

Microwave induced thermal conversion of Ethylene-Vinyl Acetate copolymer/Natural rubber composite from shoe sole scrap

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Abstract

Pyrolysis and gasification processes were utilized in order to evaluate the feasibility on production of value added fuels from ethylene-vinyl acetate copolymer/natural rubber composite (EVA/NR) which is in form of scrap shoe sole. The heat for thermal conversion was supplied via novel microwave induced heating using silicon carbide (SiC) as microwave absorber. The thermal conversion temperature ranged from 500-1,000°C which could be reached within a few minutes by microwave system depending on power levels. The conversion reaction took place in 100%Ar, 99%Ar and 1%O₂ atmosphere. It was found that the gas fraction increased when microwave power increased at all experiments and produced gas with high content of hydrogen. A comparison of microwave heating with electrical furnace showed that microwave heating produced more gas fraction. Moreover, the gas from the microwave has higher H₂ and CO₂ contents than electrical furnace.

1. Introduction

Nowadays, plastic wastes from petrochemical industry are important environmental problems because of their tremendous amount and durable nature. Variety of plastic products provides fundamental contribution to our modern society such as building materials, packaging materials, and equipments. Unfortunately, these products are a starting point of plastic waste management problems. Common ways to deal with these wastes are landfill and incineration. However these methods are not sustainable solutions in the long run. Moreover, landfill has become more difficult because of resistance by nearby populations and lack of available space in many regions. In many cases, landfill would result in contamination of soils and underground water. In the

same way, incineration generates toxic gas such as CO, SO_x, NO_x, dioxins, etc [1] depends on type of raw materials. Because of these reasons, thermal conversion under sub-stoichiometric condition is one of interesting plastic wastes treatment process.

Thermal conversion under sub-stoichiometric condition may be broadly categorized as pyrolysis and gasification. Pyrolysis is a process in which decomposition of materials (i.e. polymer) occurs in the absence of oxygen or in an inert atmosphere at high temperature to break their structure into smaller fractions such as monomer, dimer, and oligomer. Gasification is similar to pyrolysis but limited oxidizing agents in atmosphere are present and the products typically contain higher gas fraction than pyrolysis [2]. These thermal conversions differ from incineration because they allow the recovery of chemicals with added value, depend on the type of waste, time, temperature, and reactor used in the process. These products can further be used as fuels replacing petroleum products or as raw materials in many industries.

In conventional process, the system is heated by fuel burner that requires long startup/shutdown time and storage of combustible fuels. Uneven distribution of energy inside the reaction chamber and raw materials along with low efficiency are also common for conventional heating. Microwave induced thermal conversion is a novel process that uses high dielectric material which can absorb microwave radiation and then the energy is transferred to heat materials which cannot absorb microwave radiation i.e., one with a very high transparency to microwave such as plastic waste, municipal solid wastes and waste tire [3] which have a very high transparency to microwaves.

In this method, temperature can be adjusted by varying microwave power [4]. In addition, this operation requires short time to attain high temperature that is high enough for molecular fragmentation [5-9]. Due to high heating rate achieved, it may be called flash or fast pyrolysis. This heating process is very effective since heat will be evenly distributed throughout the reactor and the transformation of electricity to microwave energy is known to be very efficient results in energy saving of the overall process. In some cases, temperature of microwave heating can reach 1,000 °C in less than 6 minutes during start up period [8]. The operation of microwave system is also relatively safe as the temperature inside the reactor chamber will drop down rapidly as soon as the power is turned off with no residual heat like that of conventional heating.

The plastic waste produced by shoe manufacturers is a matter of great concern. The main component of this waste is ethylene vinyl acetate copolymer/natural rubber composite (EVA/NR) which is sole components. Shoe sole scrap is composite materials that have three layers. The top and bottom layers are consisted of 70% NR blend with 30% EVA, whereas the middle layer is made from 70% EVA blend with 30 % LDPE. It is regrettable that shoe sole scrap from industry has a large amount of about 20% by weight of EVA/NR sheet before cutting to size. Because of this reason, these scraps are usually discarded and creating problem for waste management. On the other hand, there is enormous potential to reduce shoe sole scrap by converting them to other useful products using thermal conversion method.

