Energy Recovery Study for Polyethylene and Cotton by Thermal Plasma Degradation

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Abstract

In the present study, the main focus was on plasma pyrolysis and gasification of organic waste, specifically polyethylene and cotton waste and exploring the energy recovery possibilities from the gases obtained after the plasma pyrolysis and gasification. In pyrolysis the gases formed are Syn gas (H_2 + CO), CH_4, higher hydrocarbons along with soot particles. The waste is disintegrated using thermal plasma (which is generated using graphite plasma torch) in oxygen starved environment (pyrolysis) and also in partial oxidation condition (gasification).

Experiments have been carried out by varying pyrolysis chamber temperature from 500^0C to 700^0C and polyethylene and cotton are fed into the pyrolysis chamber. It has been observed that plasma pyrolysis of polyethylene in the temperature range of 500 to 700 ^0C yields H_2 as main component around 30-40% volume basis along with CO, CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2 and soot particles whereas pyrolysis of cotton, on the other hand provides less H_2 around 15-20 %. However, it has also been observed that in plasma gasification H_2, CO, CH_4 content in the exhaust gases reduces to some extent (2-5%). The theoretical and experimental energy recovery comparisons have also been carried out.

Keywords: *Energy Recovery, Hydrogen, Polyethylene, Cotton, Thermal Plasma*

1. Introduction

Increasing population, consumerism and industrial development have led to an increase in the quantities of hazardous and municipal solid waste (MSW) generated worldwide. Various thermal processes, including incineration, pyrolysis, melting or vitrification, have been proposed for treating these hazardous wastes prior to disposal, their aim being to destroy the organic fraction and convert the inorganic fraction into an inert silicate slag, or glass, that can either be advantageously reused, or harmlessly disposed of in an inert landfill [1–3].

The organic fraction, which we destroy via technologies as suggested above still consist of energy which can be recovered in the form of hydrogen or syn gas. With this objective Plasma pyrolysis and gasification of

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polyethylene and cotton (two major components of Municipal Solid Wastes) are selected as organic waste, treated and the gas generated is studied by GC analysis for its composition.

## 2. Plasma technology fundamentals

Plasma is considered to be the fourth state of matter, consisting of a mixture of electrons, ions and neutral particles, although overall it is electrically neutral. The degree of ionisation of a plasma is the proportion of atoms that have lost (or gained) electrons and, in the case of thermal plasmas of interest for this review, this is controlled mostly by temperature. Plasma technology involves the creation of a sustained electrical arc by the passage of electric current through a gas in a process referred to as electrical breakdown. Because of the electrical resistivity across the system, significant heat is generated, which strips away electrons from the gas molecules resulting in an ionised gas stream or plasma.

The basic heat transfer mechanism involved when a particle is in contact with plasma is presented schematically as Fig. 1. The net energy contributing to heating and melting the particle (Q_n) is the difference between the conductive and convective energy transferred from the plasma to the particle, and the radiative energy loss from the surface of the particle to the surroundings [4]. This is given by equation (1),

$$Q_n = ha(T_\infty - T_s) - \sigma \varepsilon a(T_s^4 - T_a^4) \qquad (1)$$

where h is the plasma-particle heat transfer coefficient, a is the surface area of the particle, T_∞ is the plasma temperature, T_s is the particle surface temperature, T_a is the reactor wall temperature,
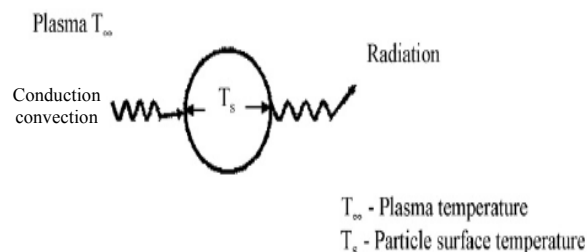
Figure 1. Basic transfer mechanism involved in the in-flight plasma heating and melting of a particle [5].

σ is the Stephan–Boltzmann constant and ε is the particle emissivity. This equation (1) represents a simplistic description of the mechanism occurring in the early stages because the surface vaporizes forming a gaseous shroud that inhibits heat transfer and, consequently, the mechanism changes [4].

