Asian Journal of Water, Environment and Pollution, Vol. 9, No. 3 (2012), pp. 59–66.

Plasma Pyrolysis/Gasification of Cotton Waste and Energy Recovery Possibilities

Pragnesh N. Dave* and Asim Joshi[1]

Department of Chemistry, K.S.K.V. Kachchh University, Bhuj – 370 001, Gujarat, India
[1]Chemical Engineering Department, Institute of Technology, Nirma University
Sarkhej-Gandhinagar Highway, Ahmedabad – 380 019
✉ pragnesh7@yahoo.com

Received July 15, 2010; revised and accepted May 7, 2012

Abstract: In this study of plasma pyrolysis of cotton, main focus was drawn on the energy recovery possibilities by generating Syn gas (H_2 + CO) by thermal pyrolysis and gasification (cracking) of cotton through plasma as heat source. Through GC analysis, we concluded that plasma pyrolysis of cotton in temperature range of 500 to 700 °C yields H_2 as main component around 15-25% volume basis and other compounds like CO, CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2 and soot (carbon). Dioxin and furan formation do not take place as we worked in higher temperature ranges and then provided sudden fast quenching to avoid De-Nevo synthesis. The theoretical and experimental energy recovery comparisons have also been done and shown.

Key words: Plasma waste treatment, hydrogen, cotton waste, energy recovery, DC plasma.

Introduction

Waste management is an important issue in both developed and developing countries nowadays. To alleviate part of our energy crisis and environmental degradation, it has become imperative to make use of appropriate technologies for recovery of resources from non-conventional sources like organic waste (Burton, 1998).

A significant, valuable percentage of today's medical waste stream consists of cotton materials, for which almost no economic recycling technology currently exists. This cotton waste is incinerated, land filled, or recycled via downgraded usage. Thermal plasma treatment is a potentially viable means of recycling these materials by converting them back into monomers or into other useful compounds (Guddeti et al., 2000).

Landfilling of plastic waste, which is presently preferred much in India, is not a solution, essentially because it has been increasingly difficult to find suitable places for building technically adequate landfills. This is due to the resistance imposed by the nearby populations and since there is the danger of leaching and soil impregnation, with the subsequent contamination of underground waters. Furthermore, this process does not allow the recovery of the valuable organic content of plastic waste.

Incineration of cotton waste to produce heat may be a possibility, but its organic content would totally be destroyed and converted only into CO_2 and H_2O. In addition, depending on its nature, combustion may produce pollutants like light hydrocarbons, nitrous and sulphur oxides, dusts, dioxins and other toxins that have a highly negative impact on the environment. End product yields and properties depend on the cotton waste composition (Pinto et al., 1999).

The problems that occurred in the earlier recycling technologies based on pyrolysis and gasification are such as low gas productivity and the wide spectrum of products. These problems are difficult to overcome due

*Corresponding Author

to only limited control of the product composition in pyrolysis and gasification processes (Huang and Tang, 2007).

Energy Recovery Potential of Cotton Waste

Total waste quantity (W) = 1.0 kg

Net Calorific Value (NCV) = 3579.93 kcal/kg

Energy recovery potential (kWh) = (NCV × W)/860

= (3579.93 × 1)/860

= 416 kWh

Power generation potential (kW) = (3579.93 × 1)/(860 × 24)

= 0.17 kW

Process Chemistry in Primary Plasma Chamber

Plasma pyrolysis of hydrocarbons proceeds through a long sequence of chemical processes that generally have condensed phase carbon and H_2 as final products.