The objective of this work is to study the thermal conversion of ethylene vinyl acetate copolymer (EVA)/natural rubber (NR) composite from shoe sole scrap by microwave induced and conventional thermal conversion processes. Investigation of product distribution at different microwave power, carrier gas, and ratio of microwave absorber (silicon carbide, SiC) is carried out in order to determine the optimum operating condition.

2. Experimental procedure

2.1 Materials

EVA/NR scrap is supplied from local company. It is first ground and sieved into evenly distributed sizes of around 0.5-1.0 mm. Thermal degradation properties of EVA/NR is determined by thermogravimetric analysis (TGA, Metler-Toledo, TGA/SDTA 851[®]) under nitrogen atmosphere at temperature between 60-600°C as well as elemental analysis using CHON/S analyzer. Microwave absorber in this research is silicon carbide (SiC) that has the same size as ground EVA/NR.

2.2 Equipments

The main reactor for thermal conversion is made of quartz tube with 0.8 and 1.3 mm inner and outer diameter, respectively. Quartz wool was placed at the bottom of the quartz tube as a raw materials retainer. Microwave oven equipped with inverter was modified and used as microwave power source to ensure smooth and continuous power supply to the reactor. Temperature inside the reactor was measured on-line by R-type thermocouple. Gas products were collected in Tedlar gas sampling bags (Cole-Parmer, USA).

2.3 Instrument

Thermal degradation of raw materials was studied by TGA and elemental analysis technique was applied to determine CHON/S composition. Pyrolysis gas and liquid products were analyzed by gas chromatography technique using a Varian CP-3800 gas chromatography coupled to Varian Saturn 2200 mass spectrometer equipped with a CP-Sil 8 CB low bleed capillary column with 1.0 micron thickness coating of 95% dimethyl polysiloxane, 0.32 mm inner diameter and 30 m long. Permanent and light hydrocarbon gases were characterized by gas chromatography equipped with a Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD).

2.4 Methodology

Before the operation, EVA/NR and silicon carbide were mixed according to predetermined volume ratio and packed into quartz tube by sandwiching EVA/NR layer between silicon carbide layers. The thermal conversion of EVA/NR composite was carried out in a single process using microwave cavity [10]. Experiments was carried out by insertion of quartz tube into microwave chamber by vertically suspending the quartz tube at the middle of the cavity and plugging type R thermocouple into the raw material bed for acquisition of temperature profile during the experiment as shown in figure 1.

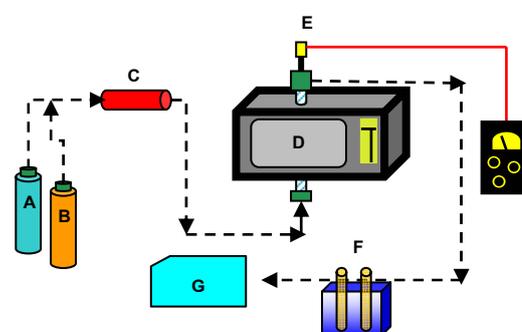


Figure 1 Schematic of microwave operation of thermal conversion set-up. **A)** argon (Ar); **B)** air zero; **C)** automatic gas flow controller; **D)** microwave oven; **E)** R-type thermocouple; **F)** condenser; **G)** gas sampling bag.

In order to maintain the atmosphere during the operation, gas with desired fraction at flow rate of 100 ml/min was passed through the reactor for 10 minutes prior to each run. Atmosphere in this operation are composed of two different components; 100% Ar and 99% Ar/1% O₂. Gas feed was controlled by automatic mass flow controllers to maintain total flow of 100 ml/min. Input power of microwave oven was varied from 110, 330, and 550 watts. Silicon carbide was employed as microwave absorber. Thus, difference amounts of silicon carbide ratio, 1:1 and 2:1, per EVA/NR was studied. Accurate measurement of temperature evolution during the process was very difficult because there are effects of microwave radiation to electronic apparatus as well as arching phenomena of thermocouple in the reactor which give rise to hot spots. Some of volatiles evolve during the operation may be condense on thermocouple which also effect the measurement. The gas product was passed through ice-cooled condenser for trapping of condensables and light gas was collected in series of gas sampling bags. First sample is collected from 0-180 seconds and the second one obtained at 181-360 seconds. After each run, dichloromethane (DCM) was used to dissolve condensable products in condenser and gas line then collected for further analysis. Weight of oil was measured by dry DCM at room temperature and weight oil after dried. The solid and oil fraction yields were directly calculated from measured weight of each fraction, while gas yield was evaluated by difference.