3. Plasma advantages and disadvantages

Thermal plasmas have numerous advantages including: high temperature, high intensity, non-ionizing radiation and high-energy density. The heat source is also directional with sharp interfaces and steep thermal gradients that can be controlled independently by chemistry. While an upper temperature limit of 2000°C can be achieved by burning fossil fuels, electrically generated thermal plasmas can reach temperatures of 20,000°C or more. Thermal plasma reactors offer a range of other advantages including:

1. High throughput with compact reactor geometry;
2. High quench rates (>106 k/s) allowing specific gas and solid material

compositions to be obtained;

3. Low gas flow rates (except for non-transferred plasma devices) are compared to the combustion of fossil fuels, thereby reducing the requirements for off-gas treatment.

A possible disadvantage, especially from an economic perspective, is the use of electrical power as the energy source [6].

4. Energy recovery potential of polyethylene and cotton

a. Cotton

Total waste quantity (W) = 1.0 kg

Net Calorific Value (NCV)

 = 3579.93 kcal/kg

Energy recovery potential (kWh)

 = (NCV x W)/860

 = (3579.93 x 1)/860

 = 416 KWh

Power generation potential (kW)

 = (3579.93 x 1)/(860 x 24) = 0.17 KW

b. Polyeyhylene

Total waste quantity = W = 1.0 kg

Net Calorific Value (NCV) = 10,273 kcal/kg.

Energy recovery potential (kWh) = (NCV x W)/860 = (10389.8 x 1.0)/860 = 12.0811 KWh

Power generation potential (kW) = (10389.8 x 1.0)/ (860 x 24) = 0.50338 KW

5. Process chemistry in primary plasma chamber

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

5.1 Formation of methane

Methane is formed by reaction between excited *CH_3 radical and H_2 as shown below, giving methane and excited Hydrogen radical [7].
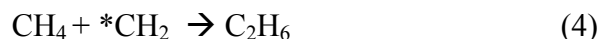
$$*CH_{3\,+}\,H_2 \rightarrow CH_4 + *H \qquad (2)$$

5.2 Thermal plasma pyrolysis of methane

Thermal decomposition of methane follows (Kassel Mechanism, 1932) [8].

$$CH_4 \rightarrow *CH_2 + H_2 \qquad (3)$$

*CH2 radical according to Kassel leads to ethane formation as follows:

$$CH_4 + *CH_2 \rightarrow C_2H_6 \qquad (4)$$

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

$$C_2H_6 \rightarrow C_2H_4 + H_2;\ C_2H_4 \rightarrow C_2H_2 + H_2;\ C_2H_2 \rightarrow 2C_{(s)} + H_2 \qquad (5)$$
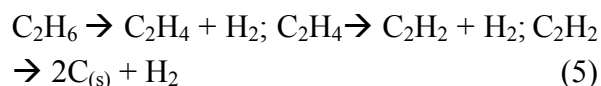
During plasma pyrolysis of methane, ethylene is formed after 10^{-6} - 10^{-5} sec and acetylene after $10^{-4} – 10^{-3}$ sec, subsequently soot formation takes place. Soot formation can be avoided if the pyrolysis gas residence time in the discharge is 10^{-3} and quenching rate 10^6 K/s. Practically such fast quenching is difficult, therefore soot formation is unavoidable.

6. Plasma pyrolysis and energy recovery system developed at facilitation center for industrial plasma technologies

As shown in Fig. 2, the system consists of the following sub-systems: plasma torch,

