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Pyrolysis of Municipal Solid Waste for Syngas Production by Microwave Irradiation

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In the present study, we discuss the application of microwave-irradiated pyrolysis of municipal solid waste (MSW) for total recovery of useful gases and energy. The MSW pyrolysis under microwave irradiation highly depends on the process parameters, like microwave power, microwave absorbers, and time of irradiation. The thoroughness of pyrolysis and product recovery were studied by changing the abovesaid variables. Pyrolysis of MSW occurs in the power rating range of 450–850 W—outside this power rating range, pyrolysis is not possible. Experiments were carried out using various microwave absorbers (i.e., graphite, charcoal, and iron) to enhance the pyrolysis even at lower power rating. The results show that the pyrolysis of MSW was possible even at low power ratings. The major composition of the pyrolysis gaseous product were analyzed with GC–MS which includes CO_2, CO, CH_4, etc.

KEY WORDS: Pyrolysis, municipal solid waste (MSW), microwave irradiation, microwave absorber, syngas.

INTRODUCTION

As the populations of urban area keep growing, the production of municipal solid waste (MSW) increases in a disproportionate way. The difficulties associated with MSW disposal have become serious problem, which do not augur well for the future generation of city dwellers and areas that are having high population density. Presently in India, a total of about 48 million tonnes of MSW is being generated annually (Pappu et al. 2007) with potential energy generation capacity of nearly 12.7 MJ/kg (Klass 1998). Such an enormous amount of MSW having tremendous energy potential must be recycled for energy generation. There are basically two types of MSW that offer opportunities for energy recovery i.e., solid waste (e.g., MSW, urban refuse, garbage, etc.) and bio-solids (e.g., sewage sludge) (Klass 1998). MSW has both organic and inorganic constituents which include paper and paper board, plastics, yard waste, wood waste, rubber and lather, textiles, aluminum, ferrous and other non-ferrous metals, and glass. The organic portion of MSW has energy generation potential which can be extracted by utilizing various conversion techniques.

There are numerous possible pathways for generating energy and producing by-products from MSW. Two principal routes that exist are physicochemical conversion and biochemical conversion. Physicochemical conversion includes combustion, thermal gasification, pyrolysis, and incineration along with a number of techniques involving microwave, plasma arc, and supercritical fluid. Biochemical route includes aerobic digestion, anaerobic digestion, anaerobic fermentation, etc. Products of these techniques include heat, fuel gases, liquids, and solids. In practice, combinations of two or more of these routes may be used, but there are numerous problems with these existing technologies. These

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existing modern techniques pose serious problems of waste disposal and impart heavy load on the Environment. On the other hand, there are restrictions on land filling, and so it is preferable to limit the volume of MSW waste being produced. Volumetric reduction of MSW is usually achieved through conventional pyrolysis as opposed to incineration to prevent the formation of dioxins, furans, and NO_x (Jones et al. 2002). Off-gases from the process are sent for further treatment, while the residue is usually an inert ash.

Pyrolysis is an endothermic process that induces the thermal decomposition of feed materials in the absence of oxygen (Blasi 2008). At present,various conventional types of pyrolytic processes exist in practice, like augers pyrolysis (Ingram et al. 2008), ablative pyrolysis (Lede et al. 1985), and rotating cone pyrolysis (Wagenaar et al. 1994). Other processes, such as fluidized bed and circulating fluidized bed pyrolyses (Lathouwers and Bellan 2001) and plasma pyrolysis (Huang and Tang 2007) have also been used and studied in detail. Pyrolysis typically occurs at temperatures between 400 and 650°C. As the pyrolysis temperature changes, the product distribution (or the form of the product) pattern is also altered. Lower pyrolysis temperatures usually produce more liquid products, whereas higher temperatures produce more gaseous products. The speed of the process and the rate of heat transfer also influence the product distribution. There are many disadvantages in the existing pyrolysis processes while converting MSW into value-added product, which includes air pollution due to SO_x and NO_x, water pollution, disposal of ash and other by-product, hazards for health safety, odor impacts, and emissions of exhaust gases i.e., CO, CO_2, etc. Further, these processes are not focused on recovery of the valuable off gases and energy. In view of the above disadvantages, we have to establish such a technology that can recover value-added products from MSW in an efficient manner without causing any adverse environmental effect, or causing only minimum environmental effect. Microwave irradiation of MSW is a promising route to accelerate the pyrolytic process, through which greater amount of useful gaseous product and less amount of liquid product recovery is possible.