For comparison, EVA/NR was operated in an electrical furnace using same quartz reactor, quantity, reaction time, and atmosphere. The temperature was set at 700°C and EVA/NR was heated to this temperature at the maximum heating rate Thermal conversion products were collect and analysis in the same manner as microwave heating experiments.

3. Results and discussion

3.1 EVA/NR analysis

The yield of the elemental composition of EVA/NR was performed using elemental analyzer and summarized in table 1. From the result, carbon content is highest with appreciable amount of oxygen. This suggested that EVA/NR is suitable for production of fuel components.

Table 1 Elemental composition of EVA/NR

Element	% Content
%C	57.6
%H	8.3
%N	1.3
%O	32.8

Thermal decomposition of EVA/NR can be observed by thermogram in figure 2. The degradation curve of EVA/NR displayed two decomposition steps. First decomposition step appeared around 300-360°C and weight loss increased from 91% to 58% of initial sample weight From literature survey [9], the first decomposition step corresponded to deacrylation group of vinyl acetate with elimination of acetic acid and formation of double bond the first step range of 250-350 °C was also observed by N. Gupya *et al* [9]. Second decomposition step was detected around 400-500°C where weight loss increased from 56% to 33% which is corresponded to the decomposition of polyene domain which comes from VA units and polyethylene domains corresponding to the initial ethylene units. The results imply that the polymer backbone and other associated organic compound were decomposed by 500°C.

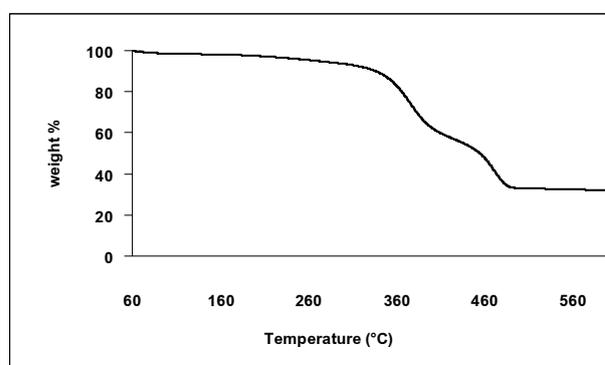


Figure 2 TGA thermogram of EVA/NR waste

3.2 Yields of different fractions

Figure 3 and figure 4 are the summary of the yields of different fractions obtained from the operation under inert and partially oxidized environments. The results indicated that increase in microwave power leads to increase in the portion of gas and decrease in solid fraction at all atmosphere and silicon carbide ratio that corresponding with findings from others using different raw materials as presented in table 2 and 3.

Table 2 Product yields from the pyrolysis of leather wastes obtained by and O. Yilmaz *et al* [15].

	Temperature	
	450 °C	600 °C
Char	44.5	38.1
Oil+Aqueous	32.0	28.9
Gas	17.8	23.6

Table 3 Effect of temperature on the product yields from electrical furnace and microwave heating of sewage sludge [12].