power supply, gas injection system, primary reaction chamber, venturi scrubber, water tank, packed bed scrubber, filter, condenser, bag filter, ID fan, chimney, buffer tank, generator set.
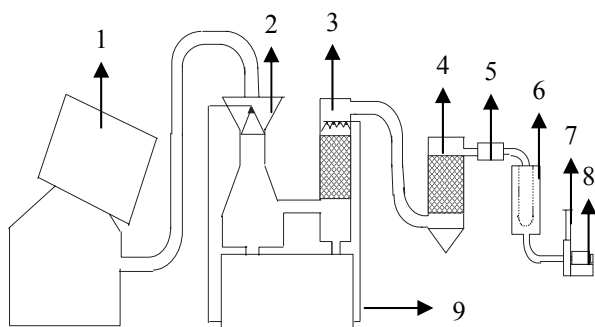
Figure 2. Plasma Pyrolysis Waste Treatment and Energy Recovery System Developed at FCIPT, Gandhinagar.
(Note: 1. Feeder system & Primary Chamber, 2. Venturi Scrubber, 3. Scrubber, 4. Filter, 5. Condenser, 6. Bag Filter, 7. Pyrolysis gas to Generator set, 8. Induced Fan, 9. Water Tank)
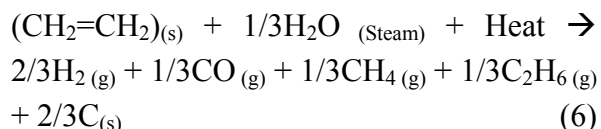
7. Energy generated from 1.0 kg polyethylene and 1.0 kg cotton

7.1 Theoretical calculation for polyethylene

We know that 1290 kcal ≈ 1.5 KWh energy is required for 1.0 kg of polyethylene to obtain maximum pyrolysis [9]. We are aiming at 15 kg/hr treatment rate. To dispose of a fixed amount of waste i.e., 15 kg/hr, 15 KWh energy is needed in the primary chamber and hence in the system. 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 Polyethylene using plasma source the required power input will be (15 X 100)/90 = 16.66 KWh ≈ 17 KWh.

Now the pyrolysis reaction for polyethylene using steam reforming is

$(CH_2=CH_2)_{(s)}$ + $1/3 H_2O$ $_{(Steam)}$ + Heat →
$2/3 H_{2 (g)}$ + $1/3 CO_{(g)}$ + $1/3 CH_{4 (g)}$ + $1/3 C_2H_{6 (g)}$
+ $2/3 C_{(s)}$ 　　　　　　　　　　　　(6)

Here, plasma pyrolysis gas components like Ethane (C_2H_6), Methane (CH_4), Hydrogen (H_2), Carbon Monoxide (CO) and Carbon ($C_{(s)}$) Soot can undergo combustion reaction to yield heat energy.
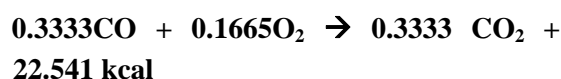
- Hydrogen

  $3H_2 + 3/2 O_2$ → $3H_2O + 3\times(57.82)$ kcal
  For (2/3) = 0.6666 moles
  $2H_2 + O_2$ → $2H_2O$ + 115.64 kcal

- Carbon Monoxide

  $CO + ½ O_2$ → CO_2 + 67.63 kcal
  For 0.3333 moles
  $0.3333 CO + 0.1665 O_2$ → $0.3333\ CO_2$ + 22.541 kcal

- Methane

  $CH_4 + 2O_2$ → $CO_2 + 2H_2O$ + 212.22 kcal
  For 0.3333 moles
  $0.3333 CH_4 + 0.6666 O_2$ → $0.3333 CO_2$ + $0.6666 H_2O$ + 70.7329 kcal

- Ethane:

  $C_2H_6 + 3.5 O_2$ → $2CO_2 + 3H_2O$ + 372.55
  For 0.3333 moles
  $0.3333 C_2H_6 + 1.16655 O_2$ → $0.6666 CO_2$ + $0.9999 H_2O$ + 124.17 kcal

- Carbon

  $C + O_2$ → CO_2 + 94.05 kcal
  For (2/3) = 0.6666 moles
  $0.6666 C + 0.6666 O_2$ → $0.6666 CO_2$ + 62.70 kcal
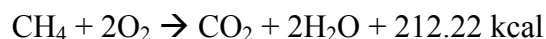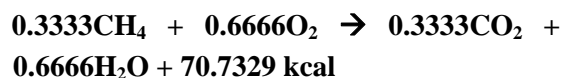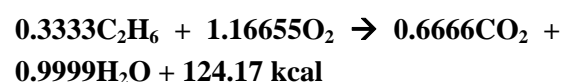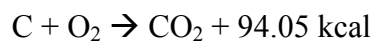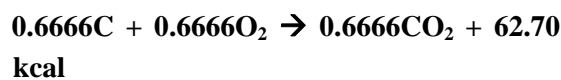
Total Energy Liberated = (124.17 + 70.7329 + 22.541 + 115.64 + 62.70) kcal = 395.783 kcal/mole = **1658.338 KJ/mole**
28 gm polyethylene yields 395.783 kcal/mole (1658.338 KJ/mole). So, 1000 gm (1.0 kg) yields [(1000×395.783)/28] = 14,135.1 kcal/kg.