Formation of Methane

Methane is formed by reaction between excited $*CH_3$ radical and H_2 as below giving methane and excited Hydrogen radical (Baeck et al., 1995).

$$*CH_3 + H_2 \rightarrow CH_4 + *H$$

Thermal Plasma Pyrolysis of Methane

Thermal decomposition of methane follows (Kassel Mechanism, 1932) (Fridman, 2008)

$$CH_4 \rightarrow *CH_2 + H_2$$

$*CH_2$ radical according to Kassel leads to ethane formation as follows:

$$CH_4 + *CH_2 \rightarrow C_2H_6$$

And further dehydrogenation of ethane leads to ethylene, acetylene and finally soot.

$$C_2H_6 \rightarrow C_2H_4 + H_2;$$

$$C_2H_4 \rightarrow C_2H_2 + H_2;$$

$$C_2H_2 \rightarrow 2C_{(s)} + H_2$$

During plasma pyrolysis of methane, ethylene is formed after 10^{-6}-10^{-5} sec and acetylene after 10^{-4}–10^{-3} sec and then soot formation takes place. Soot formation can be avoided if the pyrolysis gas residence time in the discharge is 10^{-3} and quenching rate 10^6 K/s. Practically such fast quenching is difficult hence soot formation is unavoidable.

Plasma Pyrolysis and Energy Recovery System

As shown in Figure 1, the system, developed at Facilitation Center for Industrial Plasma Technologies, consist of the following sub-systems: plasma torch, power supply, gas injection system, primary reaction chamber, venturi scrubber, water tank, packed bed

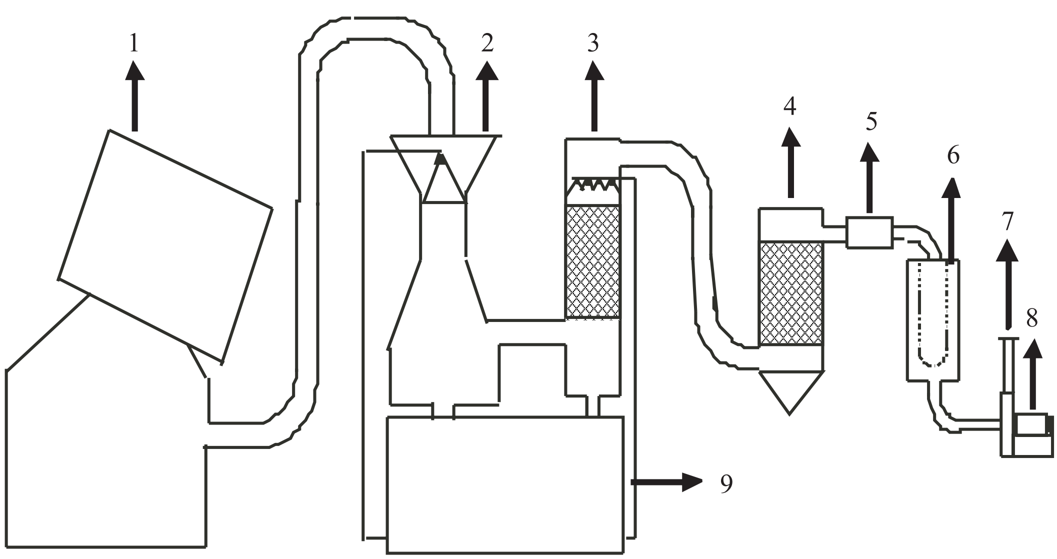

Figure 1: Plasma pyrolysis waste treatment and energy recovery system developed at FCIPT, Gandhinagar, India.

Note: 1. Feeder system and primary chamber, 2. Venturi scrubber, 3. Scrubber, 4. Filter, 5. Condenser, 6. Bag filter, 7. Pyrolysis gas to generator set, 8. Induced fan, 9. Water tank.

scrubber, filter, condenser, bag filter, ID fan, chimney, buffer tank and generator set.

Design Basis Study

Primary Chamber Volume Calculation and Gas Liberation from 1 kg Cotton

For one mole we have

$$C_6H_{10}O_{5(s)} + \text{heat} \longrightarrow CH_{4(g)} + 3CO_{(g)} + 2H_2O_{(steam)} + 2C_{(s)} + H_{2(g)}$$

Assuming ethane, acetylene, ethylene and CO_2 to be negligible as it is less in concentration (volume basis) as found in experiments.

Now, cotton molecular weight is $C_6H_{10}O_{5(s)} = (12\times6) + (1\times10) + (16\times5) = 162.0$ gm.

