TWO-STAGE PLASMA GASIFICATION OF WASTE

Pierre Carabin, Enzo Palumbo and Theodora Alexakis PyroGenesis Inc.

ABSTRACT

A novel two-stage plasma gasification process for the conversion of solid and liquid waste into synthesis gas (syngas) has been developed by PyroGenesis Inc. This paper describes this novel process, as well as its significant performance and economic advantages over conventional gasification or single-stage plasma treatment processes.

A pilot plant suitable for treating a variety of waste types (e.g. municipal solid waste, oils and solvents, plastics) has been installed at PyroGenesis' facility in Montreal. Syngas composition from this operation is shown for different operating conditions. The gas is shown to contain significant levels of CO and H_2 . Emission data from a continuous emission monitoring system are also presented and shown to meet the stringent local regulations.

INTRODUCTION

Vitrification has been shown to be an excellent method of destroying dioxins and immobilizing toxic substances such as heavy metals contaminants in ash and other waste. Vitrification technologies have successfully been demonstrated using plasma torches (1, 2) and graphite arc systems (3) as the heat source. PyroGenesis has developed a graphite arc furnace for the treatment of ash from pulp and paper power boilers. This technology has an excellent potential for the immobilization of metal contaminants in ash (4).

Gasification has the potential of producing energy from waste in a clean and efficient manner. In particular, dioxins and furans are not expected to be present in gasification systems because of the high temperatures used in gasification and the absence of oxygen precluding the formation of free chlorine and thus limiting chlorination of dioxin precursors in the gas (5). Moreover, NOx formation is also limited in gasification systems, because of the reducing environment in the system. (5) In collaboration with the US Navy, PyroGenesis has developed and demonstrated the plasma eductor concept used to gasify waste very rapidly at extreme temperatures (6, 7). The plasma eductor is an ejector combined with a plasma torch. The plasma forming gas, typically air, is used as the motive gas for the suction of waste into the plasma flame. The plasma eductor forces intimate contact between the waste and the plasma flame, ensuring instantaneous gasification.

Vitrification technologies are usually complex and expensive. Not all gasification technologies allow for the vitrification of the inorganic components in the waste. The process that is presented herein combines vitrification and gasification in the same system. It combines a low-cost graphite arc furnace developed for the vitrification of ash with and the plasma eductor, used as a secondary gasifier and designed for rapid gasification of waste. In this system, shredded waste is first fed to the graphite arc furnace, where the inorganic fraction is melted and vitrified and the organic fraction is

volatilized as a gas mixture of syngas (CO and H_2) and complex organic molecules as well as soot. The crude syngas is then fed to the secondary gasifier, which is the plasma eductor, and where the temperature of the syngas is increased, the complex organic molecules are broken down into CO and H_2 , and soot is converted to CO. Hence, a clean syngas is produced, that does not contain any organic contaminants. In addition, the secondary gasifier allows controlling the syngas composition by adjusting the amount of air and steam fed to the eductor. With this two-stage approach, vitrification and gasification parameters can also be controlled independently.

Recently, a pilot plant installation which combines the two technologies was commissioned. The system syngas quality was measured and the air emissions were tested by an external firm. The results of these tests are presented here.

DESCRIPTION OF TWO-STAGE PLASMA GASIFICATION PROCESS

PyroGenesis' two-stage gasification and vitrification process uses plasma energy to convert the organic fraction of waste into a clean fuel and the inorganic fraction into a stable inert slag. The clean gaseous fuel (or synthesis gas) can be used for the production of electricity and the inert glass can be used for construction applications or converted into other added value products.

This novel process consists of four main sub-processes (Figure 1):

- ➢ Waste preparation and feeding system
- Plasma thermal treatment system
- Synthesis gas cleaning system
- Energy recovery system

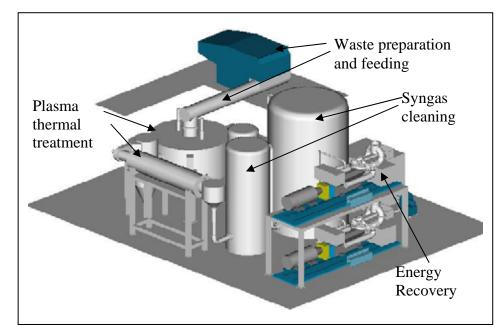


Fig. 1. System Overview

Waste is first fed to a shredder, where it is cut into small pieces roughly 2" in length. Optionally, the waste can be dried, using waste heat from the energy recovery system, in order to improve the energy efficiency of the gasification process. The vaporized moisture is mixed with the process air and fed, along with the waste, to the primary gasification furnace where it is not only treated to thermally destroy any contained hydrocarbons but also plays an important role in the chemistry of gasification.