	Temperautre		
	500 °C	800 °C	1,000 °C
Microwave heating			
Solid	30.2	25.5	22.7
Oil	7.9	9.2	8.6
Gas	61.9	65.3	68.7
Electrical furnace			
Solid	29.2	25.3	24.1
Oil	13.6	11.8	11.3
Gas	57.2	62.9	64.6

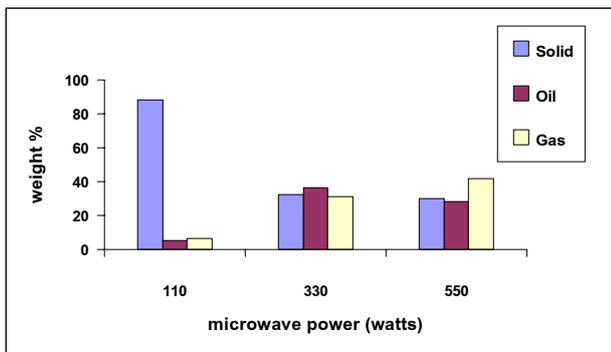


Figure 3 Distribution of products at silicon carbide ratio 1:1 under 100% Ar atmosphere.

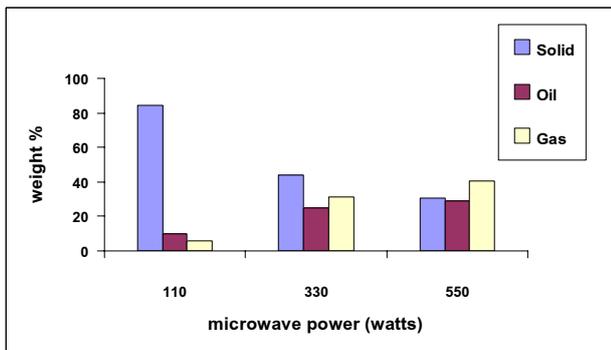


Figure 4 Distribution of products at silicon carbide ratio 2:1 under 100% Ar atmosphere.

The gas (non-condensable gases) fraction is one of the important fractions which quantity depends on thermal conversion conditions used in the experiments such as heating rates, temperature and atmosphere. From the literature [6, 10-15] and shown here in table 3, gas product increase with temperature but oil and solid products decrease, thus high heating rates and temperature tend to favor the formation of gaseous products that is corresponding to A. Domínguez *et al* [8] who found that high heating rate at temperatures higher than 650°C favored the

formation of gaseous products from pyrolyzed sewage sludge. Moreover, since temperature in microwave heating increases with microwave power, hence at 550 watt microwave power, higher gaseous products were measured than lower microwave power in both SiC ratios which shown in figure 3 and figure 4. Solid residue at 110 watt microwave power is of very high fraction because temperature of the system is not sufficient to breakdown EVA/NR and almost of them cannot decompose.

Analysis of the composition of the gaseous products revealed that H₂, CO, CO₂, and other light hydrocarbons are the main products that corresponding with A. Marcilla *et al* [13]. The operation under 99% Ar 1% O₂ can produce higher H₂ (table 4) than under 100% Ar atmosphere because when higher oxygen appears in the system, gasification process takes place and supports the formation of fuel gases. Thus, with microwave power increase from 110-550 watts, CO₂ content increase (table 5) when operated under 100% Ar and 99% Ar/1% O₂ atmosphere. In contrast, lower fraction of CO₂ was reported with other authors [8, 10, 12] that show in table 6 and table 7. The increase of CO₂ in this research may result from high oxygen content in raw material as well as high heat transfer rate to EVA/NR that molecular structure are suddenly decomposed and CO₂ is formed quickly, migrates from heated area and flushed out of reactor by carrier gas. In the other word, CO₂ production is higher than rate of CO₂ to react with carbon compound (reaction (1) and reaction (2)). Moreover, the higher CO₂ production may result from the high degree of deoxygenation of EVA during experiments (decarbonylation and decarboxylation). Some reactions between carbon containing compounds with CO₂, O₂, and H₂O may be presented by these equations.