Here, considering above reaction we can say that 162 gm of cotton will liberate maximum 1.0 mole of $CH_{4(g)}$ and $H_{2(g)}$, 3.0 moles of $CO_{(g)}$ and 2.0 moles of $C_{(s)}$ soot particles and $H_2O_{(steam).}$

Total moles of gases liberated from 162 gm of cotton will be [1 + 1 + 2 + 3] = 7.0 moles of gases. So, 15 kg cotton will liberate (7.0/0.162) × 15 = 648.15 moles of gases. Hence, in 1.0 sec amount of gases liberated from cotton will be (648.15/3600) = 0.180 moles.

Above calculations are based on NTP.

When temperature is 700 °C then volume of the gas will be [(700+273)/(25+273)] × (0.180) = 0.59 ≈ 3.3 times the volume at NTP. So, volume of gas liberated in primary chamber at 700 °C will be 0.180 × 3.3 = 0.59 moles of gases.

Now, volume of 1.0 mole of gas at NTP is 22.4 litres. So, 0.59 moles will be equal to 13.22 litres. Hence 13.22 litres of gas will be liberated per second considering 15 kg/hr feed rate of cotton in the primary chamber at 700 °C.

Waste packet have dimension approximate (200 mm × 150 mm diameter). Volume of waste packet = $\pi r^2 h$ = 18849555.921 mm^3 = 0.01885 m^3. When this packet is dropped in the primary chamber, the overall volume required in the chamber will be (13.22 + 18.85) litres = 32.07 litres = 0.03207 m^3.

If we take Factor of safety = 3.0, required primary chamber volume will be (3.0 × 0.03207) = 0.10 m^3.

Energy Generated from 1.0 kg Cotton

Theoretical Calculation

We know that around 1290 kcal ≈ 1.5 kWh energy is required for 1.0 kg of cotton or any other organic waste to get plasma pyrolysis (Nema and Ganeshprasad, 2002). We are aiming at 15 kg/hr treatment rate. To dispose a fixed amount of waste i.e. 15 kg/hr we will need 15 kWh energy in the system in the primary chamber. Feed rate considered is 1.5 kg/4 min. Hence, required energy will be 1.5 kWh in 4 min.

For plasma source the efficiency of electrical to heat energy conversion is 90% of input power. So, to treat 15 kg/hr cotton using plasma source, required power input will be (15 × 100)/90 = 16.66 kWh ≈ 17 kWh.

Now the pyrolysis reaction for cotton is

$$C_6H_{10}O_{5(s)} + \text{heat} \rightarrow CH_{4(g)} + 3CO_{(g)} + 2H_2O_{(steam)} + 2C_{(s)} + H_{2(g)}$$

Here, plasma pyrolysis gas components like methane (CH_4), hydrogen (H_2), carbon monoxide (CO) and Carbon ($C_{(s)}$) soot undergo combustion reaction to yield heat energy.

- Methane

  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 212.22$ kcal (Baeck et al., 1995)

  For 1.0 moles

  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 212.22$ kcal

- Carbon Monoxide

  $CO + ½\, O_2 \rightarrow CO_2 + 67.63$ kcal (Baeck et al., 1995)

  For 3.0 moles

  $3CO + 3/2O_2 \rightarrow 3CO_2 + 202.89$ kcal

- Hydrogen

  $3H_2 + 3/2O_2 \rightarrow 3H_2O + 3 \times (57.82)$ kcal (Baeck et al., 1995)

  For 1.0 moles

  $H_2 + 1/2O_2 \rightarrow H_2O + 57.82$ kcal

- Carbon

  $C + O_2 \rightarrow CO_2 + 94.05$ kcal (Baeck et al., 1995)

  For 2.0 moles

  $2C + 2O_2 \rightarrow 2CO_2 + 188.10$ kcal

Total Energy Liberated = (212.22 + 202.89 + 57.82 + 188.10) kcal = 661.03 kcal/mole = 2769.72 kJ/mole

162 gm cotton yields 661.03 kcal/mole (2769.72 KJ/mole). So, 1000 gm (1.0 kg) yields [(1000 × 661.03)/162] = 4,080.43 kcal/kg

Therefore, net gain in energy will be = (total energy liberated) - (energy required for pyrolysis of 1 kg cotton) = 14,135.1 – 1290 = 2790.43 kcal/kg

Experimental Calculation

Based on volume % of different compounds as found in pyrolysis gas, we calculated calorific value of pyrolysis gas which will be useful to calculate energy liberated from 1.0 kg cotton.