The shredded waste is then fed continuously to the primary gasification furnace, through an air lock. In the primary gasification furnace, similar to an electric arc furnace, the organic fraction of the waste volatilizes and separates from the inorganic portion. A schematic of the primary gasification furnace is shown in Figure 2. The inorganic portion of the waste (metals, glass, dirt, etc.) is recovered into a molten metals phase and a molten inert slag phase. The temperature of the molten waste is maintained above 1600° C.

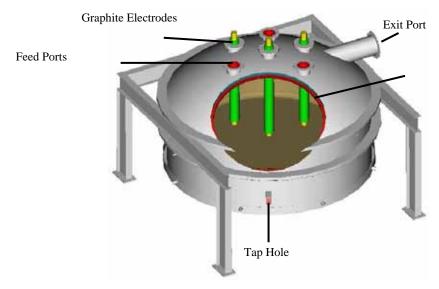


Fig. 2. Schematic of Primary Gasification Furnace

The molten metal is recovered periodically as an ingot for recycling. In a large-scale system, the slag may be removed continuously, whereas the slag is periodically removed from the pilot system. The slag can be granulated when collected in water or cast in molds, depending on the end use of the vitrified slag. The slag is a highly stable material, shown in Figure 3, which can be used for construction or other commercial uses. In a previous study, the leaching rate of elements from the slag has been shown to be several orders of magnitude below the US EPA regulations (4).



Fig. 3. Sample Products from Slag

The organic portion of the waste exits the primary gasification furnace as dirty synthesis gas, comprising primarily CO and H_2 , but also containing a certain amount of carbon soot, acid gases, moisture and partially decomposed hydrocarbons. Large dust particles are removed from the synthesis gas using a hot cyclone at the outlet of the primary gasifier and returned to the primary gasifier.

The dirty synthesis gas is then fed through a secondary gasifier, fired by a plasma torch, where the gas is reheated to 1100° C by a combination of plasma and chemical energy. The secondary gasifier is essentially a plasma driven eductor designed to mix the dirty syngas with air and moisture and expose the highly reactive mixture to the extreme temperatures of plasma. This ensures that all complex organic molecules and soot particles are converted into CO and H₂. A schematic of the secondary gasifier is shown in Figure 4.

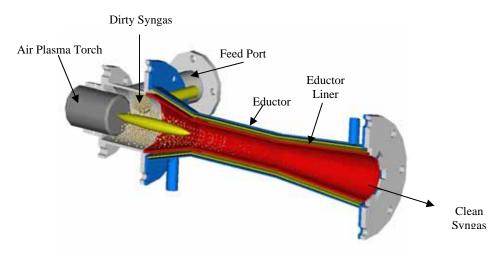


Fig. 4. Schematic of Plasma Eductor Gasifier

The synthesis gas exiting the secondary gasifier is quenched with water from 1100°C to approximately 85°C, in less than half a second, in order to freeze the thermodynamic

equilibrium of the hot syngas, and to avoid the reformation of dioxins, furans or other complex molecules.

The synthesis gas is cleaned prior to it being used for the recovery of energy. A scrubber is first used to remove any acidic HCl from the gas. Sub-cooling of the re-circulated scrubber water reduces the moisture of the gas from 50% at the outlet of the quench to below 5%. Small dust particles are removed from the gas through a Venturi scrubber. An entrainment separator removes dust and any remaining water droplets from the gas. The sulphur in the syngas (in the form of H_2S) is then removed by absorption over a bed of iron oxide impregnated packing. A HEPA filter is then used in order to remove submicron particulates from the syngas. An activated carbon filter is used to remove volatile heavy metals such as mercury. The whole system is kept under negative pressure using an induced draft (ID) fan.

In a commercial system, the clean synthesis gas may be fed to a gas engine for the production of electricity, hot combustion gases and hot water. The hot combustion gases can be used to produce steam with a heat recovery boiler. The steam can be used in part to dry the waste prior to feeding to the primary gasifier. Since the synthesis gas is cleaned before it is burned as fuel in the engine, there are no precursors to the formation of secondary pollutants such as dioxins and furans, and clean emissions are ensured.

