CHAPTER IV

RESULTS AND DISCUSSION

Discussion of the results obtained from this work is presented in two sections. The first section deals mainly on the raw materials characterization while the later focuses on the thermal conversion of raw materials at various conditions. The detailed results along with discussion are presented in this entire chapter.

4.1 Preliminary Tests

4.1.1 Elemental Analysis of EVA/NR

The elemental composition of EVA/NR sample was analyzed using an elemental analyzer. Table 4.1 shows results from the analysis.

Table 4.1 Elemental composition of EVA/NR

Element	% Content
C	57.6
H	8.3
N	1.3
O	32.7

From the result, carbon content is highest with appreciable amount of oxygen and hydrogen, thus this material can potentially be cracked or decomposed to become smaller gaseous molecules such as C_1-C_5 hydrocarbons. Carbon compound is exothermic reaction when burner which give energy to environmental. Combustion of hydrocarbon gases yields energy via exothermic reactions. This implies that EVA/NR may be suitable for production of fuel components or be utilized as chemical raw materials.

4.1.2 Thermal degradation of raw materials

Thermal degradation through pyrolysis decomposition of EVA/NR was investigated by TGA from 60-600 °C at the heating rate of 20 °C/min under inert atmosphere (N_2) of 20 ml/min flow rate. The thermogram of this analysis is shown in Figure 4.1. The degradation curve of EVA/NR exhibited 3 decomposition steps. First decomposition step took place around 300-360°C where weight loss changed from 91% to 58% of the initial weight of sample. From literature survey [26], this decomposition step corresponded to deacrylation group of vinyl acetate with elimination of acetic acid and formation of double bond as shown in Figure 4.2. According to N. Gupya et al [26], the first step occurred around 250-350°C. Second decomposition step was observed at 400-500°C in this work and 350-450°C as reported by N. Gupya et al. First and second decomposition stages found from this research was observed at higher temperature than N. Gupya et al may result from the EVA in this composite is in cellular form with partially crosslinks but EVA which N. Gupya studied was a commercial EVA in pallet form without any crosslink. Weight loss decreasing from 56% to 33% is corresponded to the decomposition of polyene domain which comes from VA units and polyethylene domains corresponding to the initial ethylene units. From the results, it may be concluded that the polymer backbone and other organic compound in the sample were absolutely decomposed by 500°C.
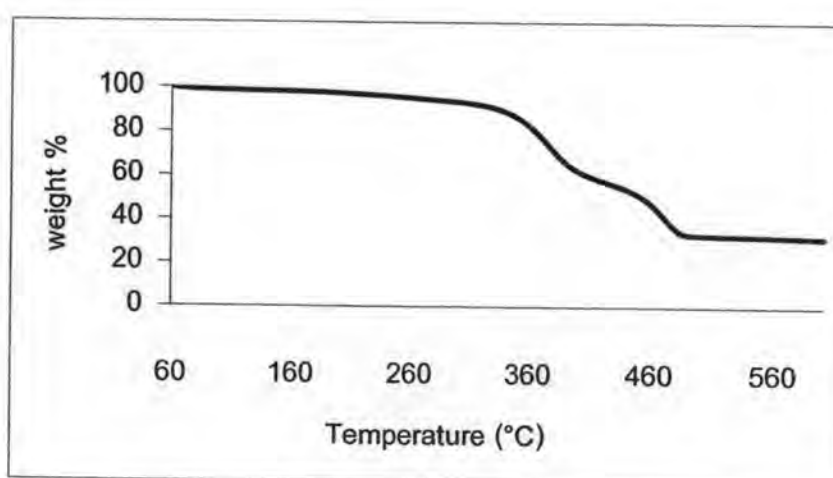

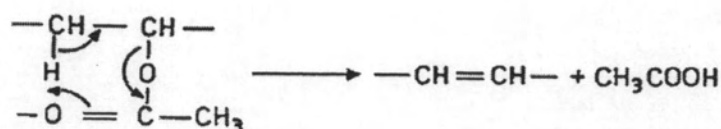Figure 4.1 TGA thermogram of EVA/NR composite.

$$-CH_2-CH- \longrightarrow -CH=CH- + CH_3COOH$$

Figure 4.2 Elimination of acetic acid and formation of double bond.

4.2 Thermal conversion products interpretation

Thermal conversion of EVA/NR composite was studied in order to investigate the influence of microwave power, carrier gas, and ratio of silicon carbide to the distribution of products. During the sample preparation, the total volume of EVA/NR and silicon carbide are 1 ml and 1.5 ml in the ratio of silicon carbide of 1:1 and 2:1, respectively. Hold time of the experiment is 360 seconds and product gas collection is separated into 2 periods, 0-180 seconds and 181-360 seconds. Gas products were characterized with Gas Chromatography with Flamed Ionized Detector and Thermal Conductivity Detector (GC/FID/TCD). FID detector is used for characterizing hydrocarbon compounds and TCD detector is used to analyze permanent gases such as H_2, CO, and CO_2. Quantitative determination of hydrocarbon gases range from C_1-C_5 and permanent gases was accomplished by comparing the GC response against standard mixed gases. The focus of this research is on the quality and quantity of hydrocarbon gases (C_1-C_5), permanent gases (H_2, CO, and CO_2), as well as phase distribution of from thermal conversion (solid, oil, and gas) at various conditions. In addition, these results were compared with yields from similar experiment using electrical furnace as heat source.

4.2.1 Product distribution

From the experiment, raw materials may be rapidly decomposed by microwave heating. Table 4.2 and 4.3 show the distribution of solid, oil, and gas products obtained from the operation at various conditions. The results indicate that raising microwave power (increase in temperature) leads to an increase in the production of gas and decrease in solid fraction at all atmosphere and silicon carbide ratio that corresponding with the literature values shown in table 4.4, table 4.5, and table 4.6. This result has effect from the reaction of solid residue with gas products and carrier gas (atmosphere)

during the operation. Moreover, higher temperature from greater microwave wattages can accelerate thermal cracking of EVA/NR molecule to convert to carbon containing products.

Table 4.2 Yield of the different fractions (wt%) obtained in thermal conversion under 100% Ar atmosphere with microwave heating and electrical furnace (700°C).

SiC :EVA/NR	Micrrowave power (watts)	Solid	Oil	Gas
1:1	110	88.3	5.1	6.6
	330	32.3	36.5	31.2
	550	29.8	28.5	41.7
2:1	110	84.5	9.7	5.8
	330	44.1	24.9	31.0
	550	30.9	28.8	40.3
	Electrical furnace	30.3	38.1	31.7

Table 4.3 Yield of the different fraction (wt%) obtained in thermal conversion under 99% Ar / 1% O_2 with microwave heating and electrical furnace (700°C).