Plasma pyrolysis of dry moisture-free cotton is carried out at three different temperatures 500, 600 and 700 °C. For the experiment the feed rate was 1.0 kg PE/4 min. First feeding of the cotton was done after starting the plasma torch and reaching 500 °C.

For cotton the best composition of plasma pyrolysis gas with high percentile of H_2, CO and CH_4 comes out to be 23.53% H_2, 1.2% CO, 21.57% CH_4, 0.24% CO_2, 5.41% C_2H_6 (ethane), 4% C_2H_2 (acetylene), 2.45% C_2H_4 (ethylene) at 700 °C, remaining is nitrogen as we have used air inside primary chamber as plasmagen gas.

Here, plasma pyrolysis gas components like ethane (C_2H_6), methane (CH_4), hydrogen (H_2), carbon monoxide (CO), C_2H_4 (acetylene) and C_2H_2 (ethylene) can undergo combustion reaction to yield heat energy.

Hydrogen	0.2353 moles	→ 13.61 kcal
Carbon Monoxide	0.01 moles	→ 0.68 kcal
Methane	0.20 moles	→ 42.44 kcal
Acetylene	0.0124 moles	→ 03.85 kcal
Ethylene	0.0245 moles	→ 08.24 kcal
Ethane	0.0541 moles	→ 20.15 kcal
	= 88.97 kcal/mol = 372.786 KJ/mol	

162 gm cotton yields 89.97 kcal/mole (372.786 KJ/mole). So, 1000 gm (1.0 kg) yields [(1000 × 89.97)/162] = 555.37 kcal/kg

Therefore, net gain in energy will be (total energy liberated) – (energy required for pyrolysis of 1 kg cotton) = 555.37 – 1290 = (–734.63) kcal/kg.

Negative value suggests that we are recovering energy less than the energy supplied to disintegrate the system. So, in plasma pyrolysis and gasification waste treatment occurs satisfactorily but energy recovery is found to be less.

Experimental Work and GC Analysis of Cotton Plasma Pyrolysis Gas and Results

Plasma pyrolysis gas obtained from primary chamber is analyzed in Gas chromatography system with N_2 as carrier gas, HP plot Q column, and TCD detector. H_2 is inorganic so we used TCD as Detector. As the difference between thermal conductivity of H_2 and He is not much higher, a small peak of helium is obtained for 100% pure H_2 feed. So we used N_2 as mobile phase to detect hydrogen. GC system configuration and parameter setting details are as given in Tables 1 and 2.

Pure Dry Cotton (1.0 kg /4 min) Plasma Pyrolysis Gas GC Analysis Result

Results of cotton pyrolysis gas composition for 500, 600 and 700 °C are as shown in Table 3. Graph is as shown in Figure 2. According to the graph we can see that between 500 and 600 °C temperatures, concentration of hydrogen and methane increase in a similar pattern, while

Table 1: GC system configuration

Model	GCMS 17A
Detectors	TCD (Thermal Conductive Detector)
Column	Capillary HP PLOT Q (PLOT - Porous Layer Open Tubular) Length: 30 m Diameter: 0.25 mm Stationary Phase: Polystyrene divinylbenzene (Porous Polymer) Mobile Phase: Nitrogen Gas (99.999% pure)

Table 2: GC parameter setting

Injection settings	Temp: 70 °C Split Ratio: 5.0 Column Flow: 3.09 ml/min
Column	HP Plot Q Temp: (60 °C for 2 minutes hold, then 10 °C rise till 100 °C) Total analysis time: 12 minutes Mobile Phase: N_2 gas
Detector	TCD Type Temp: 100 °C, Current: 78 mA