Domestic and industrial microwave ovens generally operate at a frequency of 2.45 GHz corresponding to a wavelength of 12.2 cm and energy of 1.02×10^{-5} eV (Jacob et al. 1995). However, not all materials can be heated rapidly by microwaves. Materials that absorb microwave radiation are called dielectrics; thus, microwave heating is also referred to as dielectric heating (Jones et al. 2002). Microwave heating (dielectric heating) takes place because of the presence of polar molecules, and these molecules are present in the dielectric material, which move very fast and collide with each other in high-frequency microwave electric field, as a result of which heat is generated and temperature of the inside material will go up. Microwave heating is also the phenomenon of ''hotspot'' formation, whereby regions of very high temperature form due to non-uniform heating (Hill and Marchant 1996). The amount of energy required for the microwave pyrolysis is less when compared with other pyrolysis processes (Salema and Ani 2011) because of the rapid volumetric heat generation in the system due to microwave's localized radiations. Pyrolysis can be realized with in a short time and with very high speed. As volumetric heating is not dependent on heat transfer by conduction or convection, it is possible to use microwave heating for applications where conventional heat transfer is inadequate. Hence, the microwave irradiation of MSW leads to the higher rate of pyrolysis, and more amounts of useful gaseous products may form. To improve the microwave bulk heating for non-dielectrics, the microwave absorbers were used in general. In microwave absorbing application, carbon has been used as resistive element in transforming incoming microwave into heat; by reducing the microwave reflection (Huo et al. 2008; Tomonaga 1976). The literature on the use of carbon as microwave absorber was reported in 1936, where a patented microwave absorber was created in Netherlands. On the other hand, in this present study, the authors are using two carbon materials as a microwave absorber i.e., graphite and charcoal. Further, the carbonyl iron can also be used as a good microwave absorbent at 1.18 GHz and even at a higher frequency range (Zhang et al. 2006).

In view of all these facts, the present study focused on the maximum volume reduction of MSW along with production of useful oils and gases through MSW pyrolysis at high temperatures using microwave irradiation. The process variables like microwave irradiation power and time, and the effects of three different microwave absorbers (graphite, charcoal, and iron powder) on the weight reduction of MSW were studied. Further, the composition of gaseous products was analyzed through gas chromatography analysis. The amount of char oil formed and weight reduction realized at various combinations of operating conditions were also studied in detail.

MATERIALS AND METHODS

Materials

The MSW sample was collected from the National Institute of Technology Karnataka college campus located in Surathkal, India. The % composition different fraction in MSW is shown in Table 1. The sample was dried properly and shredded in wiley mill. The shredded sample is then sieved by mesh screen (1.00/1.82 mm opening) to collect the required particle size for the experiment. The proximate analysis of the sample was performed, and it was found that the volatile content (77.94 wt%) was much higher compared with ash and fixed carbon content (Table 2). The effects of different power ratings and irradiation times on pyrolysis of MSW was studied by taking 20 g of sample having particle size (1.0/1.8 mm sieve opening) in round bottom flask. For every experimental run, the power input (100, 180, 300, 450, 600, and 850 W) and irradiation time (varying from 10 to 60 min) was kept constant, and respective readings in respect of loss in weight were noted down.

To study the effect of different microwave absorber on pyrolysis of MSW, three different microwave absorption materials, namely graphite, charcoal, and iron powder were utilized to enhance the pyrolysis at lower microwave irradiation and time. Microwave absorber of about 10 g each was mixed well with the 20 g of MSW of particle size 1.0/1.82 mm in a round bottom flask and kept in the microwave oven for different microwave power inputs (varied from 100 to 850 W) and irradiation times.