SiC :EVA/NR	Micrrowave power (watts)	Solid	Oil	Gas
1:1	110	64.7	15.8	19.5
	330	30.0	21.4	48.6
	550	23.4	23.2	53.4
2:1	110	78.3	13.9	7.8
	330	33.4	16.5	50.1
	550	33.7	17.5	48.8
	Electrical furnace	31.2	25.9	42.9

Table 4.4 Pyrolyzed products yield of sewage sludge under inert atmosphere from A. Domínguez et al [21].

Sludge Type	Solid	Oil	Gas
A	34.8	10.3	54.9
B	43.7	13.1	43.2
C	49.4	4.7	46.2
D	22.9	19.7	57.3

Table 4.5 Product yield from the pyrolysis of leather wastes obtained by and O. Yılmaz et al [27].

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

Table 4.6 Effect of temperature on the product yields from electrical furnace and microwave heating of sewage sludge [28].

	Temperautre		
	500°C	800°C	1000°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

The non-condensable gas fraction is one of the important product which amount is due to the thermal conversion conditions used in the experiments such as heating rates, temperature and reacting atmosphere. Additional gaseous product formation also occurs by the cracking, depolymerization, and condensation reactions of volatile organic compounds derived from the primary thermal conversion of EVA/NR. From the literature [14, 21, 24, 27, 28, 29, and 30], and table 4.6, 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 [23] who found that high heating rate at temperatures higher than 650°C tend to favor the formation of gaseous products from pyrolyzed sewage sludge. Temperature and heating rate in microwave heating increase with microwave power. When microwave power increase, free ion on SiC have higher activity and movement. Thus, friction between ion and internal resistance of SiC can generate heat in shorter time than lower microwave power. The heating rate in microwave heating is higher than conventional heating and this high heating rate operation may be referred to as flash or fast pyrolysis. Because of this reason, 550 watt microwave power can generate higher gaseous products than at lower power in both atmosphere which shown in Figure 4.3

and Figure 4.4. Also note that solid residue at 110 watt microwave power is very high because temperature of the system is not sufficient to breakdown EVA/NR and most of them has yet to fully decompose.
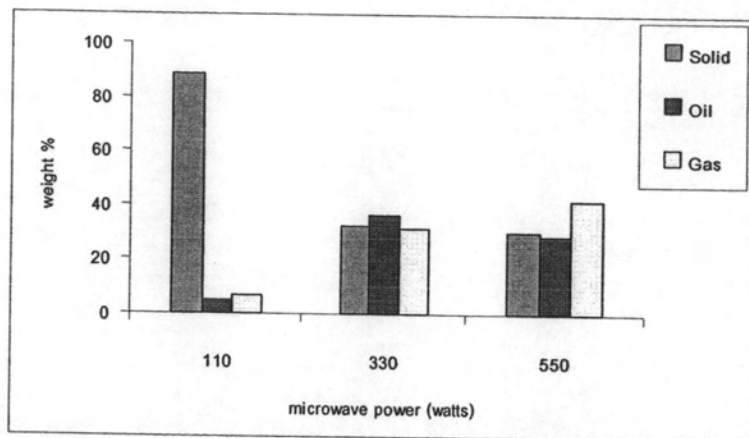

Figure 4.3 Distribution of products at silicon carbide ratio 1:1 under 100% Ar atmosphere.
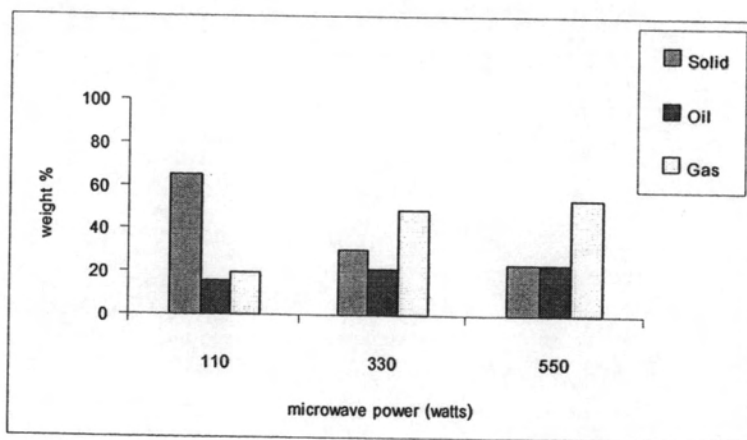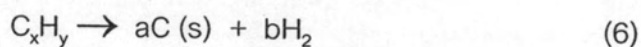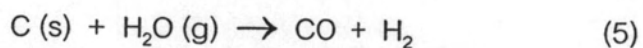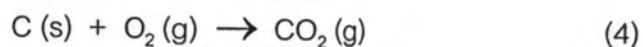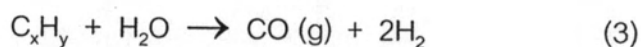

Figure 4.4 Distribution of products at silicon carbide ratio 1:1 under 99% Ar/ 1% O_2 atmosphere.

Analysis of the composition of the gaseous products revealed that H_2, CO_2, and other light hydrocarbons are main products that corresponding with A. Marcilla *et al* [29]. The operation under 99% Ar/1% O_2 can produce higher H_2 (table 4.7) than under 100% Ar atmosphere because when some oxygen presents in the system, gasification

process takes place and supports the formation of fuel gases including hydrogen. With microwave power increase from 110-550 watts, CO_2 content increase when operated under 100% Ar and 99% Ar/1% O_2 atmosphere. In contrast, lower fraction of CO_2 was reported with other authors [23, 24, 28] that show in table 4.8 and table 4.9. The increase of CO_2 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 CO_2 is formed quickly, migrates from heated area and flushed out of reactor by carrier gas. In the other word, CO_2 production is higher than rate of CO_2 to react with carbon compound (reaction (1) and reaction (2)). Moreover, the higher CO_2 production may result from the high degree of deoxygenation of EVA during experiments (decarbonylation and decarboxylation). Some reactions between carbon containing compounds with CO_2, O_2, and H_2O may be presented by these equations. Limited gas phase reactions found in this work are also confirmed by high CO_2 and very little CO detected in the product, as seen from reactions 2 and 3.