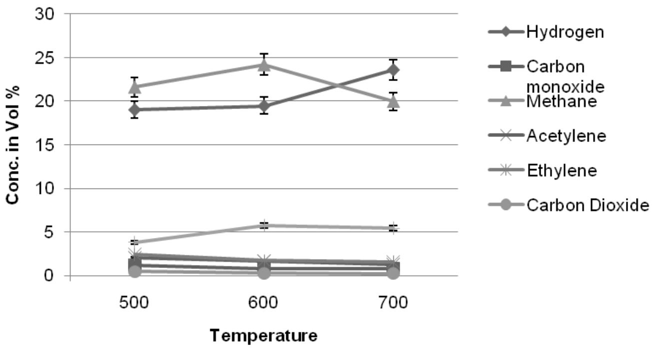

Figure 2: Graph of temperature vs conc. in volume basis of pure dry polyethylene (1.0 kg/4 min) plasma pyrolysis gas GC analysis collected at different temperatures.

that of ethane shows slight increases. From 600 to 700 °C, hydrogen conc. shoots up while methane decreases. Acetylene also shows negligible changes. Ethane conc. throughout 500 to 700 °C shows negligible changes.

SEM Analysis of Cotton Plasma Pyrolysis Soot Particles

To find out the above reason and evaluate the active sites on soot particles, we observed the surface morphologies of different sizes of soot particles using Scanning Electron Microscope (SEM).

Sample Preparation

The soot particles are taken from the inner upper wall surface of primary chamber. For SEM analysis soot particles are first dispersed in acetone by ultrasonic means for 15 minutes. Then immediately after ultrasound treatment a drop of solution is taken on a clean cover glass; we have to take note that cover glass surface is even free of any type of air dust. This cover glass is then coated with a thin film of gold by plasma sputtering for few minutes. Now the sample is ready for analysis. Pure cotton soot particles are as shown in Figures 3, 4, and 5.

Table 3: Pure dry cotton (1.0 kg/4 min) pyrolysis gas GC analysis results

Temp	H_2	CO	CH_4	C_2H_4	C_2H_2	CO_2	C_2H_6
500	19.02	1.2	21.57	2.45	2.02	0.45	3.82
600	19.45	0.81	24.15	1.7	1.65	0.28	5.73
700	23.53	0.82	19.94	1.55	1.24	0.24	5.41

