workers [9,12,16]. For this, the volatile product composition may consist of styrene, toluene, benzene, ethylbenzene, acetylene, ethylene and α-methylstyrene for polystyrene (PS) pyrolysis. However, they did not provide the volatiles composition data under the oxygen-rich conditions. In this investigation, the composition of organic volatile products has been examined by GC-MS for SBR incineration; and exhaust gas from reactor was accumulated for species identification. A typical chromatogram for major products of degradation of a 24 mg SBR sample for the heating rate of 10 K/min and 20% oxygen concentration is shown in Fig. 11. Fig. 11 indicates that among the organic species in the gas by-products include 1-butane, 2-propanone, 1-methylcyclopentene, benzene, toluene, 1–4 ethenylcyclohexene, xylene, styrene and propylbenzene. It is worth noting that McNeill et al. [9] reported the volatiles included styrene, toluene, benzene, ethylbenzene for PS pyrolysis; and those species are also found in the volatile product composition of SBR incineration in this work. This finding suggests that the

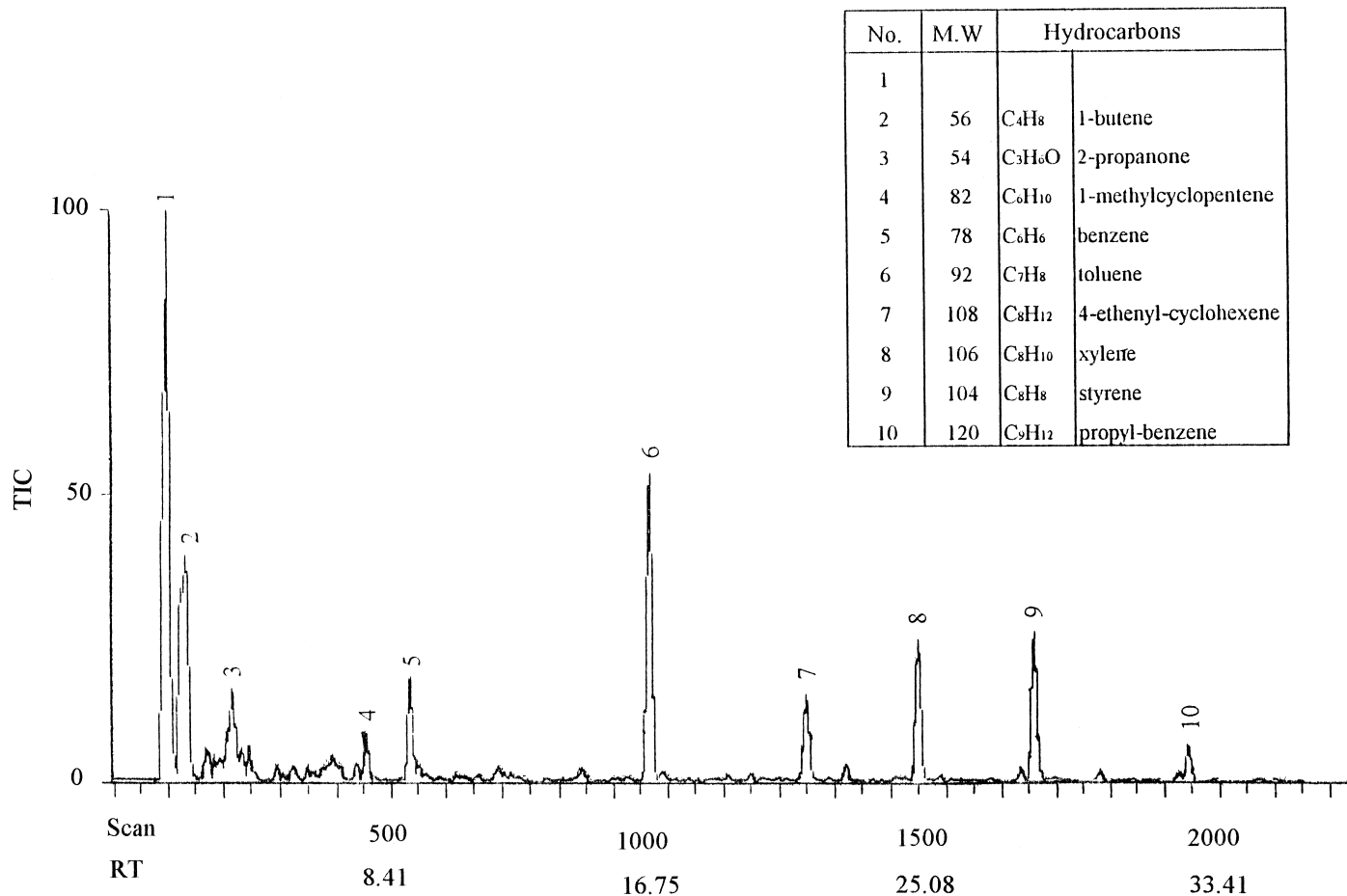| No.	M.W	Hydrocarbons	
1			
2	56	C_4H_8	1-butene
3	54	C_3H_6O	2-propanone
4	82	C_6H_{10}	1-methylcyclopentene
5	78	C_6H_6	benzene
6	92	C_7H_8	toluene
7	108	C_8H_{12}	4-ethenyl-cyclohexene
8	106	C_8H_{10}	xylene
9	104	C_8H_8	styrene
10	120	C_9H_{12}	propyl-benzene

Fig. 11. Identifications of hydrocarbon products measured at the outlet of the incinerator for 20% oxygen, 0.9 l/min flow rate and 10 K/min heating rate.

aromatics hydrocarbons with benzene-ring account for a large portion of hydrocarbons under nitrogen-rich and oxygen-rich conditions. These hydrocarbons forming are probably owing to the involvement of the free radicals produced from SBR decomposition and monomers recombination processes.

4. Conclusions

This work investigates thermal decomposition of SBR by a lab-scale incinerator for the heating conditions of 2, 5, 10 and 20 K/min with oxygen–nitrogen as the carrier gas. Effects of oxygen composition in the range of 5% to 20% at a fixed flow rate 0.9 l/min are also examined. These results demonstrate that the heating rate obviously affects the volatiles concentrations of SBR decomposition. A rising heating rate not only causes the proportion of gas products to increase but also the reaction region to shift toward a high temperature region. Two reaction stages are found in CO_2, CO and THC formation. When oxygen content in carrier gas increases, CO_2, CO and THC concentration increase as SBR decomposes relatively. When oxygen is present, the apparent activation energy of volatile composition is lowered, the presence of oxygen reduces the apparent activation energy and enhances the reaction rates. The major species of organic hydrocarbons are butane, propanone, benzene, toluene, xylene, styrene and 4-ethenyl-cyclohexene for the incineration of SBR.

Acknowledgements

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