The Gasification of Residual Plastics Derived from Municipal Recycling Facilities

The Environment and Industry Council (EPIC)
Canadian Plastics Industry Association

May 2004

Introduction

Gasification is a simple and commercially proven technology that has been practised for over 50 years. The process involves the conversion of materials having Carbon and Hydrogen in their chemical structure into clean synthesis gas, "syngas", a mixture of Hydrogen (H_2) and Carbon Monoxide (CO). "Syngas" can be used as a source of energy for combustion processes used to generate electricity (gas turbine or internal combustion engine) or as a source of chemical building blocks from which a wide assortment of commercial chemicals may be manufactured. In addition the Hydrogen may be extracted and used in fuel cells.

In 1999 a survey conducted under the auspices of the U.S. Department of Energy identified 160 commercial gasification plants in operation, under construction or in the planning, design stages in the world. The capacity of these plants when operational will produce an amount of energy equivalent to 770,000 barrels of oil per day.

Although most feedstocks for use in gasifiers are based on coal and petroleum by-products or residues such as tars, heavy oils and petroleum coke many other materials are being considered for gasification.

Many developing nations with ever increasing demands for electrical power are not rich in conventional fossil fuels. Their economies are often based on agriculture and as a result there are large quantities of agricultural residues which one calls bio-mass. Even in the developed world many industries, especially the agricultural and forest product sectors generate large quantities of waste the disposal of which is becoming increasingly difficult and costly. At the same time emphasis is being placed on the search for renewable sources of energy. As a result of all of these currents there is a great deal of work being conducted on the gasification of bio-mass and plants scaled to meet local circumstances are being erected. At the present time in the United States, bio-mass is the (non-hydro) renewable energy source with the largest generating capacity (about 7000 megawatts).

In addition, interest in the gasification of other residues including those from municipal waste collection is increasing. Why landfill certain wastes if they can be transformed into products that can be used as sources of chemicals or clean burning fuels?

The Gasifier: Its Operation

Gasification is not incineration. The chemical process of gasification is markedly different from that of incineration.

With out becoming too technical gasification is designed to maximize the conversion of feedstock to Carbon Monoxide (CO) and Hydrogen (H_2) while incineration converts the feedstock into Carbon Dioxide (CO_2) and water (H_20). Gasifiers typically operate at temperatures in the range of 1200°C to 2000°C. At these extreme temperatures chemical bonds are broken thermally. In addition, a gasifier operates with an atmosphere deficient in oxygen. This is called a reducing atmosphere. Such an atmosphere prevents the formation of the oxides of Sulphur and Nitrogen that contribute to the formation of smog and acid gases. The United States Environmental Protection Agency (EPA) defines gasification in the manner stated in the footnote below.[1]

Dioxin and furan compounds are not expected to be present in the syngas from gasifiers for two reasons. First, the high temperatures in the gasification process destroy any dioxin or furan compounds or precursors in the feed. Secondly, the reducing environment precludes the formation of free chlorine from HCl, thereby limiting chlorination of any species in the syngas.

The Gasifier: Plastics as a Feedstock

Many plastics, particularly the polyolefines, have high calorific values and simple chemical constitutions of primarily carbon and hydrogen. As a result, waste plastics are, from a chemical point of view, ideal candidates for the gasification process. Because of the myriad of sizes and shapes of plastic products size reduction is necessary to create a feed material of a size less than 5cm in diameter. Some forms of waste plastics such as thin films may require a simple agglomeration step to produce a particle of higher bulk density to facilitate ease of feeding.

A plastic, such as high-density polyethylene, processed through a gasifier is converted essentially to carbon monoxide and hydrogen and these materials in turn may be used to form other chemicals including ethylene from which the polyethylene is produced. This is true feedstock recycling, “closing the loop” as some might wish to call it.

In regions where electrical power is generated primarily through the burning of coal the substitution of plastics for coal in facilities with the good conversion efficiencies that result from co-generation (the production of electricity and steam), can provide more benefit, in terms of the reduction of greenhouse gas emissions, than the mechanical recycling of the plastic.