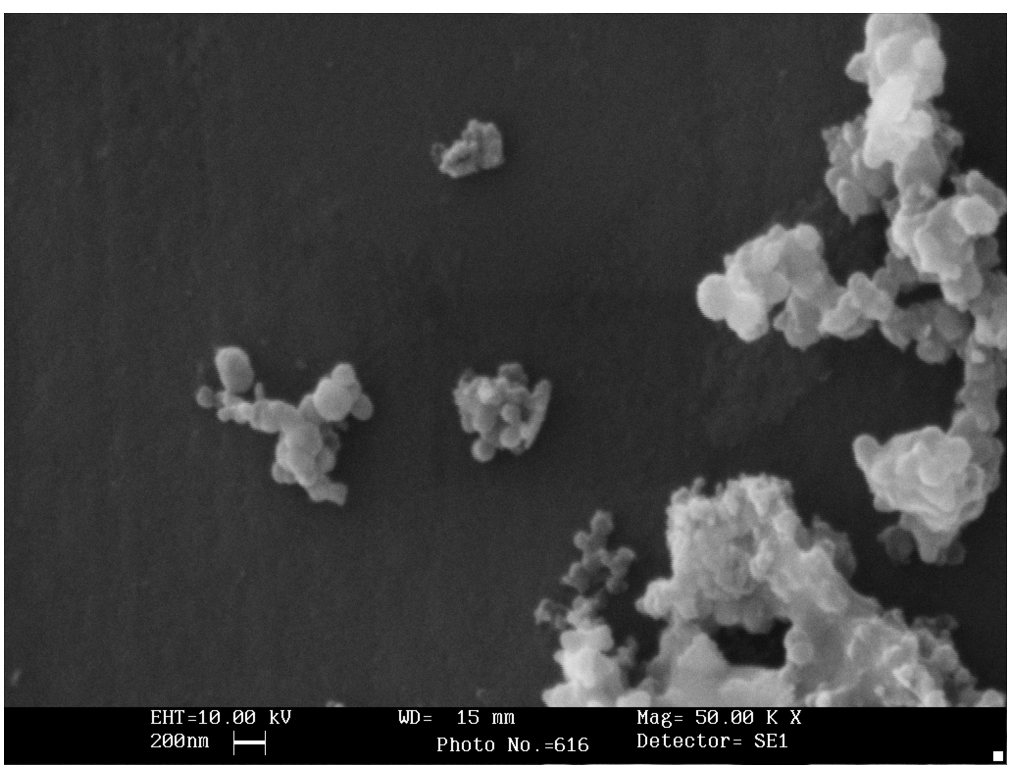

Figure 3: SEM photo of cotton soot particles generated during plasma pyrolysis treatment 200 nm range.

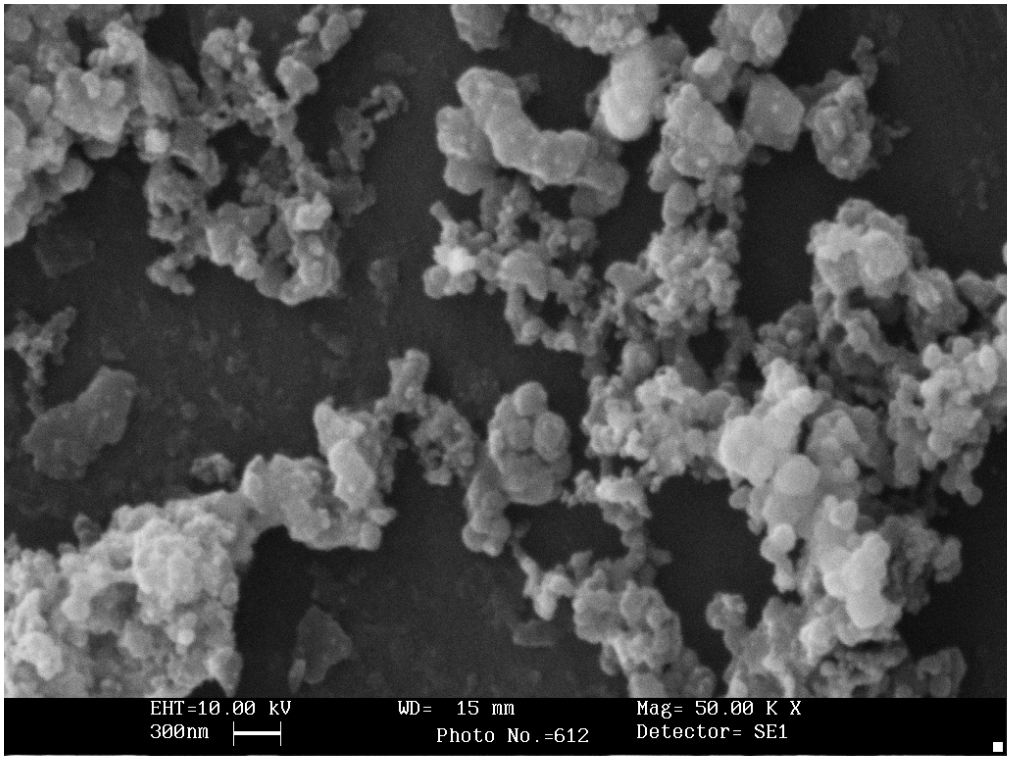

Figure 4: SEM photo of cotton soot particles generated during plasma air gasification (25 litre/min) treatment 300 nm range.