$$C\,(s) \;+\; CO_2\,(g) \;\rightarrow\; 2CO\,(g) \qquad\qquad (1)$$

$$C_xH_y \;+\; CO_2\,(g) \;\rightarrow\; 2CO\,(g) \;+\; H_2 \qquad\qquad (2)$$

$$C_xH_y \;+\; H_2O \;\rightarrow\; CO\,(g) \;+\; 2H_2 \qquad\qquad (3)$$

$$C\,(s) \;+\; O_2\,(g) \;\rightarrow\; CO_2\,(g) \qquad\qquad (4)$$

$$C\,(s) \;+\; H_2O\,(g) \;\rightarrow\; CO \;+\; H_2 \qquad\qquad (5)$$

$$C_xH_y \;\rightarrow\; aC\,(s) \;+\; bH_2 \qquad\qquad (6)$$

Light hydrocarbon and heavy hydrocarbon productions are observed by Gas Chromatography with flame ionization detector. Hydrocarbon gases increase when microwave power increases as shown in Figure 4.5. At 110 watt microwave power, the equivalent amount of hydrocarbon (as GC respond) was low but when operated at 330

and 550 watt microwave power, the hydrocarbon production significantly increased because greater molecular fragmentation rate occurs at higher temperature. Moreover, operation under 99% Ar/1%O_2 can generated higher hydrocarbon gases than 100% Ar because of the enhancement by gasification reactions occur by oxygen presented in carrier gas.

Figure 4.6 and Figure 4.7 show chromatograms which obtained from the analysis of gas product. When compare at 110 watt microwave power between 100% Ar and 99% Ar/1%O_2 atmosphere, higher contents of hydrocarbon gas are found in 99% Ar/1% O_2 that can be noticed from peak intensity in Figure 4.6 and Figure 4.7. This trend is similar among experiments at 330 and 550 watt microwave power as well as electrical furnace. In the other word, with higher microwave power, hydrocarbon gases are generated at higher amount at all atmospheres and are higher than that of electrical furnace heating. At 100% Ar atmosphere for 110 watt microwave power, hydrocarbon production is very low because heating intensity is not sufficient to appreciably decompose EVA/NR.
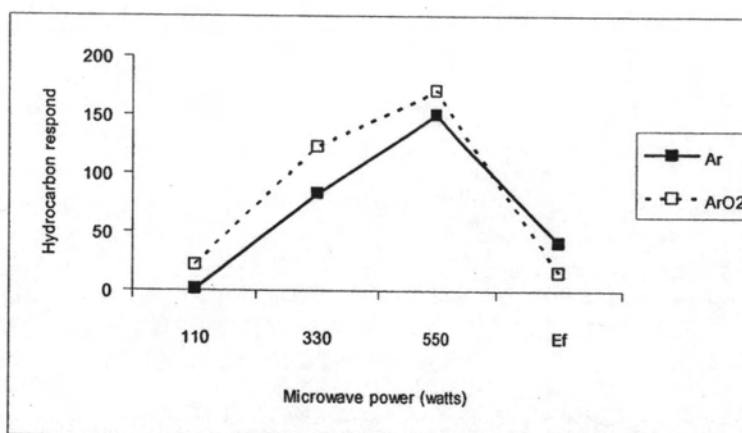

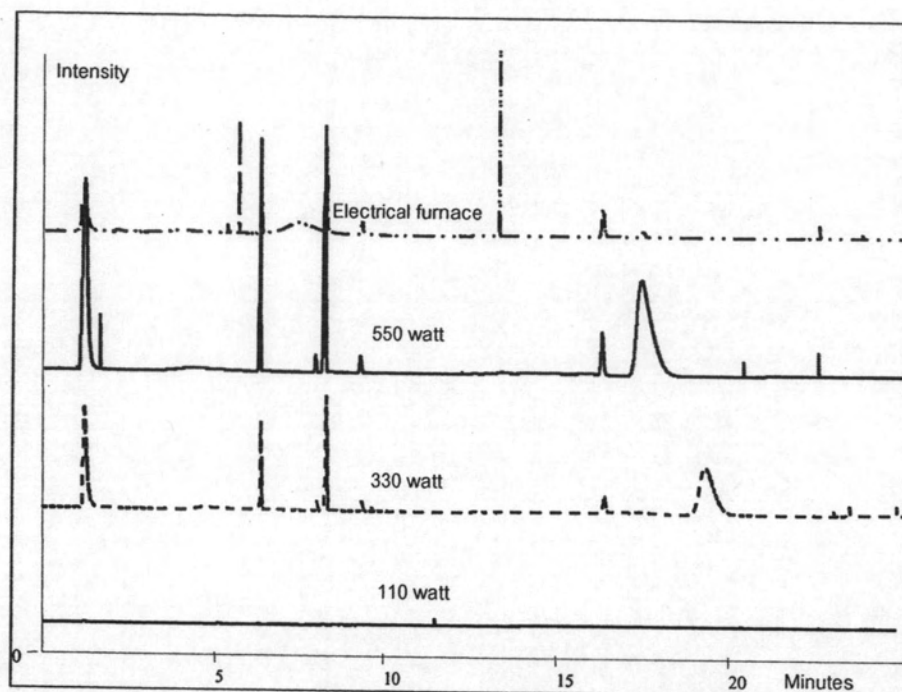**Figure 4.5** Hydrocarbon respond ($\times 10^{-4}$) compare between 100% Ar and 99% Ar/1%O_2.

Figure 4.6 Chromatogram from the operation under 100% Ar atmosphere at different microwave power.
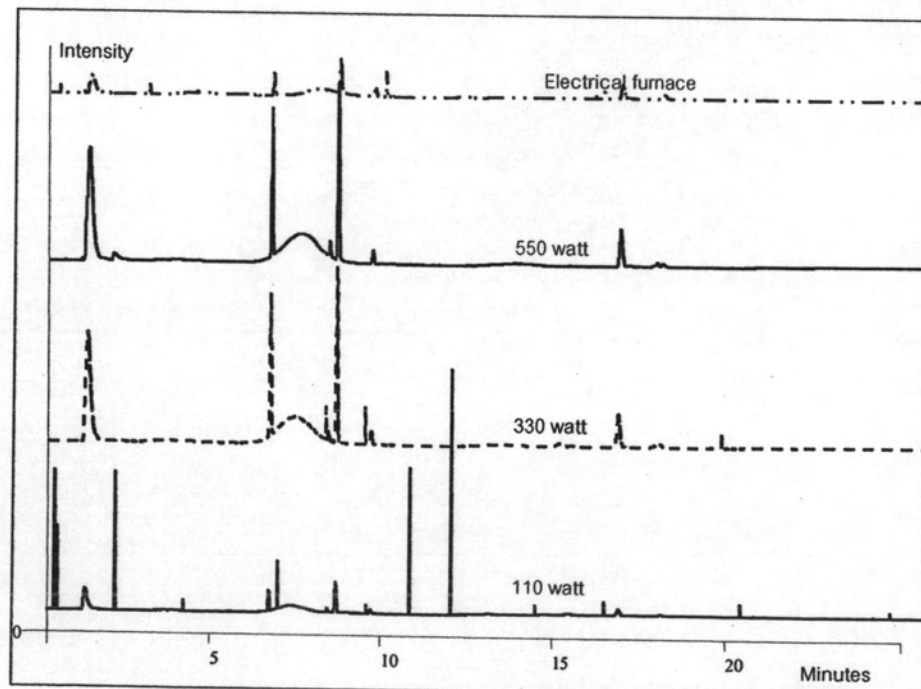

Figure 4.7 Chromatogram from the operation under 99% Ar/1% O_2 at different microwave power.