The plastics industry supports the mechanical recycling of its products where this recycling can be shown to be environmentally and economically sustainable. For products that don’t meet these two criteria or are residues from the preparation for reprocessing and reprocessing itself, the industry advocates energy recovery through efficient processes such as gasification.

Plastics are a relatively small portion of the municipal waste stream, generally around eight percent by weight. A substantial component of the plastics in the stream

[1] Gasification has been defined for the U.S. EPA as: “ a process that converts carbonaceous materials through a process involving partial oxidation of the feedstock in a reducing atmosphere in the presence of steam at temperatures sufficient to convert the feedstock to synthesis gas, to convert inorganic matter in the feedstock (when the feedstock is a solid or semi-solid) to a glassy solid material known as vitreous frit or slag, and to convert halogens into the corresponding acid halides.”

(particularly rigid containers) currently is being recycled mechanically. As a result can sufficient residual material be collected to operate even a small (5 megawatt) gasifier producing electricity for a local grid?

An integrated gasification process generating 5 megawatts of electrical energy at an efficiency of 37% (the average of the processes studied by the U.S. Dept. of Energy) requires a feedstock delivering 48,650 MJ (megajoules) of energy per hour. High-density polyethylene (HDPE) has a calorific value of 43.5 MJ per kilogram. Therefore, the operation of a 5 megawatt facility would require 1118 kilograms of HDPE per hour, 26.8 tonnes per day or 9800 tonnes per year.

Analyses of the composition of municipal solid waste recently conducted in various parts of Canada indicate that plastics do make up about 8 percent of the waste stream. Detailed analyses of the plastics streams show that approximately 58 percent of the plastics can be considered to be recoverable while the remaining 42 percent are said to be unrecoverable because the materials have been too badly contaminated by or are mixed in with other garbage. Of the recoverable 58% an all bottle collection capturing 80 percent of plastic bottles for mechanical recycling would leave 34 percent of the plastics in the waste stream potentially recoverable but without markets for their disposition. This material would be admirably suited for gasification. 34 percent of the plastics in the waste stream represent 2.75 percent of municipal solid waste.

The average per capita generation of municipal solid waste as recently measured in five communities across Canada is 350 kilograms. On this basis a region having a population of just over 1 million could provide a plastic feed to a 5megawatt gasifier generating electricity. If other carbonaceous wastes such as paper were incorporated with the plastics even moderate size communities could support the operation of a gasifier. A five megawatts generator is sufficient to supply the annual electrical needs of approximately 4600 Canadian homes.