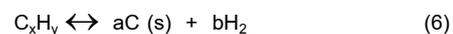
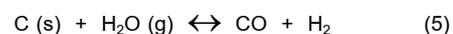
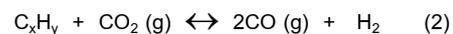
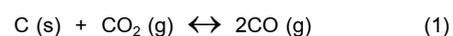


Table 4 Conversion to H₂ from the operation with silicon carbide ratio 1:1

Microwave power	Weight x10 ⁴ (g)	
	Ar	Ar/O ₂
110	0.0	0.0
330	0.3	1.1
550	61.1	190.8
Electrical furnace	0.0	0.0

Table 5 Conversion to CO₂ from the operation with silicon carbide ratio 1:1

Microwave power	Weight x10 ⁴ (g)	
	Ar	Ar/O ₂
110	174.7	25.8
330	55.0	93.5
550	121.4	215.7
Electrical furnace	128.2	106.4

Table 6 Composition of H₂ and CO₂ (%vol) of sewage sludge at different temperature from microwave heating obtained by A. Domínguez *et al* [12].

	Temperature		
	500 °C	800 °C	1,000 °C
H ₂	35.6	38.2	40.0
CO ₂	28.4	22.7	17.7

Table 7 Comparison of H₂ and CO₂ (%vol) from electrical furnace of sewage sludge obtained by A. Domínguez *et al* [12].

	Temperature		
	500 °C	800 °C	1,000 °C
H ₂	9.3	25.8	29.9
CO ₂	56.6	39.1	32.0

In 99% Ar/1% O₂, the weight of CO₂ increase with higher microwave power, because carrier gas have O₂ that gasification of EVA/NR would produce CO₂, reaction (4), at higher rate than from reaction (1) and (2). Microwave heating favors the production of H₂ via reaction (2) and (3) and CO₂ than electrical furnace (table 4, 6, and 7). This result is corresponding with A. Domínguez *et al* [8] that shown in table 8.

Table 8 Comparison of H₂ and CO₂ (% vol) from pyrolysis of sewage sludge at same temperature obtained by A. Domínguez *et al* [8].

	Microwave heating	Electrical furnace
H ₂	38.0	29.0
CO ₂	9.7	11.8

3.3 Effect of microwave power

From the results, when operating at 330 and 550 watt microwave powers, all of EVA/NR are converted to solid residue, oil, and gas product, except for 110 watt microwave power where temperature is lower than decomposition temperature of EVA/NR that almost of EVA/NR are still like as before the testing because microwave power is not sufficient to generated ample heat. Conversely, these affect are found clearly in 330 and 550 watt microwave power.

At higher microwave power, gases were produced in time range from 0 to 180 seconds. In contrast, gas collect time from 181 to 360 seconds have low concentration because reaction temperature can be raised 500-700 °C in 30-60 seconds and almost of EVA/NR is transform to gas product by then. Conversely, at 110 watt microwave power, gas content variation between 0-180 and 181-360 seconds cannot be observed. Moreover, higher at higher microwave power, oil products from the reaction were pyrolyzed simultaneously and help increase gas product fraction. Similarly, A. Domínguez *et al* [12] also reported the energy distribution of products for electrical furnace and microwave heating that show in figure 5. They found that, in the case of microwave heating the recovery of energy is very close to 100% at all temperature. This may be due to the fact that the increase in pyrolysis or microwave power increases the products of gas.

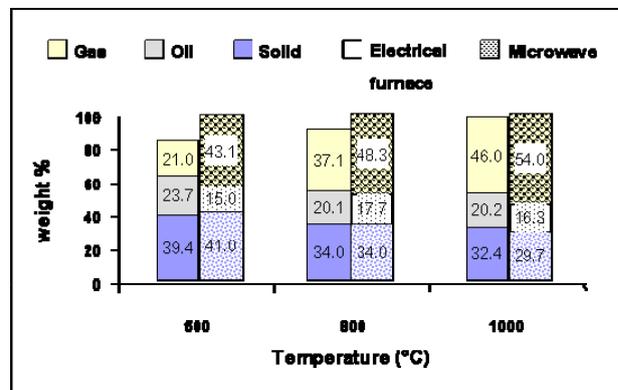


Figure 5 Energy distributions in each fraction from microwave heating and electrical furnace obtained by A. Domínguez *et al* [12].