Table 1. % Composition of Different Fraction in MSW

S. No.	Component of MSW	% Composition (Approx)
1	Paper	7–10
2	Plastics	0.87–0.96
3	Metals	0.4–0.8
4	Glass	0.39–0.86
5	Organic matter	35.4–43.7
6	Inert	28.7–39

Table 2. Proximate Analysis of MSW

Sample	Moisture Content (wt%)	Volatile Content (wt%)	Ash Content (wt%)	Fixed Carbon (wt%)
MSW	4.6379	77.94	5.32	16.73

Experimental Setup for Pyrolysis of MSW

The pyrolysis process was carried out in the single-mode (focused) Samsung house-hold microwave device with 2.45-GHz frequency. The maximal incident power of micro-wave generator was 850 W and minimum power was 100 W. The MSW sample was taken into the sample holder (i.e., 250-mL round bottom flask) as shown in Figure 1. The sample holder was properly placed in the pathway of microwave radiation. A circular hole of 15 mm in diameter was cut at the top of the microwave oven chamber, through which a mercury seal tube was connected to the flask externally to hold the condenser. The mercury seal connection from the stationary condenser enables the rotation of the round bottom flask which was placed on the turntable. Due to the rotation of the round bottom flask,the entire MSW contained in the flask may get well exposed to the microwave irradiation. The asbestos material was used as a microwave leak-proof agent, which was provided at the top of the cavity where the hole was drilled. Then, the microwave generator was turned on and switched to the designated power. The temperature existing in the flask during microwave irradiation was hard to measure, since, many

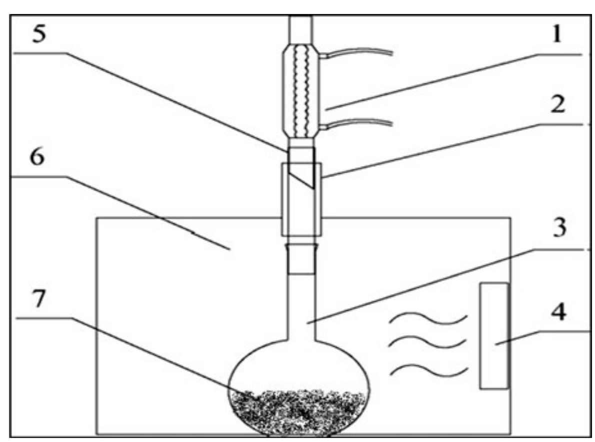


Figure 1. The microwave-assisted reactor (1, water-cooled condenser; 2, mercury seal (glass tube connector in it); 3, round bottom flask; 4, magnetron; 5, glass tube; 6, microwave oven cavity; and 7, MSW sample in sample holder).

of the thermocouples could suffer interference due to the electromagnetic radiation. Further, the temperature measured by the thermocouple may not to be realistically true because of the nature of heating (volumetric heating) through microwave. The vapors produced during the experiment were immediately cooled by the condenser. The gas along with the char oil was collected in the receiving flask. Collected gases were analyzed by gas chromatography (GC–MS). The weight loss of the MSW and the volume of char oil formed were also recorded for the subsequent analysis.

The shredded and sieved MSW samples of 10 g, particle sizes of 1–1.8 mm, were taken for the analysis in the sample holder as shown in Figure 1. The microwave generator was turned on and switched to the designated power range (450–850 W). The designated power input was maintained for a duration of 15–20 min. At this power input and irradiation time, the temperature approximately reaches to 450–600°C, which was measured immediately after the irradiation using mercury thermometer. At this temperature, pyrolysis process started to set in, and gases including vapors were produced. To enhance the pyrolysis rate, about 10 g each of the microwave absorbers like graphite, charcoal, and iron powder were added to the sample. The gases and vapors are allowed to pass through the condenser, and the condensate was collected in the receiving flask. The gases which are collected in the gas bladder or the receiving flask were analyzed by GC.