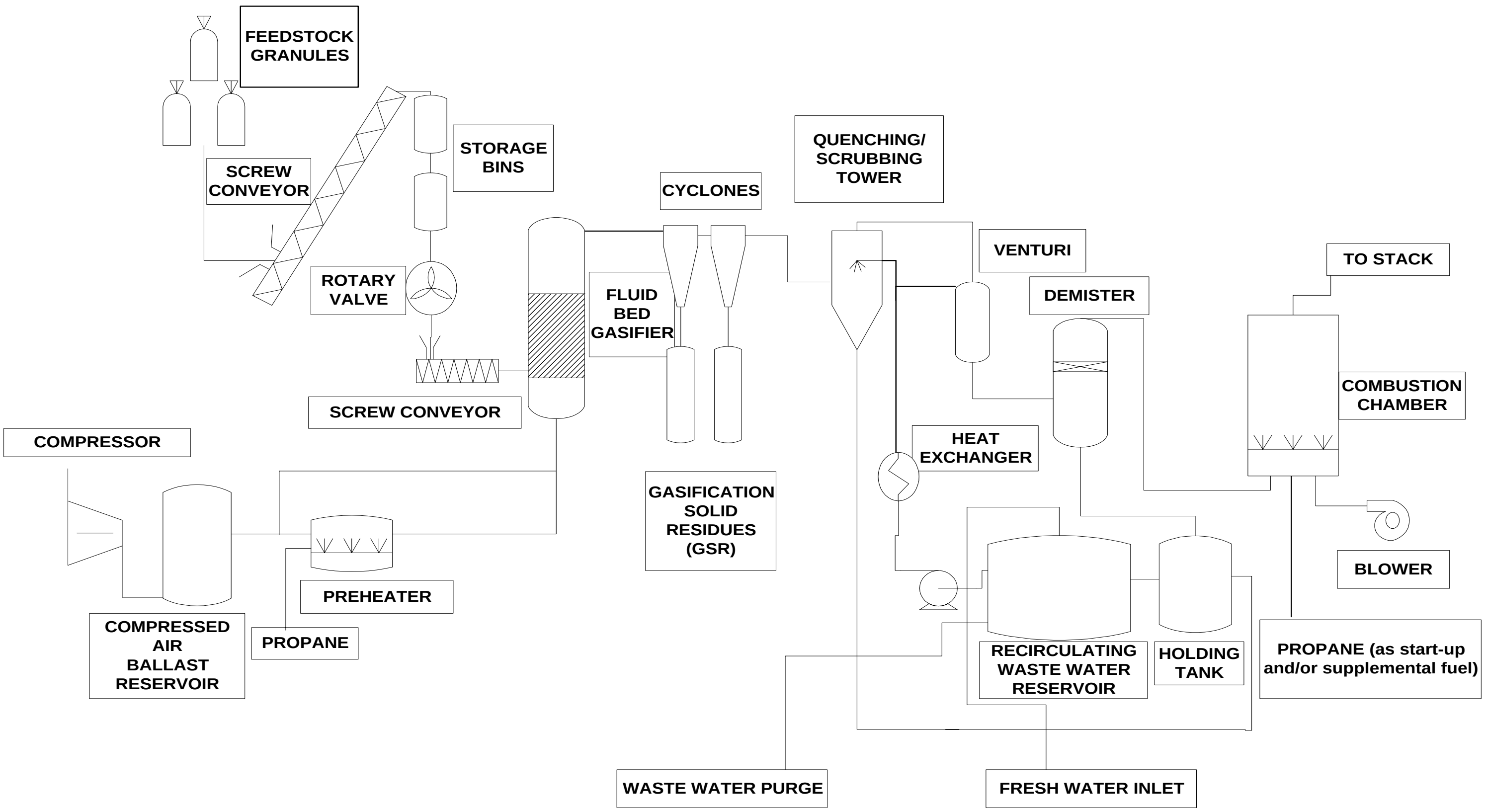
Testing the Gasification of Plastic Residues

In 2001 the Environment and Plastics Industry Council (EPIC) of the Canadian Plastics Industry Association carried out a series of preliminary experiments to test the gasification of plastic residues in the Ottawa laboratories of the CANMET Division of Natural Resources Canada. Although small in scope the information gleaned from these tests was very encouraging and led EPIC to consider a much larger, more sophisticated, series of trials in the facilities of ENERKEM Technologies Inc. located in Sherbrooke Quebec.

ENERKEM an off growth company from the University of Sherbrooke has developed what is known as the BIOSYN™ gasification process. ENERKEM is a cooperator of a commercial facility based on the process in Spain using contaminated plastic drums as a feedstock. In Sherbrooke ENERKEM maintains a fully instrumented pilot plant with a the capacity to gasify 100 to 150 kilograms of material per hour.

For the technically inclined reader figure 1 is a schematic representation of the BIOSYN process.

Figure 1 The BIOSYN^{TM} Process



In late 2002 EPIC contracted with ENERKEM to carry out a series of experiments in which plastics residues taken from an Ontario municipal recycling programme were to be gasified. The residues used as feedstocks for the experiments would normally have been disposed of by landfilling. In order to determine with precision and accuracy the various chemical species emitted by the process to atmosphere, water and land, EPIC engaged the services of *Arthur Gordon Environmental Evaluators Ltd.* a Quebec based independent testing contractor to carry out a detailed chemical analysis. The analytical methods employed by Arthur Gordon Ltd. followed standards recognized by the Canadian Government or the U.S. EPA. A complete list of the species for which an analysis was carried out is available in the full report describing the experiments.