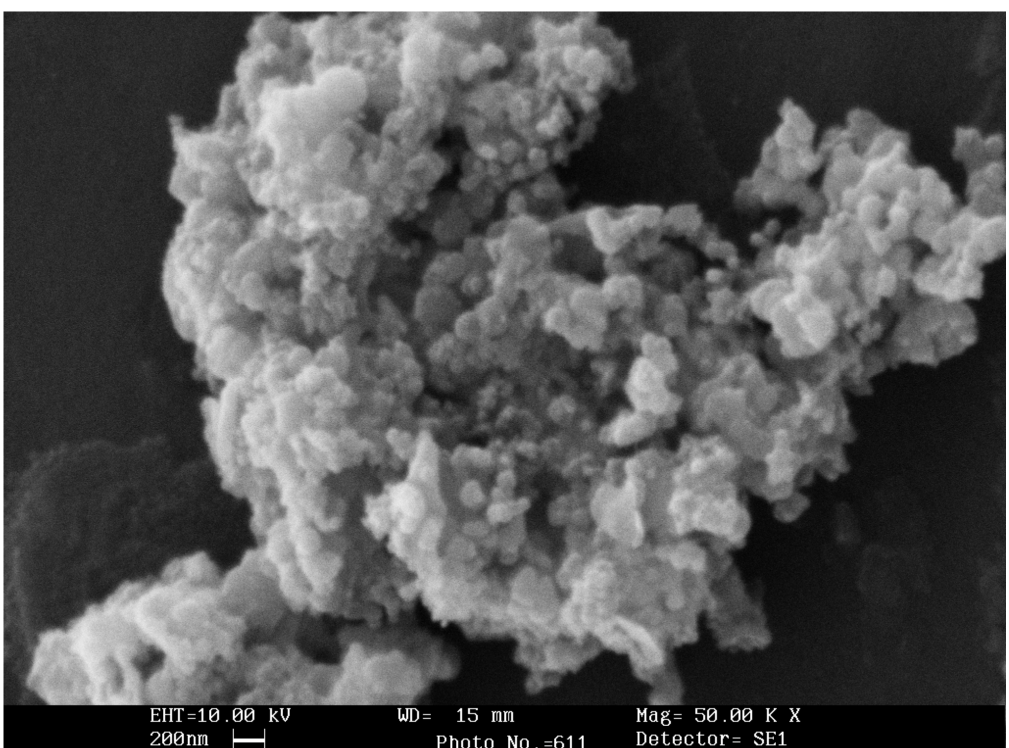

Figure 5: SEM photo of cotton soot particles generated during plasma air gasification (25 litre/min) treatment 200 nm range.

SEM of Cotton Plasma Pyrolysis Soot Particle

The soot particles are agglomerated as visible in the photo. The particle size range is about 150 to 300 nm size. The particles appear to have curved edges but no specific symmetrical structure could be judged. In Figures 4 and 5, as visible, we can see that soot particles are fused in each other and majority appear to be spherical.

Experimental Work and GC Analysis of Cotton Plasma Gasification Gas and Results

Gasification is a process for converting carbonaceous materials to a combustible or synthetic gas (e.g., H_2, CO, CO_2 and CH_4). In general, gasification involves the reaction of carbon with air, oxygen, steam, carbon dioxide, or a mixture of these gases to produce a gaseous product that can be used to provide electric power and heat or as a raw material for the synthesis of chemicals, liquid fuels, or other gaseous fuels such as hydrogen.

Pure Dry Cotton (1.0 kg/4 min) Plasma Gasification by Air (25 litre/min) Gas GC Analysis Result

Results of cotton gasification (25 litre/min) gas composition for 500, 600 and 700 °C are as shown in Table 4. Graph is shown in Figure 6. According to the graph we can see that between 500 and 600 °C temperatures concentration of hydrogen shows slight increase and between 600 and 700 it increases and methane on the contrary decreases; acetylene conc. also increases.

Pure Dry Cotton (1.0 kg/4 min) Plasma Gasification by Air (50 litre/min) Gas GC Analysis Result

Results of cotton gasification (50 litre/min) gas composition for 500, 600 and 700 °C are as shown in Table 5. Graph is shown in Figure 7. According to the graph we can see that between 500 and 700 °C temperatures, concentration of hydrogen is much low and methane is higher. Both hydrogen and methane conc. value are not much deviated. Ethane shows slight rise in concentration between 600 and 700 °C. Figure 8 shows GC peaks for 700 °C reading.