Analyses of Gaseous Products and Oil

The analyses of gaseous products were done using chromatography equipment (GC–MS) i.e., CHROMPACK CP 9001 with POROPACK (2 m) and CHROMO-SOLE (2 m)-packed Columns for analysis of CO_2 and CO, having an oven temperature of 42°C and detector temperature of 200°C. The VARIAN CP 3800 molesive 5 Å capillary column ($1\times 11/8'' \times 2$ mm) was utilized for the analysis of remaining hydrocarbon gases having oven and detector temperatures of 35 and 250°C, respectively. The 0.5 mL of sample was injected, and the chromatography Column was kept on up to 15–18 min. The other by-product which was obtained along with the pyrolysis gases is char oil or pyrolytic oil and char; nearly 0.8–1.2 mL of char oil was obtained at every experimental run. The pH of char oil was analyzed by Equip-tonics digital pH meter. Physical parameters of char oil, i.e., specific gravity and density of char oil were determined by standard methods.

RESULTS AND DISCUSSION

The Effects of Different Powers and Irradiation Times on Pyrolysis of MSW

The effects of different microwave power inputs and irradiation times on pyrolysis of MSW are shown in Figure 2. From the experimental results, it was observed that the pyrolysis is not possible at the microwave power input of 100, 180, and 300 W, as the amount of energy input and temperature intensity which are required for pyrolysis of MSW were not realized at these lower power inputs. The amount of energy which is required to drive fast pyrolysis process is nearly 10–15% of total energy derived from biomass (Laird and Agron 2008). But, for the power input of 600–850 W, the energy required to drive the reaction was realized very quickly, and the necessary pyrolysis was started within a shorter period of irradiation time i.e., 10–25 min, resulting in a significant amount (i.e., 1–4 g) of weight loss. Although the weight loss happened at higher power rating, the weight reduction is in the lower side. The result shows that the MSW could not absorb the microwave energy fully. Hence, microwave absorber/promoter is required to promote the pyrolysis at lower microwave power input of MSW in efficient manner.

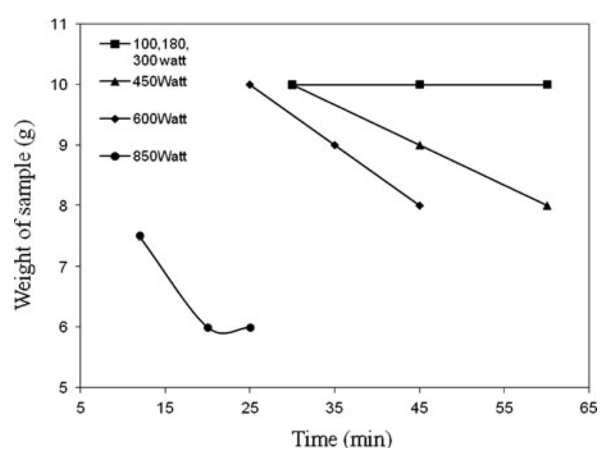


Figure 2. Effect of microwave power on pyrolysis of MSW without microwave absorber.

The Effects of Different Microwave Absorbers on Pyrolysis of MSW

In general, different sources of carbon materials can act as a microwave absorber. Charcoal is one of the forms of carbon which can be used as a microwave absorber (Huo et al. 2008) for the pyrolysis of MSW, it has similar property of carbon. The experiment was carried out with charcoal in a powder form. About 10 g of charcoal was mixed well with the 20 g of MSW in a round bottom flask and kept in the microwave oven at different power inputs and irradiation time. Figure 3 shows the effect of microwave power and irradiation time on the weight loss of MSW. From the graph, it was observed that the loss in weight of MSW was increasing from 5 to 11 g with decrease in irradiation time from 55 to 10 min at 450 W microwave power input. Due to the experimental constrains (The glass container was not able to withstand higher temperature), the maximum microwave power input was fixed at 450 W. Similarly, with the increase of microwave power input from 100 to 450 W, the loss in weight was increasing, however, with subsequent decrease of irradiation time. As charcoal absorbed the maximum incident microwave energy, having less reflection losses (Yusof et al. 2005), it gets burnt out, and simultaneously, the material, which was in contact with the charcoal powder, would also get burnt,, and the energy input along with temperature which is required for pyrolysis can be realized in shorter duration.