With regard to atmospheric emissions, analyses were done for dioxins and furans, polychlorinated biphenyls (PCB's), chlorophenols (CP), chlorobenzenes (CB), heavy metals such as Lead, Mercury and Cadmium, particulate matter and hydrochloric acid as well as the oxides of Sulphur, Nitrogen etc. amongst other species. In addition the chemical species making up the “syngas” were determined using the technique of gas chromatography.

All of the water used for cooling the process and scrubbing the gases produced, as well as any water produced from the chemical reactions, was accumulated and analyzed before treatment for discharge to the local sewer system. These analyses considered oils and greases, poly-aromatic hydrocarbons, pesticides, suspended solids, biological oxygen demand (BOD), heavy metals and a number of other chemicals.

Solid residues were “leached” using standard procedures and analyzed for heavy metals, Arsenic, Barium, Selenium and Boron. In addition the solids were also analyzed to determine their residual Carbon content.

In order to determine the extent of the conversion of the feedstock into “syngas” detailed elemental analyses of the feedstocks were carried out.

The Experiments

As mentioned previously, two samples of plastic residues were tested. Sample 1 consisted of post consumer plastic film collected in the Regional Municipality of Ottawa. The film was shredded and agglomerated by friction to produce a small prill or pellet at Sol Plastics in Montreal. Sample 2 was a mixture of plastics (#3 to #7) that formed the residues from the plastics sorting line at the materials recovery facility (MRF) used by Ottawa. At the MRF # 1 plastics (PET) and # 2 plastics (high density polyethylene, HDPE) are sorted from the stream and baled for sale. The materials making up sample 2 were shredded by a private operator in Quebec and shipped in boxes to ENERKEM.

The gasification of each of the samples was carried out separately with the gasifier being cleaned following the trial of the first sample. Both samples were fed to the unit at a rate of 100 kilograms per hour. The duration of each run was approximately eight hours. The protocols governing the testing for dioxins and furans required that sampling be conducted for at least four hours under stable conditions. This condition was easily met.

Both runs were carried out without incident. The materials were easily injected into the unit. Stable conditions were achieved in a short period of time and all the sampling and analytical equipment on site operated without problem. The more sophisticated analyses were carried out off site at laboratories having recognized capability in dealing with particular species such as dioxins.

Results and Analysis

Mass Balance

In these experiments emphasis was placed on accounting for all of the carbon in the initial samples as the materials were gasified. This was done by comparing the carbon in the samples against the carbon contained in the species produced by gasification.

Mass Balance

	Sample 1	Sample 2
Carbon converted to gas	93.2%	94.1%
Carbon in solid residues	0.1%	0.2%
Carbon in wastewater	0.2%	0.1%
Carbon in tar	6.3%	5.9%
Closing	99.8%	100.2%

The accounting for carbon is quite reasonable for this type of experiment approaching 100% closures for both tests.

Energy Balances

Because their chemical composition consists primarily of Carbon and Hydrogen plastics have high energy content. Polyethylene could be thought of as "frozen natural gas" in that its energy content, which can be released by burning, is very similar to that of natural gas.

In the experiments the energy available in the samples was measured before gasification and then accounted for in the chemical species produced by gasification and in the losses incurred through processes such as cooling. The balance is shown in the table below.

Energy Balance

	Sample 1	Sample 2
Feed energy converted to "syngas" energy	71.8%	76.9%
Heat loss from solid residue recovery	0.01%	0.02%
Chemical energy in solid residue	0.1%	0.1%
Chemical energy in water	4.9%	4.7%
Heat loss from cooling	13.5%	14.3%
Closing	90.3%	96.1%

The energy balances clearly show that plastics exhibit high energy efficiencies in gasification since the energy in the feed is largely converted to energy in the "syngas".