Therefore, **Net gain in energy will** = (total energy liberated) - (energy required for pyrolysis of 1kg Polyethylene) = 14,135.1 - 1290 = **12,845.1 kcal/kg**
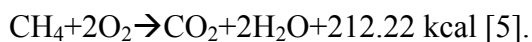
7.2 Theoretical calculation for cotton
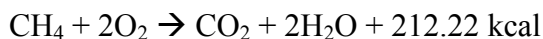Now the pyrolysis reaction for Cotton is,

$$C_6H_{10}O_5(s) + heat \rightarrow CH_4(g) + 3CO(g) + 2H_2O(steam) + 2C(s) + H_2(g) \qquad (7)$$
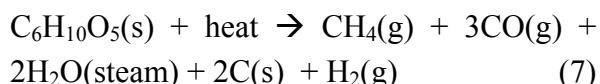
Here, plasma pyrolysis gas components like methane (CH_4), hydrogen (H_2), carbon monoxide (CO) and carbon ($C_{(s)}$) soot undergo combustion reaction to yield heat energy.
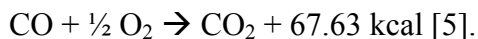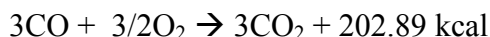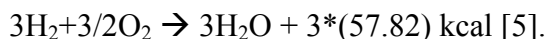
- Methane
  $CH_4+2O_2\rightarrow CO_2+2H_2O+212.22$ kcal [5].
  For 1.0 moles
  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 212.22$ kcal

- Carbon Monoxide
  $CO + \frac{1}{2} O_2 \rightarrow CO_2 + 67.63$ kcal [5].
  For 3.0 moles
  $3CO + 3/2O_2 \rightarrow 3CO_2 + 202.89$ kcal

- Hydrogen
  $3H_2+3/2O_2 \rightarrow 3H_2O + 3*(57.82)$ kcal [5].
  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 [5].
  For 2.0 moles
  $2C + 2O_2 \rightarrow 2CO_2 + 188.10$ kcal
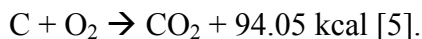
Total Energy Liberated = (212.22 + 202.89 + 57.82 + 188.10) kcal = 661.03 kcal/mole = 2769.72 KJ/mole
162 gm Cotton yields 661.03 kcal/mole (2769.72 KJ/mole). So, 1000 gm (1.0 kg) yields $[(1000\times661.03)/162]$ = 4,080.43 kcal/kg.

Therefore, Net gain in energy will = (total energy liberated) - (energy required for pyrolysis of 1kg Cotton) = 14,135.1 - 1290 = **2790.43 kcal/kg**

8. Experimental work and GC analysis of polyethylene plasma pyrolysis gas & results
Plasma pyrolysis gas obtained from primary chamber was analyzed in Gas chromatography system with N_2 as carrier gas, HP plot Q column, and TCD detector. TCD detector was used to measure the composition of gasses. 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. Therefore, N_2 was used as mobile phase to detect hydrogen. GC system configuration and parameter setting details are as presented in Tables 1 and 2.

Table 1. GC system configuration.

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

Table 2. GC parameter setting.

Injection Settings	Temp – 70 ^{0}C Split Ratio – 5.0 Column Flow - 3.09 ml/min
Column	HP Plot Q Temp – (60 ^{0}C for 2 minutes hold then 10^{0}C rise till 100 ^{0}C) Total analysis time 12 minutes Mobile Phase – N_2 gas
Detector	TCD Type Temp – 100 ^{0}C, Current – 78 mA

9. Plasma pyrolysis and air gasification results for PE

As shown in Tables 3,4,5 and Figs. 3,4,5,the results for plasma treatment of polyethylene and gas composition at three different temperatures 500°C, 600°C, 700°C.