The new two-stage gasification process offers several advantages over traditional low temperature gasification including minimal pre-treatment requirements, ability to treat a wide array of wastes and no ash production. The ash is replaced by inert slag, usable as construction material or other commercial uses. Compared to other single stage plasma gasification processes, this technology offers a higher level of safety, energy efficiency and the ability to control syngas composition. Furthermore, it is a very compact system.

PILOT PLANT OPERATION

A two-stage gasification pilot plant having a capacity of 0.5 to 2.5 tonnes per day, depending on the type of waste, has been commissioned at PyroGenesis Inc. in Montreal, Quebec, Canada (Fig. 5). The pilot plant system is essentially as described in the previous section, except that there is no energy recovery operation. The clean syngas produced is combusted in an afterburner and the off-gas is vented into the atmosphere. The system is designed to accept both solid and liquid feeds of various types, including municipal solid waste (MSW), oils, solvents, and plastics.



Fig. 5. Two-stage gasification pilot plant facility

During the commissioning of the pilot plant operation, the system was tested with incinerator ash, methanol, mixed plastics, and surrogate MSW.

Primary Gasifier

The impact of air flow in the primary gasification unit on the gross heating value of the syngas was studied. In these tests, surrogate MSW was used with a nominal composition shown in Table I. The results are shown in Figure 6. In these tests, the air flow was varied between 0 to 21 Nm3/h, resulting in heating values as high as 6 MJ/m^3 and as low as 1 MJ/m^3 .

Mixture	Nominal Composition Weight %	Composition Details	
Paper	22.0	Office paper	
Cardboard	14.5	Corrugated Cardboard	
Plastics	13.0	Polyethylene: Milk Jugs, Soda Bottles	
Glass	7.5	Soda glass: Bottles, Windows	
Metals	7.5	Tin Cans, Steel and Aluminum	
Wood	10.0	Plywood & Lumber	
Food	21.0	High Fiber plant (Cauliflower & Celery), beans, pea	
Textiles	4.5	Rags	

Table I -Surrogate Municipal Solid Waste Composition

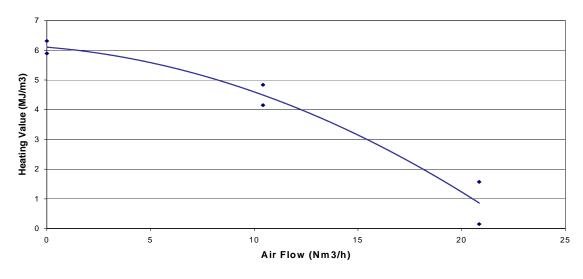


Fig. 6 Effect of Primary Gasification air on Heating Value

Secondary Gasifier

In another series of tests using surrogate MSW (Table I), syngas samples were taken from a slipstream at the secondary gasifier chamber for various operating conditions. The slipstream passed through a cold trap and filter before being aspirated into a 2-L Tedlar bag. The syngas sample was then analysed for O_2 , CO, H_2 , and CO₂ using a Burrell apparatus.

The feed rate into the primary gasification and vitrification unit varied between 20 and 25 kg/h. The airflow into the primary gasification unit was approximately 10 Nm³/h. At the secondary gasifier, the plasma current was varied between 400 and 450 amps, and the air flow rate was varied between 12 and 14.4 Nm³/h.

Table II shows the syngas composition for two samples, measured at the outlet of the secondary gasifier. The syngas composition was measured for two samples under the same operating conditions, namely 14.4 Nm³/h air, 450 amps, and 25 kg/hr MSW. The syngas samples were relatively rich in CO and H₂ and the gross heating values was 4.45 MJ/m^3 on average, making them suitable for use in an internal combustion engine.

Test no	CO ₂	O ₂	СО	H ₂	N ₂ (Balance)	Gross heating value
30a	7.7 %	0.8 %	29.0 %	8.8 %	53.7 %	4.6 MJ/Nm ³
30b	8.1 %	0.4 %	28.0 %	8.2 %	55.3 %	4.3 MJ/Nm ³
Average	7.9 %	0.6 %	28.5 %	8.5 %	54.5 %	4.45 MJ/Nm ³

Table II -Syngas Analysis and Gross Heating Values

In another test series, the impact of feed rate on syngas composition was investigated. In this test (no. 32), the air flow and feed rate were reduced to $12 \text{ Nm}^3/\text{h}$ and 20/kg/hr, respectively. The syngas compositions and heating values obtained were compared with the results of test no. 30 (Table III). Within the range of parameters tested at the secondary gasifier, there was no clear impact on the gross heating value of the syngas produced. In future test work, the secondary gasifier parameters will be varied over a wider range.