In the experiments the "syngas" was burned in a combustion chamber. In large scale situations the "syngas" could be used to power an engine generating electricity or it could be used as a source of chemicals to form new chemicals or the Hydrogen could be extracted for use in fuel cells.

Emissions to Atmosphere

As stated above, in these experiments the "syngas" produced was burned. The emissions passing into the atmosphere from the flue stack on the combustion unit were analyzed. It should be noted in passing that the only means of egress for gases produced in the gasification unit is through the flue stack. Exhaustive results on flue gas analyses are presented in the test reports from Arthur Gordon Ltd. Using guidelines produced by the province of Ontario as a reference point all emissions, adjusted at 11 vol% Oxygen, are well below the allowable limits. The main results from the analyses are summarized in the table below.

Summary of Atmospheric Emissions

No	Categories	Descriptions	Sample 1	Sample 2	Ontario limits	Units
1	Continuous sampling (average)	O_2	11	11	-	%
		CO_2	8.68	7.94	-	%
		CO	0.9	1.3	50	mg/Rm^3
		SO_2	1	1	56	mg/Rm^3
		NO_x	48.6	47.1	110	PPMV
		Total Hydrocarbon (equiv. CH_4)	15	10	100	mg/Rm^3
2	Dioxin/Furan	TEQ equivalent	0.005	0.03	0,08	ng/Rm^3
3	Particles	Total	4.5	4.4	17	mg/Rm^3
4	HCL	Total	2.3	1.5	27	mg/Rm^3
5	Metals	Chrome	20.08	7.73	-	µg/Rm^3
		Cadmium	1	7.46	14	µg/Rm^3
		Mercury	0.62	3.82	20	µg/Rm^3
		Lead	35.27	44.19	142	µg/Rm^3
6	PCB	Total	0.1	0.11	-	µg/Rm^3
7	Chlorophenols	Total	0.64	0.33	-	µg/Rm^3
8	Chlorobenzene	Total	0.51	0.55	-	µg/Rm^3

The measured levels of dioxins and furans, already as much as 16 times lower than the Ontario emission limits, could be further decreased to essentially whatever level is desired by (a) filtering the air used for combustion and (b) additional gas conditioning steps. A commercially built unit would incorporate (a) and (b) to reach levels that correspond to "analytically detectable limits" (0.0015 ng/Rm^3).

Solid Residues

The quantities of solid residues remaining after the gasification of the plastics were very small. The residue from Sample 1 was 0.82% of the plastic processed while that from Sample 2 was 1.37%. Following leaching of the residues it was determined that any quantities of heavy metals, Cadmium, Chromium, Lead and Mercury were below the limits of detection. As a result it may be stated that the residues would comply with environmental regulations if they were used as ground cover.

Emissions to Water

In order to understand the analytical results and their significance it is necessary to remember that no water was purged from the system during the tests. In fact, the initial tap water charged into the holding reservoir continuously receives additional water from: (i) the humidity present in the feedstock; (ii) the water added to the gasifier to moderate the bed temperature and to create a partial pressure of steam capable of reforming some of the intermediate molecules resulting from depolymerization; and (iii) the water produced during the gasification. Although some of the water leaves the process as moisture in the gas, the net result is that the amount of water in the reservoir increases with time. During an 8.6 hour run the quantity of water increased by 307 litres.

The gasification process generates some particulates (organics and inorganics) and, as well, volatile organic intermediates. Cyclones can capture particulates down to 10 µm. Smaller particulates as well as volatile organics are captured by the scrubbing system and accumulate in the scrubbing water. The following table shows the accumulated amounts at the end of the runs.