The graphite powder, another carbonaceous material, can also be used as a microwave absorber for the pyrolysis of MSW (Huo et al. 2008). In the present study, the effect of graphite powder was studied on pyrolysis and the values were compared with pyrolysis without microwave absorber. From Figure 4, it was observed that, with the use of graphite as a microwave absorber the irradiation time required for pyrolysis is around 10 min and uniform weight loss of 13 g was achieved. Also, it was observed that without using graphite as a microwave absorber, the pyrolysis of MSW was achieved in 18–20 min irradiation time for equivalent weight loss of 13 g. This was because graphite acts as a good absorber material by absorbing the incident microwave radiation and reducing refection of microwave radiation (Yusof et al. 2005). As the graphite powder gets heated by dielectric phenomenon (Acierno et al. 2004), the irradiation time required for pyrolysis was reduces by 10 min.

The magnetic materials and ferromagnetic material which acts as a good microwave absorber include iron powder and recycle magnet. Iron powders have distinct absorbing properties like high particle density and good absorbing wave band (An et al. 2008). Figure 5 shows that with the use of iron as an absorber, the loss in weight of MSW is increasing from 3 to 10 g with respective decrease in irradiation time from 50 to 8 min. Similarly with the increase of microwave power input from 100 to 450 W, the loss in weight is increasing with decrease of irradiation time. The high intensity of pyrolysis was possible at lower power level itself, due to low reflection coefficient, lower permittivity, and higher permeability of the iron powder (Zhang et al. 2006).

On comparing the graph of charcoal versus iron as a microwave absorber (Fig. 6), it was noticed that iron and charcoal acts as a good microwave absorber for pyrolysis of MSW, and both these absorbers have nearly the same effect on pyrolysis of MSW at low microwave power input and irradiation time with significant weight loss of sample. In general, with the use of these absorbers, pyrolysis was gradually

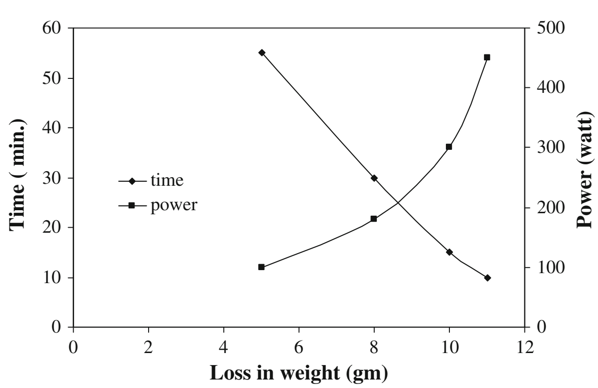


Figure 3. Effect of charcoal as a microwave absorber.

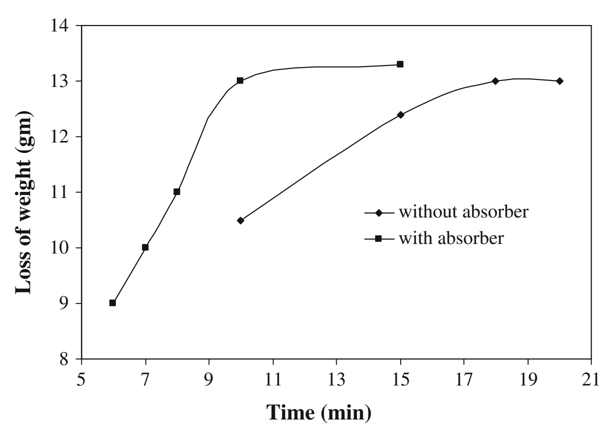


Figure 4. Pyrolysis rate with and without graphite as a microwave absorber at 850 W microwave power.

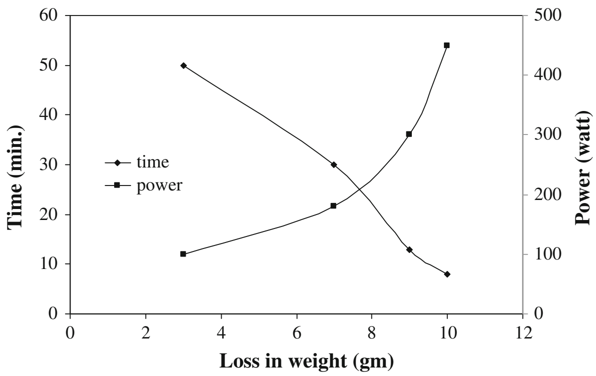


Figure 5. Effect of iron as a microwave absorber.