Test no	Feed rate	Air flow	CO ₂	O ₂	СО	H ₂	N ₂ (Balance)	Gross heating value
30	25 kg/h	14.4 Nm3/h	7.9 %	0.6 %	28.5 %	8.5 %	54.5 %	4.45 MJ/m ³
32	20 kg/h	12 Nm3/h	6 %	1.2 %	25.6 %	12 %	55.2 %	4.5 MJ/m ³

Table III - Syngas Analysis and Gross Heating Value at Lower Feed Rate

Another test was carried out to characterize the impact of the gas cleaning system on gas composition. In this test (no. 34), gas samples were taken at the secondary gasifier and after the gas cleaning section (Table IV). The gas analysis was essentially the same before and after the gas cleaning section, indicating that that there was no infiltrating air in the system.

Table IV - Syngas Analyses Before and After the Cleaning Section

Test no	CO2	O ₂	со	H ₂	N₂ (Balance)	Gross heating value
34a (before cleaning)	8.2 %	1.2 %	22.5 %	18 %	50.1 %	4.9 MJ/Nm ³
34b (after cleaning)	6.5 %	1.6 %	22 %	18.5 %	51.4 %	4.9 MJ/Nm ³

Air emissions

The pilot plant system is equipped with a continuous emission monitoring and analysis system (CEMAS) for analyzing inorganic compounds and total hydrocarbons (THC) in the stack off-gas. Specification for the CEMAS analyser is given in Table V.

This system is in operation at all times to ensure that all particulate and inorganic emissions are kept to a minimum. In addition, the emissions were sampled and analyzed by an external firm, to validate the values obtained by the CEMAS. The feed material for these tests was again simulated MSW with nominal composition as shown in Table I. The feed rate was maintained between 20-25kg/h. A summary of the results is shown in Table VI.

Measurement Principle	A multi-component emission monitoring system for simultaneously measuring HCl, CO, NO, NO ₂ , SO ₂ , H ₂ O, CO ₂ , O ₂ . The infra-red-active components are measured at high temperature (180°C) using a Fourier Transform Infra Red (FTIR) Bomem Inc. spectrometer. The O ₂ measurement is performed using an electrochemical sensor and the organic carbon content is measured using a flame ionization detector				
Measurement Range	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
Sampling Method	Extractive with sample conditioning				

Table V – Specifications for the CEMAS FTIR Analyser

Table VI - Emissions Adjusted to Reference O	Conditions of Local Regulations
--	---------------------------------

Parameters	Limit Values	Avg. Measured Values
Particulate (mg/Rm ³) ^a	15	<3.5
Carbon monoxide (mg/Rm ³)	50	36
Hydrochloric acid (mg/Rm ³)	30	0.33
Sulphur dioxide (mg/Rm ³)	50	18
Hydrofluoric acid (mg/Rm ³)	1	BDL^{b}
Nitrogen Oxides ^c (mg/Rm ³)	200	124
Arsenic (As) (µg/Rm ³)	50	BDL
Beryllium (Be) (µg/Rm ³)	10	BDL
Cadmium (Cd) (µg/Rm ³)	15	BDL
Mercury (Hg) (µg/Rm ³)	50	BDL
Lead (Pb) (μ g/Rm ³)	70	BDL
Thallium (Tl) (µg/Rm ³)	1	BDL
Other Metals ^d (µg/Rm ³)	500	BDL
Total Hydrocarbon (µg/Rm ³)	30	0.8

 ^a Rm³ refers to a meter cubed of gas at the reference conditions of the local regulations.
^b Below detection limit.
^c Expressed as NO₂.
^d Sb, Cr, Co, Cu, Sn, Mn, Ni, Se, Te, and V

The particulate and gaseous inorganic emissions were well within the limits of the local regulations and were in line with results obtained from the CEMAS. Although dioxins and furans were not measured during this series of tests, the total hydrocarbons were very low, which is a strong indication that dioxins and furans did not form.