Solid residue and oil fraction were decreased when microwave power increase in 100% Ar and 99% Ar/1%O₂ at all silicon carbide ratio. At 330 and 550 watt, gas and oil fraction yields were very similar because temperature increased from heat generated and transferred by SiC to raw material was at the same level on both wattages. This may due to the limitation of SiC on microwave absorption and heat transfer. When compare gas product between microwave heating and electrical furnace in figure 6 and figure 7, one can see that microwave heating

produced higher gas fraction than electrical furnace, especially in 99% Ar/1% O₂ atmosphere that described earlier.

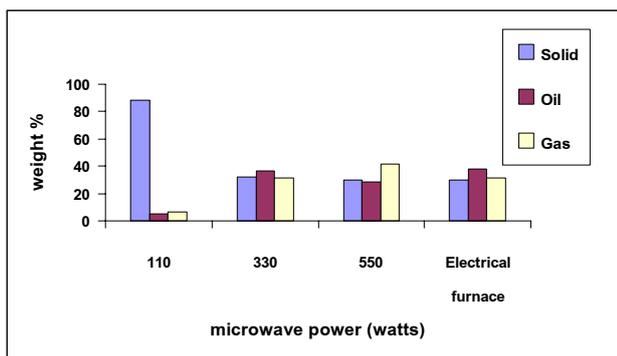


Figure 6 Product distributions between microwave heating and electrical furnace under 100% Ar atmosphere.

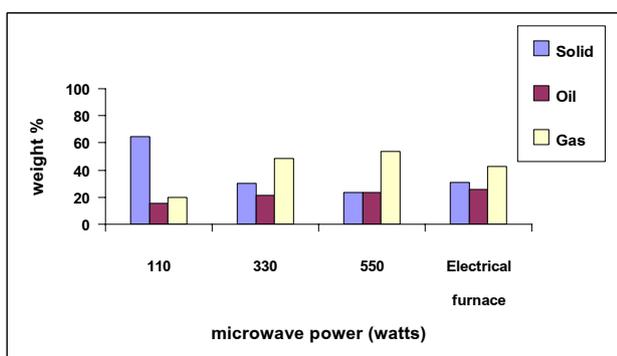


Figure 7 Product distributions between microwave heating and electrical furnace under 99% Ar/1% O₂ atmosphere.

Figure 6 and figure 7 are comparable with figure 5 from the research by A. Domínguez *et al* [12], increase in pyrolysis temperature leads to an increase in the production of gas and a decrease in solid and oil fraction. Solid fraction of microwave heating is close to electrical furnace but its oil fraction from microwave heating is clearly lower than that of electrical furnace. Moreover, gas fraction of microwave heating is higher than electrical furnace at all temperature. When electrical furnace is carried out on the sewage sludge mixed with microwave absorber, there is decrease in the oil yield and increase in gas portion with respect to the values obtained in electrical furnace in the absence of microwave absorber.

3.4 Effect of reacting gas

When compared the operation under 100% Ar and 99% Ar/1% O₂. Operation under 100% Ar atmosphere, generated higher light hydrocarbon than H₂. In contrast, H₂, CO, and CO₂ were obtained for atmosphere with 99% Ar/1% O₂. Light hydrocarbon contents were decreased from simultaneous reactions of gas, oil, and solid residue produced during operation. This is the gasification reactions where reactions of hydrocarbon and carbon in char with oxygen generate CO, CO₂ and H₂ which also reduced yields of oil, and solid residue (compare between

figures 3-4 and figures 8-9). On the other hand, these reactions are not dominant in electrical furnace and solid content is not different but oil fraction decrease and increase in gas fraction when operate under 99% Ar/1% O₂ that was shown in table 9. Under 99% Ar/1% O₂ atmosphere, higher content of H₂ and CO₂ than under pyrolysis condition can be measured. It is known that microwave heating favors the heterogeneous reactions between the pyrolysis gases and solid residue [12]. Reactions (2) and (6) may therefore be favored by the microwave heating. This would partly explain higher H₂ content in gases obtained from microwave heating compared with electrical furnace. In electrical furnace products distribution are different between 100% Ar and 99% Ar/1% O₂ that show in figure 10. Gas fraction in electrical furnace is higher in 99% Ar/1% O₂ in the same reason with microwave heating that described earlier.