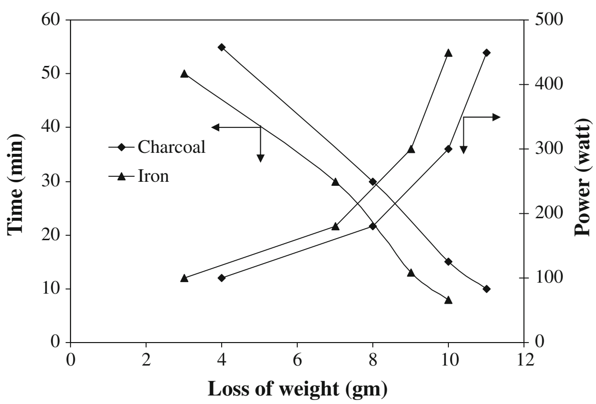


Figure 6. Comparison of charcoal and iron as a microwave absorber.

started from 100 W power input, and significant effect was observed at power input of 450 W within a shorter irradiation time. Even though iron powder accelerates the pyrolysis process, the removal of iron powder after the pyrolysis required additional treatment before the ash content is sent to other purpose/landfill. Further, the charcoal maybe a good absorber for the industrial/large scale operation of MSW pyrolysis, as the nature of the charcoal is identical with the charcoal/ash produced during the pyrolysis. In this direction, further research is required to enhance the ash property to utilize it in a better way as a microwave absorber within the process.

The Product Analysis

The compositions of the gaseous products produced from the pyrolysis at 450 W microwave power input for 10-min irradiation time are shown in Table 3. The major gases produced during pyrolysis of MSW include CO, CO_2, and CH_4 having 30.31%, 16.99%, 9.54%, respectively, and small amounts of propane isobutene, and isopentane, including traces of hydrogen were found. The percentage composition of each gas was estimated from the peak areas shown in the chromatographic Figures 7 and 8.

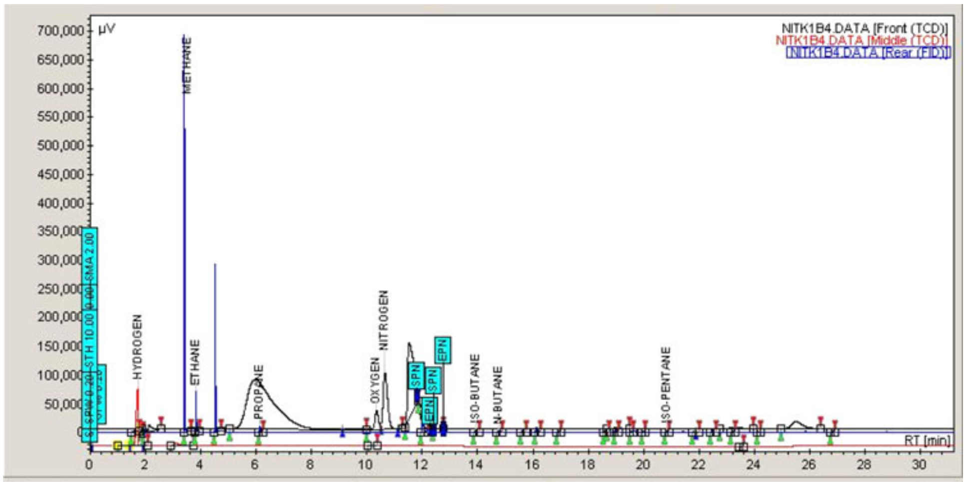
Table 3. Gas Chromatographic Analysis of Gases Product

S. No.	Compound	Quantity (%)
1	Methane	9.54
2	Ethane	0.52
3	Propane	0.08
4	Isobutene	0.03
5	*n*-Butane	0.02
6	Isopentane	0.01
7	Hydrogen	Traces
8	Carbon dioxide	16.99
9	Carbon monoxide	30.31
10	Nitrogen	42.5