Figure 4.8 and Figure 4.9 show formation of hydrocarbon gas species from C_1-C_5 at different atmosphere and calculated as weight percent of carbon content in raw materials (EVA/NR). Hydrocarbon species of C_3+C_4 are the highest yield at all atmosphere, microwave power, and heating system. This result may due to the depolymerization of EVA/NR (monomer of EVA is C_2 and monomer of NR is C_4). The second important species is C_5 and the last is C_1+C_2 which may come from random scission of polymeric main chain. Thermal conversion by microwave heating shows the higher yield of hydrocarbon than electrical furnace. As expected, the production of hydrocarbon gas at lower microwave power show the low percent of carbon as percent of carbon input in raw materials but and increase directly with microwave power. When considering at 550 watt microwave power, at 100% Ar atmosphere, the production of C_3+C_4 and C_5 is about 56% and 14%, respectively. With partial oxidation atmosphere of 99% Ar/1% O_2, C_3+C_4 and C_5 is about 85% and 0.7%, respectively. The higher weight percent of C_3+C_4 at 99% Ar/1% O_2 is influenced from gasification reaction of EVA/NR to smaller molecules, especially C_3+C_4, resulting in conversion of C_5 to C_3+C_4 hydrocarbon gases. The higher C_3+C_4 contents are observed at all microwave power due to similar reason. This finding is more profound in microwave heating than in electrical furnace heating.
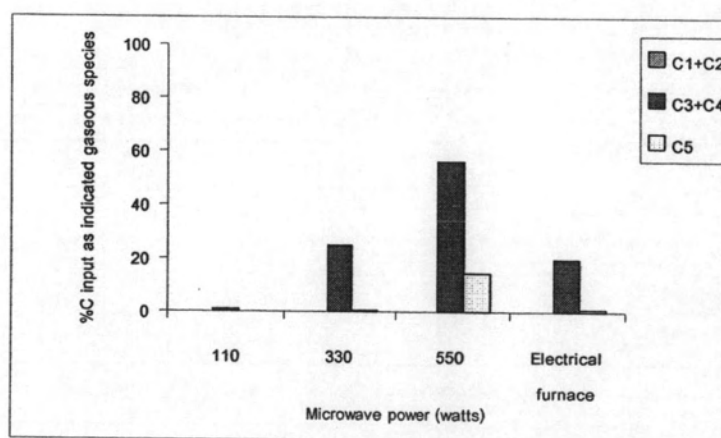

Figure 4.8 Carbon input as indicated gaseous species from C_1 to C_5 at 100% Ar atmosphere.
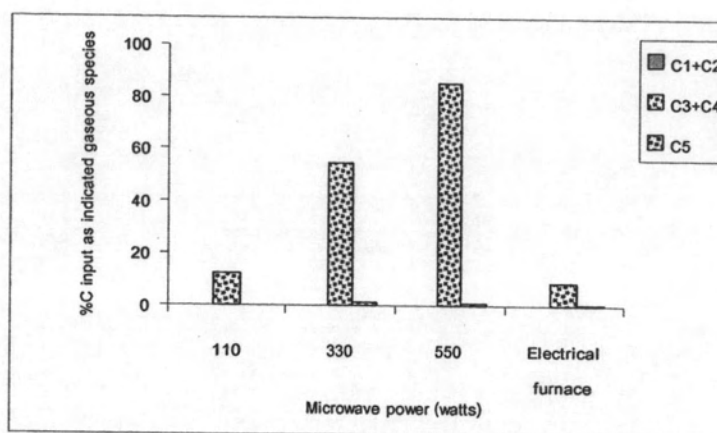
Figure 4.9 Carbon input as indicated gaseous species from C_1 to C_5 at 99% Ar/1% O_2 atmosphere.

In Figure 4.10, at 110, 330 watt microwave heating, and electrical furnace heating, the production of light hydrocarbon and heavy hydrocarbon is not different. In contrast, for 550 watt microwave power, light hydrocarbon is produced at higher content. At 99% Ar/ 1% O_2 atmosphere, hydrocarbon production is higher than 100% Ar because carbon component such as solid residue were converted to H_2, CO, and CO_2 by O_2 accelerate the fragmentation of EVA/NR to hydrocarbon compound (Figure 4.5) via gasification reactions as shown in equations 3, 4, and 6.

Furthermore, it is clear that light hydrocarbon yield in the thermally conversed gases is higher than heavy hydrocarbon content from 110 to 550 watt and electrical furnace under 99% Ar/1% O_2 (Figure 4.11). The same argument can only be made for experiments at 330 and 550 watt under 100% Ar atmosphere (Figure 4.10). The lower content of heavy hydrocarbon may be describe by two conversion processes. First conversion is the transformation to light hydrocarbon, this conversion is occurred when heavy hydrocarbons from cracking of the molecule of EVA/NR have sufficient time or energy and further converted to smaller molecule that observed in 330 watt, 550 watt, and electrical furnace (compared with 110 watt microwave power). Second one is the conversion to permanent gaseous products such as H_2, CO, CO_2, and CH_4. The important factor beside heat is oxygen that present in reacting atmosphere to induced gasification reaction of heavy hydrocarbon as shown in reaction 2, 3. This process can be confirmed by the Figure 4.12-4.14 that display yield of H_2, CO_2, and CH_4,