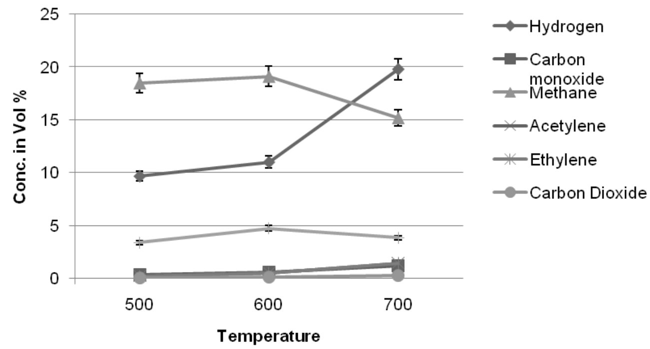

Figure 6: Graph of temperature vs conc. in volume basis of pure dry cotton (1.0 kg/4 min) plasma gasification by air (25 litre/min) gas GC analysis collected at different temperatures.

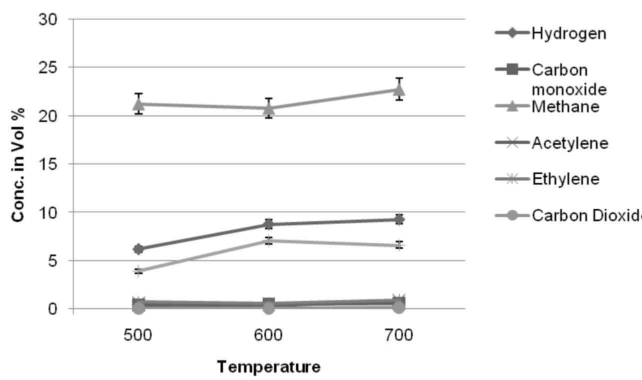

Figure 7: Pure dry cotton (1.0 kg/4 min) plasma gasification by air (50 litre/min) gas GC analysis collected at different temperatures.

Table 4: Pure dry cotton (1.0 kg/4 min) gasification (25 litre/min) as GC analysis results

Temp	H_2	*CO*	CH_4	C_2H_4	C_2H_2	CO_2	C_2H_6
500	9.705	0.38	18.478	0.263	0.263	0.085	3.411
600	11.036	0.613	19.097	0.538	0.538	0.172	4.767
700	19.815	1.228	15.213	1.457	1.457	0.288	3.874

Table 5: Pure dry cotton (1.0 kg/4 min) gasification (50 litre/min) as GC analysis results

Temp	H_2	*CO*	CH_4	C_2H_4	C_2H_2	CO_2	C_2H_6
500	6.188	0.432	21.244	0.74	0.557	0.098	3.937
600	8.803	0.557	20.797	0.58	0.359	0.109	7.09
700	9.289	0.609	22.766	0.96	0.841	0.196	6.612

Conclusion

With the results obtained for plasma pyrolysis of cotton, we can conclude that plasma pyrolysis can be a solution for safe solid waste disposal of organic wastes in an environmental friendly manner. Even energy recovery in the form of syn gas or Hydrogen is commercially possible. So we can say that it is a green technology.

Not only for organic waste but also for hazardous waste, low level nuclear waste and infectious bio-medical waste this technology can be utilized with few modifications and energy recovery is also possible there from.

References

Baeck, H.J., Shin, K.S., Yang, H., Lissianski, V. and W.C. Gardiner (1995). Reaction between CH_3 and H_2 at Combustion Reaction. *Korean Chem. Soc.*, **16:** 6.

Burton, J.M. (1998). Sustainable waste management – A case study from the UK water industry. *Water Sci Technol*, **38:** 51.

Fridman, A. (2008). Plasma Chemistry. Cambridge University Press, Cambridge, U.K.

Guddeti, R.R., Knight, R. and E.D. Grossmann (2000). Depolymerization of Polyethylene Using Induction-Couple Plasma Technology. *Plasma Chem. and Plasma Process*, **20:** 46.

Huang, H. and L. Tang (2007). Treatment of Organic Waste Using Thermal Plasma Pyrolysis Technology. *Energy Conver. and Manage.*, **48:** 1331.

Nema, S.K. and K.S. Ganeshprasad (2002). Plasma Pyrolysis of Medical Waste. *Current Sci.*, **83:** 271.

Pinto, F., Costa, P., Gulyurtlu, I. and I. Cabrita (1999). Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield. *Journal of Analytical and Applied Pyrolysis*, **51:** 39.