From the chromatographic result of MSW pyrolysis (Figs. 7, 8), it was observed that the pyrolysis gaseous products have more percentages of CO, CO_2, and CH_4 which have good calorific values along with ethane, propane, isobutane, and *n*-butane. The calorific values of all gaseous products was calculated, using ideal gas equation and energy balance equation, which was nearly equal to 125.59 kJ/kg. Char oil which was obtained as a bi-product from microwave-induced pyrolysis was nearly 0.8–1.2 mL; it was acidic in nature having pH 3.21; and its specific gravity is 1.165. The major compounds in char oil are alkanes from C_{12} to C_{32}, polycyclic aromatic hydrocarbon and polar compounds including phenol and its derivative (Huang et al. 2008).

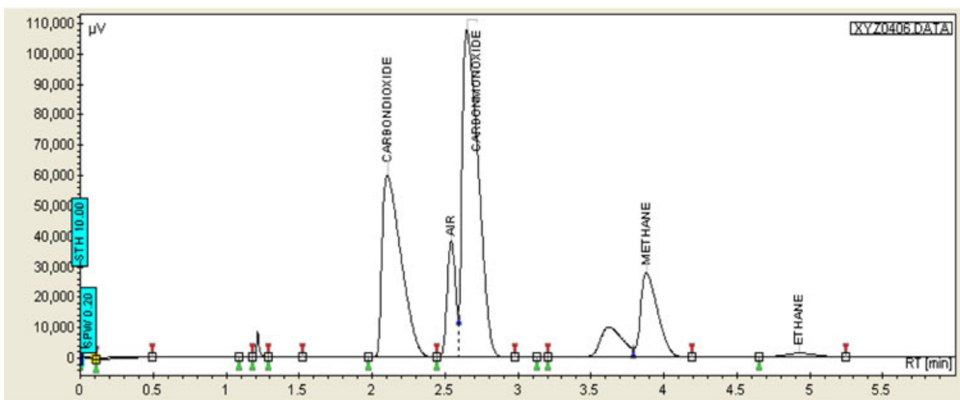
CONCLUSION

The pyrolysis of MSW was subjected to different microwave power inputs and irradiation times, and use of different microwave absorber. From the analysis of the experimental data, it was concluded that, pyrolysis of MSW would take place only at a higher microwave power input i.e., greater than 450 W. Below these powers, input pyrolysis was impractical without microwave absorbers. Graphite, charcoal, and iron were considered as a microwave absorber for pyrolysis of MSW and with the use of these absorbers, pyrolysis of MSW is possible even in the low microwave power input i.e., lesser than 450 W, where conventional pyrolysis was not possible.



#	Name	Time [Min]	Height [μV]	Area [μV.Min]	Quantity [%]
3	METHANE	3.40	691717.7	12948.9	9.54
4	ETHANE	3.83	69740.6	1341.9	0.52
6	PROPANE	6.14	8641.9	321.8	0.08
8	ISO-BUTANE	13.95	2805.5	152.5	0.03
9	N-BUTANE	14.78	1897.1	100.7	0.02
17	ISO-PENTANE	20.84	933.2	42.7	0.01
Total			1115190.2	24869.7	10.19

Figure 7. Gas chromatogram of hydrocarbon gases.



#	Name	Time [Min]	Area [μV.Min]	Quantity [%]
6	CARBONDIOXII	2.10	8976.3	16.99
7	AIR	2.54	2547.9	0.00
8	CARBONMONC	2.65	13583.0	30.31
11	METHANE	3.88	3720.3	10.39
12	ETHANE	4.93	282.4	0.56
Total			31113.2	58.25

Figure 8. Gas chromatogram of CO and CO_2 gases.

The syngases obtained from pyrolysis of MSW include CO (30.31%), CO_2 (16.99%), CH_4 (9.54%), and traces of ethane, propane, isobutane, and *n*-butane having calorific value of 125.59 kJ/kg. The feasibility and practicability of this technology to be utilized in the syngas production from MSW need to be researched intensively in terms of effect and optimization of the operating variables.

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