**Table 3.** Gas composition result for PPPE in (volume mole%).

Temperature	Hydrogen	Carbon Monoxide	Methane	Carbon Dioxide	Ethane	Acetylene
500	34.55	1.06	14.24	0.49	9.97	2.027
600	39.32	2.09	13.94	1.102	8.89	4.408
700	40.92	1.09	19.015	0.794	8.25	1.848

Table 4. Gas composition result for PGPE25 (volume mole%).

Temperature	Hydrogen	Carbon Monoxide	Methane	Carbon Dioxide	Ethane	Acetylene
500	18.32	0.37	13.01	0.129	7.19	0.3415
600	25.58	0.972	10.29	0.236	6.51	2.1
700	29.95	1.667	7.82	0.646	6.79	5.399

Table 5. Gas composition result for PGPE50 gas composition result (volume mole%).

Temperature	Hydrogen	Carbon Monoxide	Methane	Carbon Dioxide	Ethane	Acetylene
500	9.882	0.255	17.74	0.076	4.6	0.4
600	16.82	1.348	11.15	0.652	5.52	3.31
700	20.51	2.774	9.498	1.156	6.07	8.78
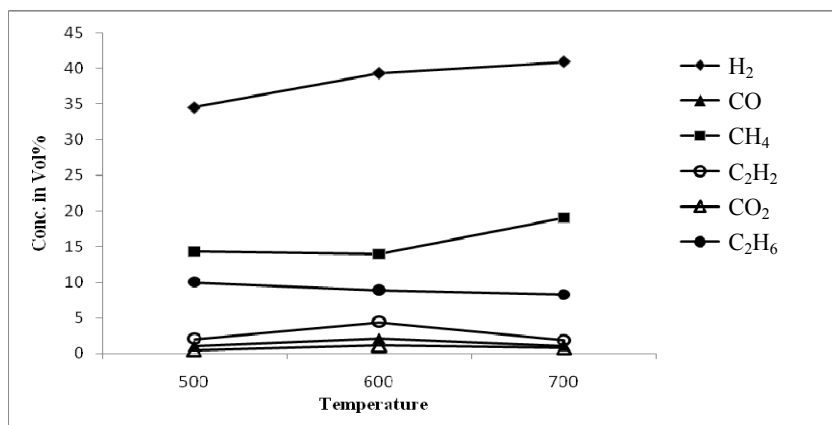
Figure 3. Graph of gas composition for PPPE as a function of temperature
(Unit X axis – °C, Y- Axis – Volume Mole %).
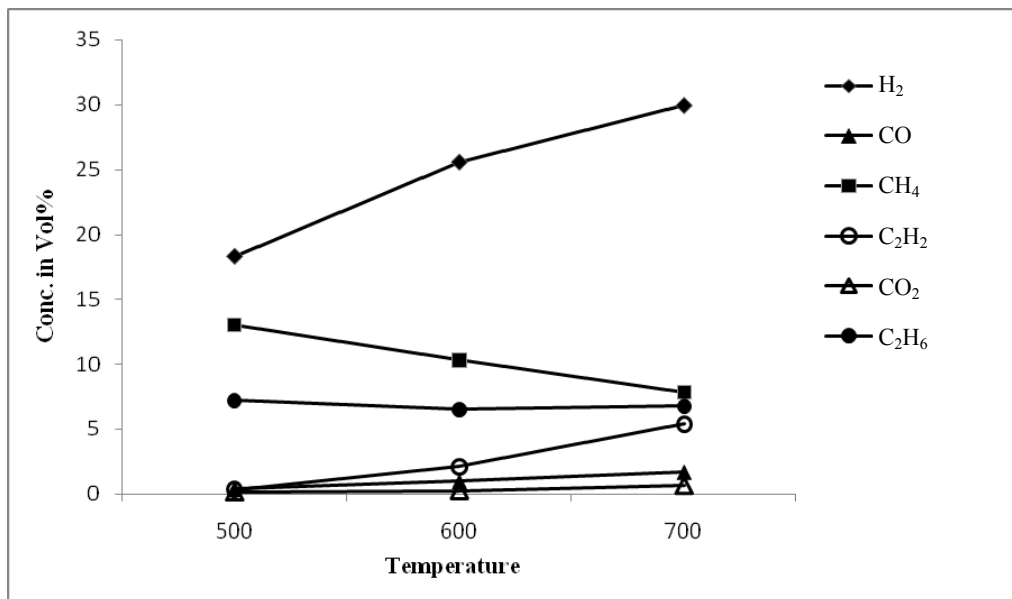
Figure 4. Graph of gas composition for PGPE25 as a function of temperature
(Unit X axis – °C, Y- Axis – Volume Mole %).
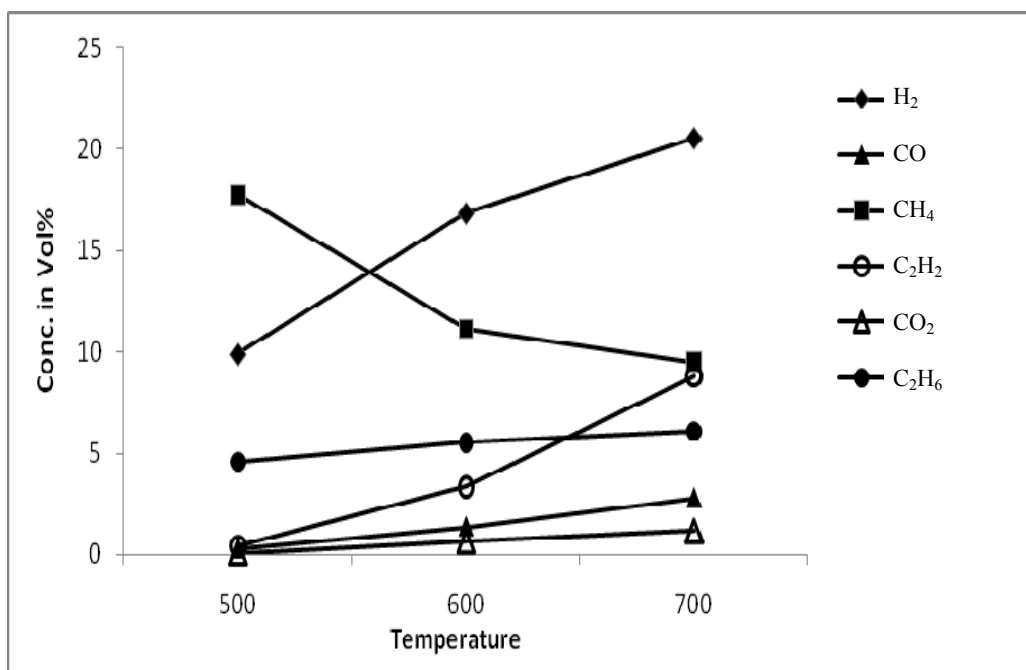
Figure 5. Graph of gas composition for PGPE50 as a function of temperature
(Unit X axis – °C, Y- Axis – Volume Mole %).