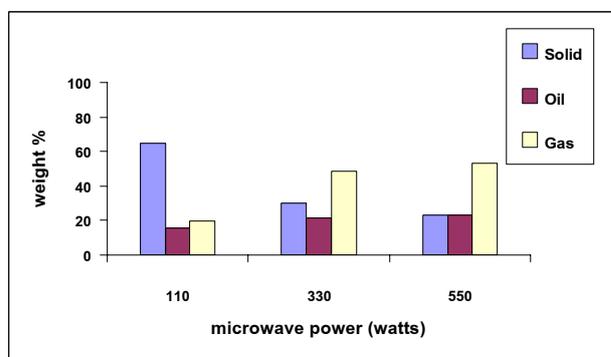


Figure 8 Distributions of product at silicon carbide ratio 1:1 under 100% Ar/1% O₂ atmosphere.

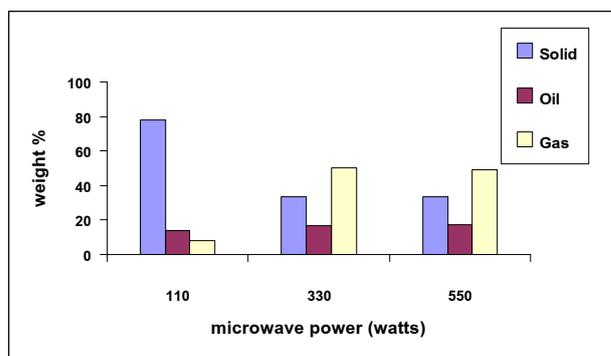


Figure 9 Distributions of product at silicon carbide ratio 2:1 under 100% Ar/1% O₂ atmosphere.

Table 9 Yield of different fraction obtained in thermal conversion with electrical furnace at 700°C.

Atmosphere	Weight %		
	Solid	Oil	Gas
Ar	30.3	38.1	31.7
Ar/O ₂	31.2	25.9	42.9

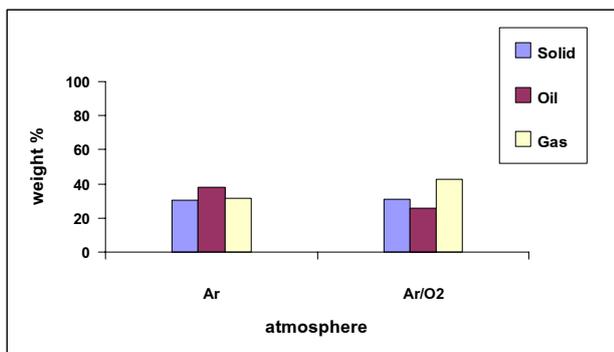


Figure 10 Distributions of product from electrical furnace compare between 100% Ar and 99% Ar/1% O₂ atmosphere.

3.4 Effect of silicon carbide ratio

The effect of silicon carbide ratio is not prominent due to limitation of distribution of microwave radiation in microwave oven. In the case of 1:1 silicon carbide, volume of raw materials (EVA/NR) in quartz tube is mostly in the area that microwave can uniformly radiate. In contrast for 2:1 ratio, it was later found that about 20% by volume of raw materials are out of area of direct microwave radiation, thus conversion cannot appreciably take place. All of the experiments, the qualitative composition of products are the same regardless of the ratio of silicon carbide. Because of this reason, it is recommended that microwave oven should have multimode apparatus to generate a standing wave pattern where more uniform radiation may achieved as compared to this research that utilized single mode microwave oven.

4. Conclusion

By applying microwave induced thermal conversion of EVA/NR waste by SiC as microwave absorber, EVA/NR can be rapidly heated with higher rate as microwave power increases. Thermal conversion under atmosphere of 1%O₂ balanced Ar generates higher content of H₂, and CO₂ than in 100% Ar atmosphere. In addition, higher production of H₂ and CO₂ was achieved in the microwave heating than that of conventional electrical furnace. Due to its high efficiency and ease of operation, further process design would enable this conversion method to become another option to conventional polymeric waste treatment which can be effectively practiced on-site for production of green energy from waste.

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