respectively. From the result, H_2, CO_2 and CH_4 yields sharply increase in 550 watt because temperature in operation is suffcient for gas formation via secondary reactions. Moreover, higher yield of H_2, CO_2 and CH_4 can be observed in operation under 99% Ar/1% O_2 atmosphere.
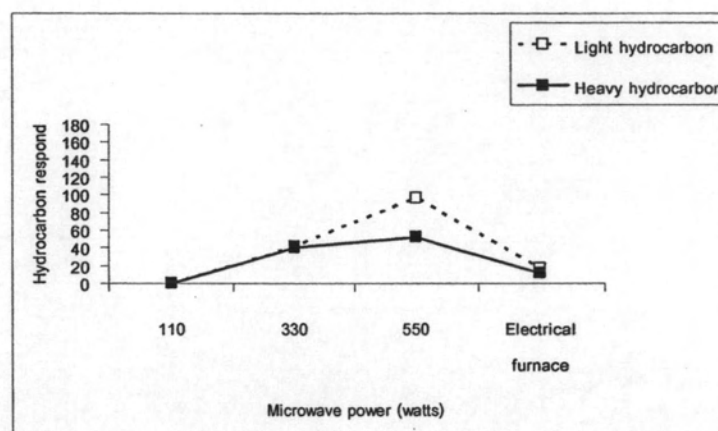
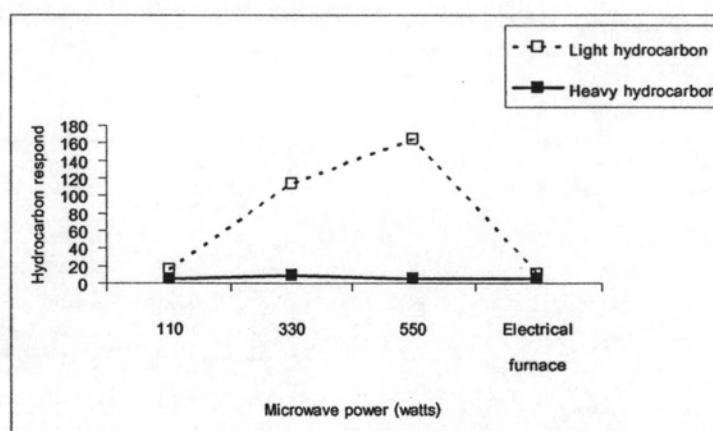**Figure 4.10** Hydrocarbon responds ($\times 10^4$) under 100% Ar atmosphere.

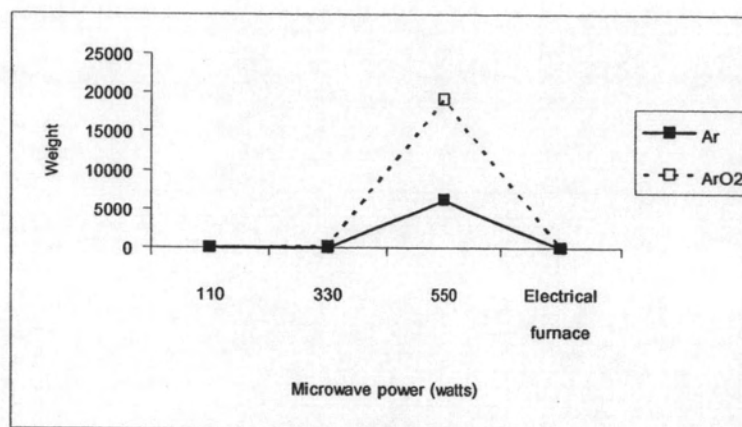**Figure 4.11** Hydrocarbon responds ($\times 10^4$) under 99% Ar/ 1% O_2 atmosphere.

Figure 4.12 Amount of H_2 ($\times 10^{-6}$g) formed at different microwave power compare between 100% Ar and 99% Ar/1%O_2.
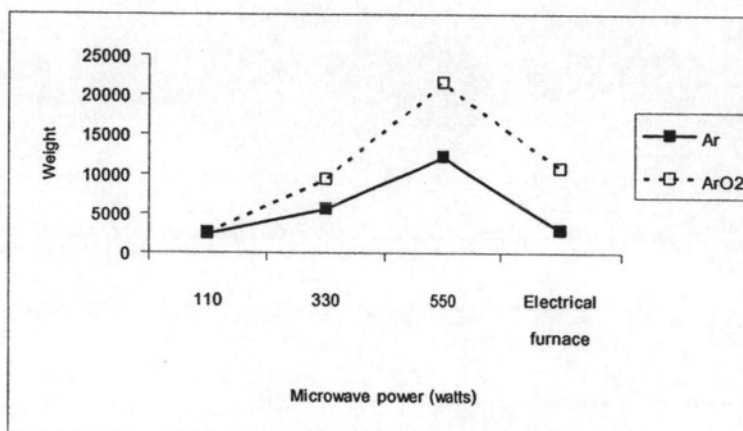

Figure 4.13 Amount of CO_2 ($\times 10^{-6}$g) formed at different microwave power compare between 100% Ar and 99% Ar/1%O_2.

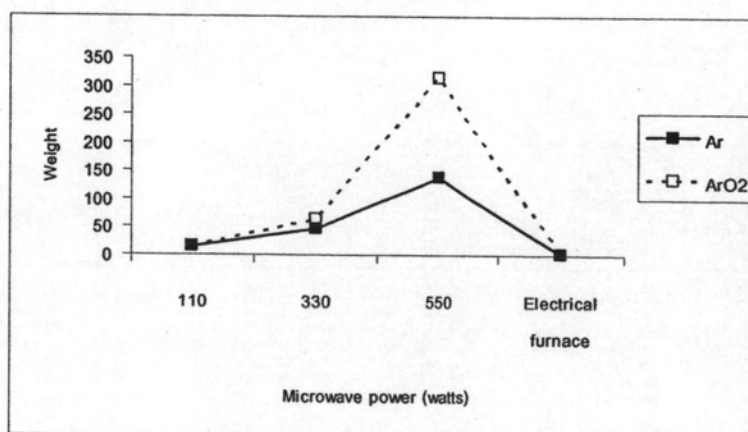**Figure 4.14** Amount of CH_4 ($\times 10^{-6}$g) formed at different microwave power compare between 100% Ar and 99% Ar/1%O_2.

Table 4.7 Amount of H_2 ($\times 10^{-4}$ g) from the operation with silicon carbide ratio 1:1.

Microwave power (watts)	Weight (g)	
	Ar	Ar/O2
110	0.00	0.03
330	0.25	1.10
550	61.12	190.77
Electrical furnace	0.02	0.02

Table 4.8 Amount of H_2, CO_2, and CH_4 from thermal conversion of sewage sludge at different temperature using microwave heating as obtained by A. Domínguez et al [28].

	Temperature (°C)		
	500	800	1,000
H_2	35.6	38.2	40
CO_2	28.4	22.7	17.7
CH_4	7.25	7.13	6.74

Table 4.9 Amount of H_2, CO_2, and CH_4 (%vol) from thermal conversion of sewage sludge using electrical furnace as obtained by A. Domínguez et al [28].

	Temperature		
	500 °C	800 °C	1,000 °C
H_2	9.3	25.8	29.9
CO_2	56.6	39.1	32.0
CH_4	11.3	10.9	10.7

Table 4.10 Amount of CO_2 ($\times 10^{-4}$) from the operation at silicon carbide ratio of 1:1.