10. Plasma pyrolysis and air gasification results for cotton

The Tables 6,7,8 and Figs. 6,7,8 present the results for plasma treatment of cotton and gas composition at three different temperatures 500°C, 600°C, 700°C.

**Table 6.** Gas composition results for PPC (volume mole%).

Temperature	Hydrogen	Carbon Monoxide	Methane	Carbon Dioxide	Ethane	Acetylene
500	17.92	0.861	20.484	0.34	3.18	1.63
600	18.27	0.669	23.1	0.18	5.07	0.8
700	22.43	0.746	18.76	0.21	4.55	0.77

Table 7. Gas composition result for PGC25 (volume mole%).

| Temperature	Hydrogen	Carbon Monoxide	Methane	Carbon Dioxide	Ethane	Acetylene
500	11.24	0.467	23.44	0.108	4.27	0.337
600	13.36	0.664	20.15	0.212	4.9	0.513
700	23.88	1.511	19.54	0.393	5.32	1.513

Table 8. Gas composition result for PGC50 (volume mole%).

| Temperature	Hydrogen	Carbon Monoxide	Methane	Carbon Dioxide	Ethane	Acetylene
500	10.5	0.631	21.21	0.215	5.867	0.771
600	10.34	0.436	24.36	0.088	7.294	0.324
700	10.53	0.636	23.52	0.209	6.906	0.588
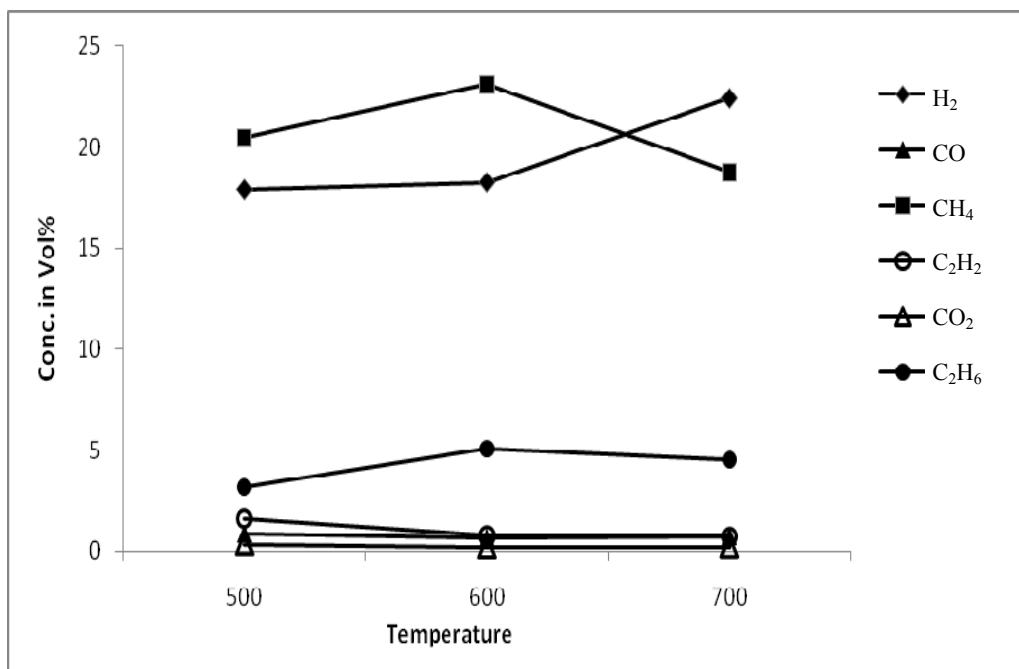
Figure 6. Graph of gas composition for PPC as a function of temperature
(Unit X axis – °C, Y- Axis – Volume Mole %).
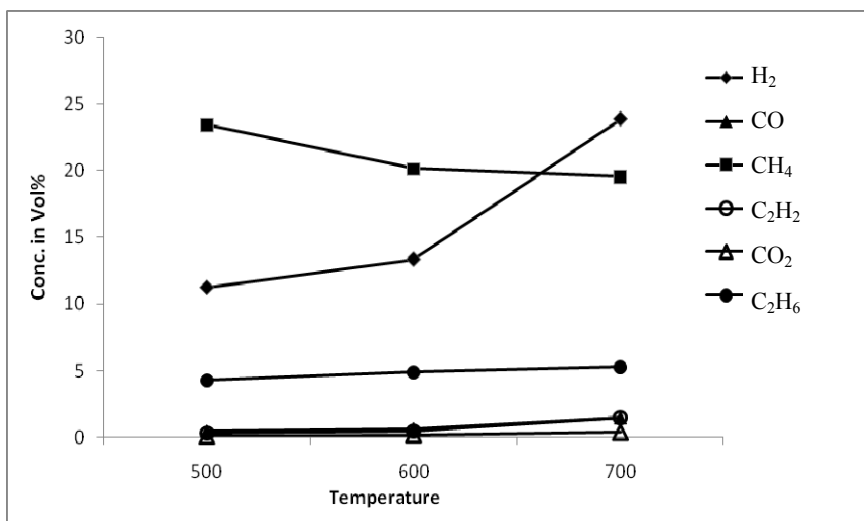
Figure 7. Graph of gas composition for PGC25 as a function of temperature
(Unit X axis – °C, Y- Axis – Volume Mole %).
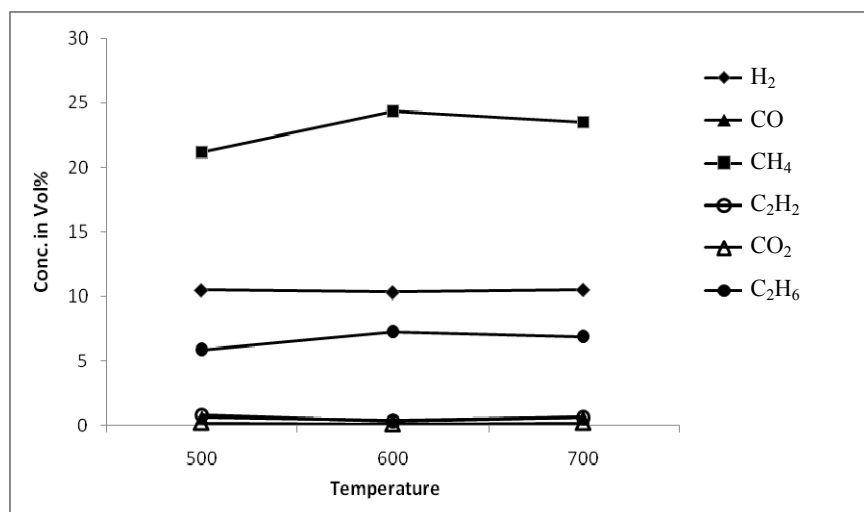
Figure 8. Graph of gas composition for PGC50 as a function of temperature
(Unit X axis – °C, Y- Axis – Volume Mole %).