Figure 7 shows the unadjusted continuous emissions results for one 2-hour sampling campaign. The CO, SO₂, and NO_x emissions are relatively stable during the two hour period, indicating that the production of syngas was also relatively stable. Fairly early in the sampling campaign, there was a very short duration of high NO_x emission. This was due to an interruption in the feed. Because of the high temperature at the secondary gasifier, a large amount of NO_x is generated. In normal operation and in the presence of syngas, the NO_x is typically reduced by the carbon in the syngas to form diatomic nitrogen. If feed levels are too low or feed is interrupted, there is no source of carbon available in the secondary gasifier to reduce the NO_x. Therefore, NOx level in the syngas could be used as an indicator of feed interruptions and trigger an alarm for the system operator.

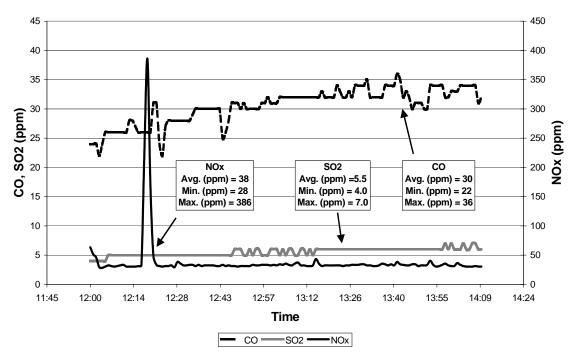


Fig. 7 Concentration of CO, SO₂, and NO_x during one 2-hour sampling Campaign

CONCLUSION AND FUTURE WORK

A new two-stage gasification process has been tested at the pilot stage and shown to produce air emissions that are well within the stringent local requirements for the main inorganic contaminants.

In the future, an external firm will be contracted to determine whether the emissions from the pilot plant operation also meet the stringent local regulations for organic emissions, including dioxins and furans. Based on our preliminary work, we are confident that these regulations will also be met.

In addition, further characterization tests of the secondary gasifier will be carried out. Along with determining the effect of secondary gasifier parameters on the heating value of syngas, the impact on the formation of soot will be determined. It has been qualitatively observed that, under certain operating conditions, the formation of soot can be significantly reduced by the secondary gasifier. Future tests will focus on quantifying these effects.

A CDN\$4.8 millions grant was recently received for the scale-up of this technology from the Canadian Government Sustainable Development Technology Canada (SDTC) fund. It is intended that this 50 TPD demonstration system be tested with both municipal solid waste (MSW) and industrial waste.

REFERENCES

- Tzeng,C. C., Kuo, Y.Y., Huang, T. F., Yu, Y.J, Lee, H. Y., Lin, D. L., Kuo, P. C., Hung, T. M., Sun, K. S., Luo, C. S., "The Study on Plasma Vitrification Technology for the Treatment of Radioactive and Hazardous Wastes", <u>Proceedings of the 2000 International Conference on Incineration and Thermal</u> <u>Treatment Technologies, Portland</u>, OR, (May 2000)
- Jimbo, H., "Plasma Melting and Useful Application of Molten Slag", <u>Waste</u> <u>Management</u>, Vol. 16, Nos 5/6, pp 417-422 (1996)
- Oden, L. L. and O'Connor, W., ASME/US Bureau of Mines Investigative Program Report on <u>Vitrification of Residue (Ash) from Municipal Waste</u> <u>Combustion Systems</u>, CRTD-Vol. 24 (1994)
- 4. Carabin, P., Alexakis. T., LeRoy, R., Drouet, M., and Tsantrizos, P., "Vitrification and Gasification of Pulp and Paper Hog Fuel Boiler Ash", Proceedings of the 2000 International Conference on Incineration and Thermal Treatment Technologies, Portland, OR, (May 2000)
- 5. Orr, D. and Maxwell, D., <u>A Comparison of Gasification and Incineration of Hazardous Wastes</u>, Report DCN 99.803931, (March 2000)
- Kaldas, A., Alexakis, T. and Tsantrizos, P., "Optimization Of The Marine Plasma Waste Destruction Technology", <u>Proceedings of the 2003 International</u> <u>Conference on Incineration and Thermal Treatment Technologies</u>, Orlando, FL, (May 2003)
- Alexakis, T., Tsantrizos, P.G., Manoliadis, P., Beverly, D. and Pelletier, S. "A Plasma-Arc-Assisted Thermal Treatment System For Shipboard Waste", <u>Proceedings of the 2002 International Conference on Incineration and Thermal Treatment Technologies</u>, New Orleans, LA, (May 2002).