Microwave power (watts)	Weight (g)	
	Ar	Ar/O2
110	24.64	25.76
330	55.05	93.52
550	121.40	215.65
Electrical furnace	128.20	106.40

Table 4.11 Amount of CH_4 ($\times 10^{-4}$) from the operation at silicon carbide ratio of 1:1.

| Microwave power (watts)	Weight (g)	
	Ar	Ar/O2
110	0.15	0.15
330	0.47	0.65
550	1.37	3.14
Electrical furnace	0.03	0.02

In 99% Ar/1% O_2, the amount of CO_2 increase with microwave power, because carrier gas have O_2 that gasification of EVA/NR would produce CO_2, reaction (4), at higher rate than from reaction (1) and (2). Microwave heating favors the production of H_2 via reaction (2) and (3) with CO_2, and CH_4 than electrical furnace (table 4.7, table 4.10, and table 4.11). This result is different to A. Domínguez et al [8] that shown in table 4.12. This difference may be due to dissimilar systems of heating and set up. Microwave heat the EVA/NR and SiC directly, causing the sample to attain a much higher temperature than the surrounding environment and CO_2 have shorter time for reaction with other products. In contrast, in electrical furnace heating, the sample is heated by conduction and convection so that the reactor walls and the surrounding atmosphere are at higher temperatures than in the case of microwave heating thus CO_2 have more time to react with other products during conversion, thus CO_2 content decrease.

Table 4.12 Comparison of H_2, CO_2, and CH_4 (% vol) from pyrolysis of sewage sludge at same temperature obtained by A. Domínguez et al [23].

	Microwave heating	Electrical furnace
H_2	38.0	29.0
CO_2	9.7	11.8
CH_4	4.4	18.4

4.2.2 Effects 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 products, except for 110 watt microwave power where temperature is lower than the decomposition temperature of EVA/NR that most of EVA/NR is still intact because microwave power is not sufficient to generated ample heat for conversion. Measurement of temperature profile during this microwave-induced thermal decomposition is shown Figure 4.15. Note that uncertainty of about ± 50°C is possible for this kind of measurement due to the difficulty of determining the temperature during the experiments under microwave irradiation. This variation is resulting from arching of thermocouple which occur between the tip of the thermocouple and SiC, making it infeasible to perform real time temperature logging.
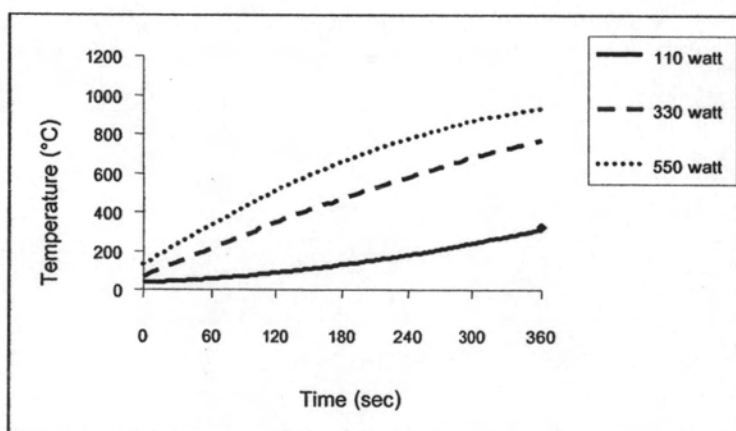

Figure 4.15 Temperature profile at different microwave power.

The formation of the gaseous products is a consequence of oil decomposition, the decomposition of solid residue at high temperatures and reactions between species

formed during the decomposition. At higher microwave power, most of gases were produced during the first 180 seconds. In contrast, gas collected from 181 to 360 seconds have a low concentration because reaction temperature has already reached 450-600°C in the first 180 seconds which display in Figure 4.15 and most 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 can not be observed. Moreover, at higher microwave power, oil products from the reaction were pyrolyzed simultaneously and help increase gas product fraction. Similarly, A. Domínguez et al [28] also reported the energy distribution of products for electrical furnace heating and microwave heating that show in Figure 4.16. 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 the extent of pyrolysis or microwave power increases the gas products.
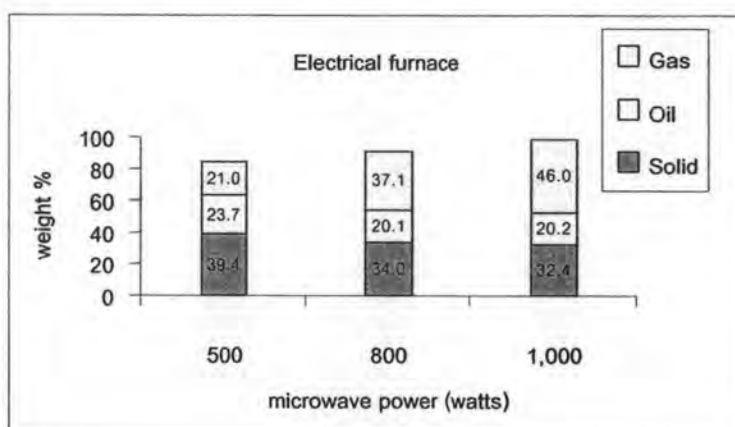
(a)
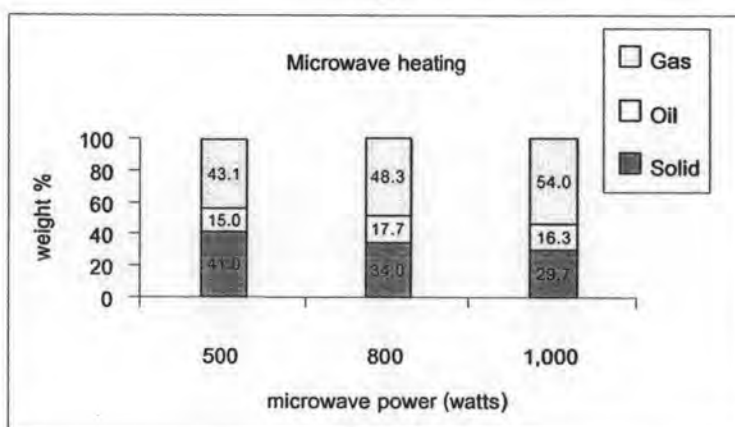
(b)

Figure 4.16 Product distributions from microwave heating (a) and electrical furnace (b) obtained by A. Domínguez et al [28].