11. Experimental energy recovery calculation of PPPE, PPC, PGPE25, PGPE50, PGC25 & PGC50 gases

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

Plasma pyrolysis of dry moisture free polyethylene 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 Polyethylene (PE) was done after starting the plasma torch and temperature reaching to 500°C.

For PE the best composition of plasma pyrolysis gas with high percentile of H_2, CO and CH_4 has been chosen from the mean readings of experiment no. 2,3,4. The result comes out to be 40.92% H_2, 1.09% CO, 19.01% CH_4, 0.79% CO_2, 8.25% C_2H_6 (Ethane), 1.848% C_2H_2 (acetylene) at 700 ^0C, remaining nitrogen is balanced. The air inside primary chamber was used as plasmagen gas.

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

Hydrogen - 0.41 moles $\rightarrow$ **23.71 kcal**
Carbon Monoxide - 0.01 moles $\rightarrow$ **00.68 kcal**
Methane - 0.19 moles $\rightarrow$ **40.32 kcal**
Acetylene - 0.018 moles $\rightarrow$ **05.59 kcal**
Ethane - 0.082 moles $\rightarrow$ **30.55 kcal**

= 100.85 kcal/mol
= 422.563 KJ/mol

28 gm polyethylene yields 100.85 kcal/mole (422.563 KJ/mole). So, 1000 gm (1.0 kg) yields [(1000×100.85)/28] = 3601.79 kcal/kg Therefore, **Net gain in energy will be** = (total energy liberated) - (energy required for pyrolysis of 1kg Polyethylene) = 3601.79 - 1290 = **2311.79 kcal/kg.**

Similarly other gases calorific values were calculated and compared for energy recovery as shown in Table. 9

12. Conclusions

From our experimental result, we conclude that disposal of both cotton and polyethylene is more efficient with plasma treatment. However, the energy recovery is found to be commercially possible from polyethylene only as in the case of cotton it is not too high.

Table 9. Calorific values of PPPE, PPC, PGPE25, PGPE50, PGC25 & PGC50 gases.

Process System	Gas calorific value obtained		
	kcal/mol	kcal/kg	Net gain in energy (kcal/kg)
PPPE	100.85	3601.79	2311.79
PGPE25	77.06	2752.14	1462.14
PGPE50	83.65	2987.50	1697.50
PPC	72.59	448.09	-841.91
PGC25	80.82	498.89	-791.11
PGC50	83.99	518.46	-771.54

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