Summary of the Characteristics of Wastewater

	Categories	Descriptions	Sample 1	Sample 2	Units	
1	Oil and grease	Animal & Vegetal	153	45	mg/L	
		Mineral & synthetic	77	18	mg/L	
2	PAH	Total	73 000	21 000	µg/L	
3	Pesticides	Mirex	<0.5	<0.05	µg/L	
		Aldrine	<0.5	<0.05	µg/L	
4	PCB	Total	<1	<0.5	µg/L	
5	Inorganics	Suspended solids (total)	72	16	mg/L	
		Phosphorus (total)	<0.1	<0.1	mg/L	
		Fluoride	4.4	2.2	mg/L	
6	Other organics	Cyanide (total)	12	4.7	mg/L	
		BOD_5	510	270	mg/L	

		TKN	80	24	mg/L	
7	Metals	Silver	<0.05	<0.05	mg/L	
		Aluminum	1.2	1.1	mg/L	
		Cadmium	<0.05	0.2	mg/L	
		Copper	0.07	0.06	mg/L	
		Mercury	<0.0002	<0.0002	mg/L	
		Lead	0.13	0.52	mg/L	
		Zinc	0.2	0.4	mg/L	
8	Others	Phenols (4-AAP)	69	46	mg/L	

In a commercial facility the wastewater would be treated through a three-step process:

(1) A physical-chemical pre-treatment to remove as much organic and inorganic material as possible by direct application of flocculants and coagulants;

(2) A wet oxidation treatment, to partially oxidize the PAH and the phenols, as well as other components including metal ions. Efforts in this direction have been carried out by ENERKEM in the period June – August, 2002. The polyaromatic hydrocarbons (PAH) and phenols are converted to acids, aldehydes and ketones at 260 – 320 C. This facilitates further biological degradation;

(3) Biological treatment under aerobic conditions converts the acids present in the wet oxidized wastewaters into biomass and CO2. The net result is clean water plus a biological sludge.

Such a 3-step wastewater treatment process can be incorporated into the overall gasification process and guarantee that regulations concerning purge to the sewage system will be met. This is the situation in the petrochemical industries where wastewater treatment has become a “routine” unit operation.

For the wet oxidation step the required heat can be provided by the recovery of the sensible heat of the hot “syngas” after the cyclones and prior to the quench step.

CONCLUSIONS

The results obtained during the testing program lead to the following conclusions:

1. Environmental

- Gasification of granulated plastic residues from municipal recovery facilities via the BIOSYN^{TM} process has shown that it can produce a synthetic gas that, upon combustion, results in atmospheric emissions of particulates, metals and organics well below the accepted emission limits in Ontario;

- All emissions, adjusted at 11 vol% O2, are well below allowable limits (Ontario as reference). For example, CO, NO_x, SO_2, dioxins and furans were below the strictest emissions limits in Canada;

- In both tests very small quantities of gasification solid residues (GSR) have been found. The solid residues contain most of the inorganic material initially present in the waste pellets and some unconverted carbon. Lixiviation (leaching) tests have shown that such residues comply with environmental regulations and can be used without any treatment as ground cover in embankments or a matrix for compost.

- The wastewater resulting from the scrubbing operations has been characterized. It needs to be treated. Technologies to treat this type of wastewater are known and operational all over the world.

2. Process considerations

- During the experiments the BIOSYN^{TM} gasification process was operated at conditions normally used, by ENERKEM, for similar types of feedstocks

- The synthetic gas produced combusts very well due to its significant energy content (Higher Heating Value) (10.6 MJ/Nm^3). No propane was necessary to supplement the energy input to the burner.

- The energy efficiency (energy value in the gas divided by the energy value of the feed) was 71.8% for Sample 1 and 76.9% for Sample 2. This corresponds to carbon conversions of 93.2 and 94.1 % respectively.

- The operations went smoothly and no major difficulties were encountered. The different modules of the process train functioned very well and only minor maintenance was needed throughout the runs.

FINAL SYNTHESIS (made by ENERKEM Technologies): ***based on the results of the pilot testing, a commercially designed gasification facility will be well within all known or anticipated environmental guidelines.***