Solid residue and oil fraction decreased when microwave power increase in 100% Ar and 99% Ar/1%O_2 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 comparing the gas product between microwave heating and electrical furnace in Figure 4.17 and Figure 4.18, microwave heating generated higher gas fraction than electrical furnace, especially in 99% Ar/1% O_2 atmosphere as described earlier. The decrease in solid fraction with temperature (microwave power) is mainly attributed to an increase in devolatilization of the organic materials. However, the influence of temperature on oil production is not apparent.
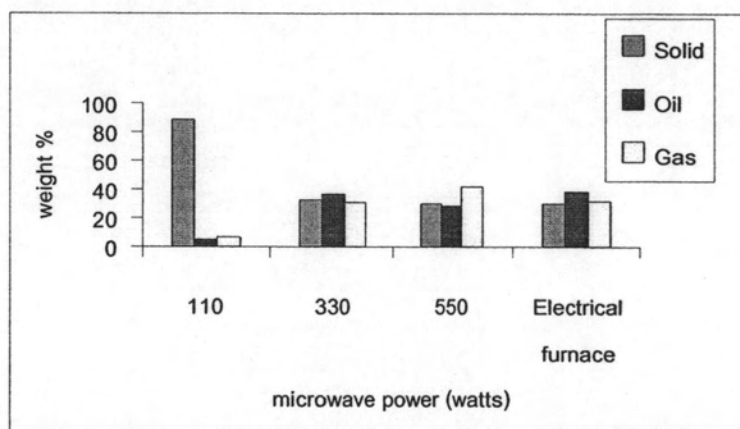

Figure 4.17 Product distributions between microwave heating and electrical furnace under 100% Ar atmosphere.
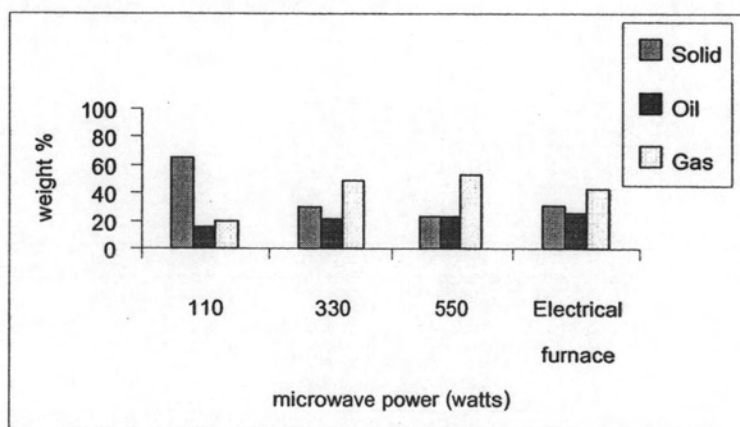

Figure 4.18 Product distributions between microwave heating and electrical furnace under 99% Ar/1% O_2 atmosphere.

Figure 4.17 and Figure 4.18 are comparable with Figure 4.6 from findings by A. Domínguez *et al* [28]. 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 heating but its oil fraction from microwave heating is clearly lower than that of electrical furnace heating. Moreover, gas fraction of microwave heating is higher than electrical furnace heating at all temperature. When electrical furnace heating 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.

4.2.3 Effects of reacting gas

When compared the operation under 100% Ar and 99% Ar/1% O_2. Operation under 99% Ar/1% O_2 atmosphere generated higher amounts of light hydrocarbon and H_2. Hydrocarbon contents increased from simultaneous reactions of gas, oil, and solid residue produced during the operation. This is the gasification process where reactions of hydrocarbon and carbon in char with oxygen generate CO, CO_2 and H_2 which also reduced yields of oil, and solid residue (compare between Figures 4.3-4.4 and Figures 4.19-4.20). On the other hand, these reactions are not dominant in electrical furnace heating and the solid content is not different but oil fraction decreased and increase in gas fraction when operate under 99% Ar/1% O_2 that was shown in table 4.14. Under 99% Ar/1% O_2 atmosphere, higher content of H_2 and CO_2 than under pyrolysis condition can be measured. It is known that microwave heating favors heterogeneous reactions between the pyrolysis gases and solid residue [28]. Reactions (2) and (6) may therefore be favored by the microwave heating. This would partly explain higher H_2 content in gases obtained from microwave heating compared with electrical furnace. In electrical furnace heating products distribution are different between 100% Ar and 99% Ar/1% O_2 that shown in Figure 4.21. Gas fraction in electrical furnace heating is higher in 99% Ar/1% O_2 by similar reason as microwave heating that described earlier.
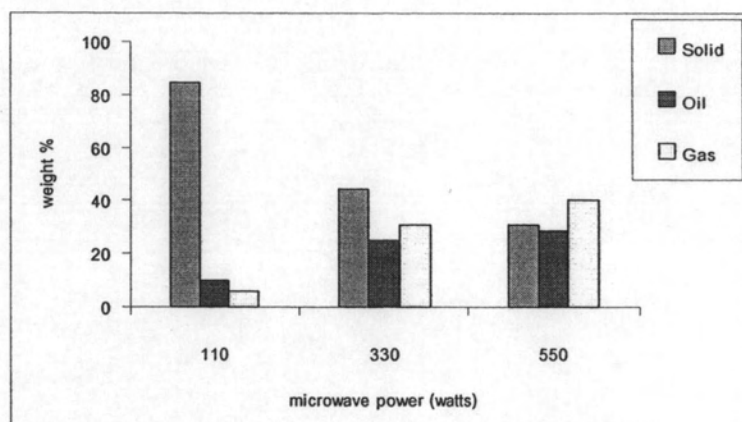
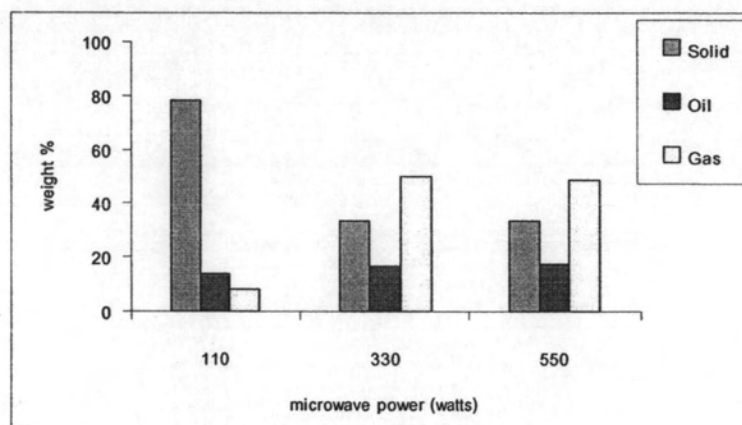**Figure 4.19** Distributions of product at silicon carbide ratio 2:1 under 100% Ar atmosphere.

Figure 4.20 Distributions of product at silicon carbide ratio 2:1 under 99% Ar/1%O_2 atmosphere.

Table 4.13 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
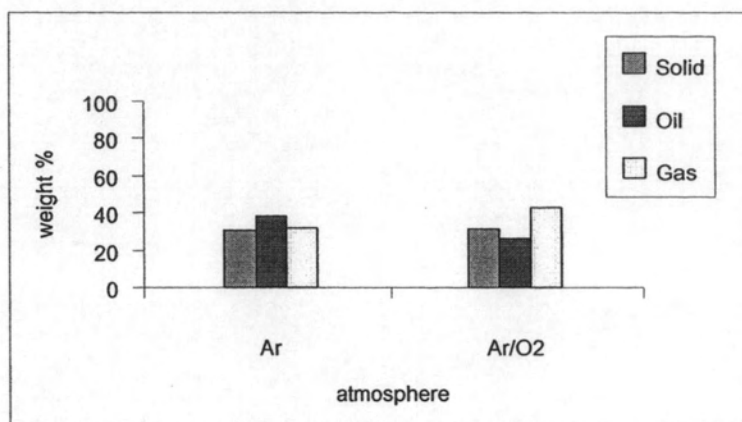
Figure 4.21 Distributions of product from electrical furnace compare between 100% Ar and 99% Ar/1% O_2 atmosphere.

4.2.4 Effect of silicon carbide ratio

The effect of silicon carbide ratio is not evident due to limitation of distribution of microwave radiation in microwave oven as observed in Figure 4.22 and Figure 4.23, at the same atmosphere, when compare between 1:1 and 2:1 silicon carbide ratio. 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 which can notice from the solid residue at ratio 2:1 is higher especially 100% Ar atmosphere. All of the experiments, the qualitative composition of products are quite   similar regardless of the ratio of silicon carbide. Because of this reason, it is recommended that the microwave oven should have multimode apparatus to generate a standing wave pattern where more uniform radiation may be achieved as compared to this research that utilized single mode microwave oven.
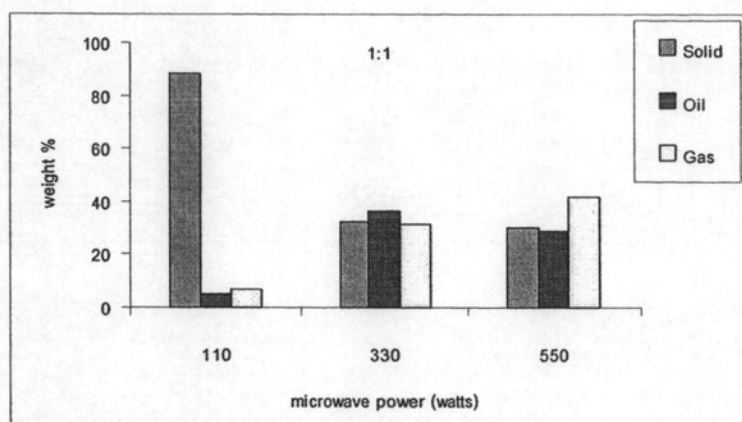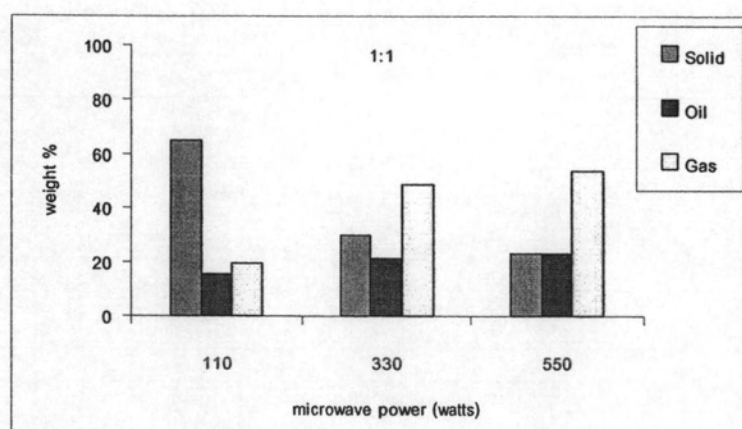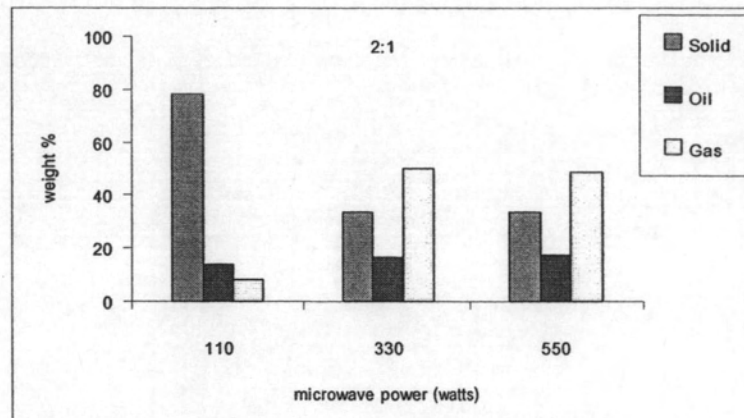
(a)
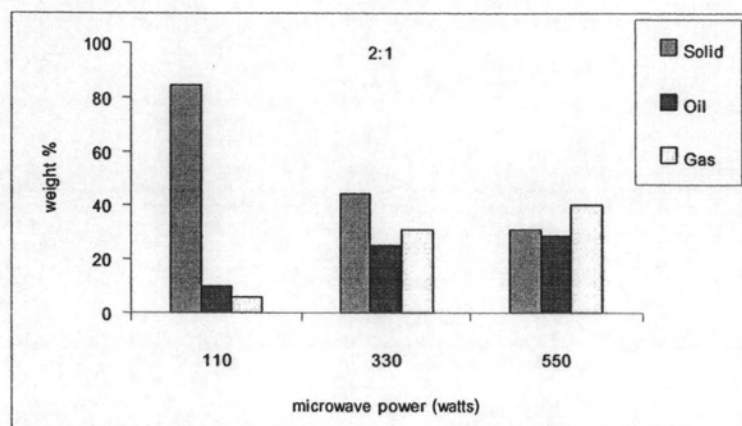
(b)

Figure 4.22 Product distributions (a) 1:1 and (b) 2:1 silicon carbide ratio at 100% Ar atmosphere.

(a)

(b)

Figure 4.23 Product distributions (a) 1:1 and (b) 2:1 silicon carbide ratio at 99% Ar/1% O_2 atmosphere.