DETERMINING ACCURATE HEATING VALUES OF NON-RECYCLED PLASTICS (NRP)

Demetra A. Tsiamis and Marco J. Castaldi

Earth Engineering Center | City College

City University of New York

March 23. 2016

Earth Engineering Center
CITY COLLEGE of NEW YORK

DETERMINING A MORE ACCURATE HEATING VALUE OF NON-RECYCLED PLASTICS (NRP)

BACKGROUND

Mechanical recycling of post-use plastics into new products can conserve resources and reduce energy use and greenhouse gas emissions. However, some plastics are not recycled in commercial markets. These non-recycled plastics (NRP), found in the municipal solid waste (MSW) stream, could provide an abundant source of alternative energy

NRP currently are not recovered to their full potential. According to the Earth Engineering Center of Columbia University's (EEC-Columbia's) "2014 Energy and Economic Value of Municipal Solid Waste (MSW), Including Non-Recycled Plastics (NRP), Currently Landfilled in the Fifty States" only about 6.8% (2.66 million tons) of post-use plastics in the U.S. were recycled in 2013 and 9.9% (3.9 million tons) were thermally converted to energy at the 85 waste-to-energy facilities in the U.S. These facilities displace fossil energy and produce useful heat and electricity from mixed, non-recycled waste, including NRP. The majority of NRP in the US, approximately 82.7% (32.5 million tons), is currently landfilled. This represents a loss of a valuable alternative energy resource. There is a significant opportunity to transform the abundant energy in NRP into electricity and heat and to commercialize new processes that produce higher value fuels and chemical feedstocks. (1)

In 2011, EEC-Columbia estimated that the average heating value for NRP in the waste stream was 31.96 MJ/kg. This estimate was contained in the report "Energy and Economic Value of Non-Recycled Plastics (NRP) and Municipal Solid Wastes (MSW) that are Currently Landfilled in the Fifty States." The report determined how much NRP was landfilled in the US and then estimated how much energy could be generated if all of the landfilled NRP were hypothetically converted to energy. EEC-Columbia's engineers used a U.S. Energy Information Administration (EIA) report titled "Methodology for Allocating Municipal Solid Waste to Biogenic and Non-Biogenic Energy" to estimate the heating values of each plastic resin (#1 - #7) in the waste stream. Then, using the tons of each resin landfilled, EEC-Columbia was able to calculate the NRP heating value of 31.96 MJ/kg that was used in its report. (2)

It was later discovered from a survey of additional sources that some of the energy values used in EIA's report underestimated the energy in certain plastic resins – such as low density polyethylene (LDPE). Underestimating the energy value of the NRP resulted in an underestimate of its energy potential. In 2014, EEC-Columbia released an updated report for the ACC. The report, "2014 Energy and Economic Value of Municipal Solid Waste (MSW) Including Non-Recycled Plastics (NRP), Currently Landfilled in the Fifty

States," used a variety of literature resources to estimate the energy value of NRP in MSW. The energy value used in the 2014 report was 35.7 MJ/kg, an increase of 11.7% from the value used in the 2011 report. (1)

Policymakers, communities across the country, and other key stakeholders are making important decisions about utilizing NRP as a potential energy resource. Therefore, it is critical that the energy value for NRP is as accurate as possible since it is a necessary piece of information in the design of efficient energy recovery technologies. The energy value of the input fuel, NRP in this case, must be reliably known to accurately design an energy recovery unit, such as a boiler. ACC tasked engineers from the Earth Engineering Center at City College of New York (EEC|CCNY) to address the discrepancies in NRP heating value in the literature by experimentally determining the heating value of NRP. EEC tested actual non-recycled plastics found in the waste stream and compared the experimental results to values presented in the literature.

EXECUTIVE SUMMARY

An EEC-Columbia 2014 literature study, "2014 Energy and Economic Value of Municipal Solid Waste (MSW), Including Non-Recycled Plastics (NRP), Currently Landfilled in the Fifty States" found that the weighted-average, lower heating value of NRP is 35.7 MJ/kg. This is significant because it means that NRP has a higher energy value than several conventional fuel sources routinely used in the U.S. and globally. NRP has an energy value that is 19% higher than petroleum coke, 37% higher than U.S. coal, and 87% higher than wood (1). There are several discrepancies in the technical literature regarding the heating value of NRP. The purpose of this study is to address these discrepancies by experimentally determining the heating values of as-received, contaminated, non-recycled plastics. All non-recycled plastics in this study were tested at EEC|CCNY labs and for the remainder of this report, all experimentally determined heating values will be referred to as "EEC|CCNY" values.

The weighted-average, lower heating value (LHV) of NRP was determined by EEC|CCNY by taking the mass average of the experimentally determined individual resin heating values of resins #1-6 typically found in MSW and weighting it based on the mass percent breakdown of NRP by resin type. This resulted in an average overall NRP heating value of 35.7 MJ/kg (30.8 MMBtu/ton). That amount could theoretically power 2.0 million more homes compared to the number of homes powered by an equivalent mass of coal. Figure 1 compares the EEC|CCNY LHV for NRP to LHV reported in the literature. It also compares the energy content of NRP to that of conventional sources of energy.

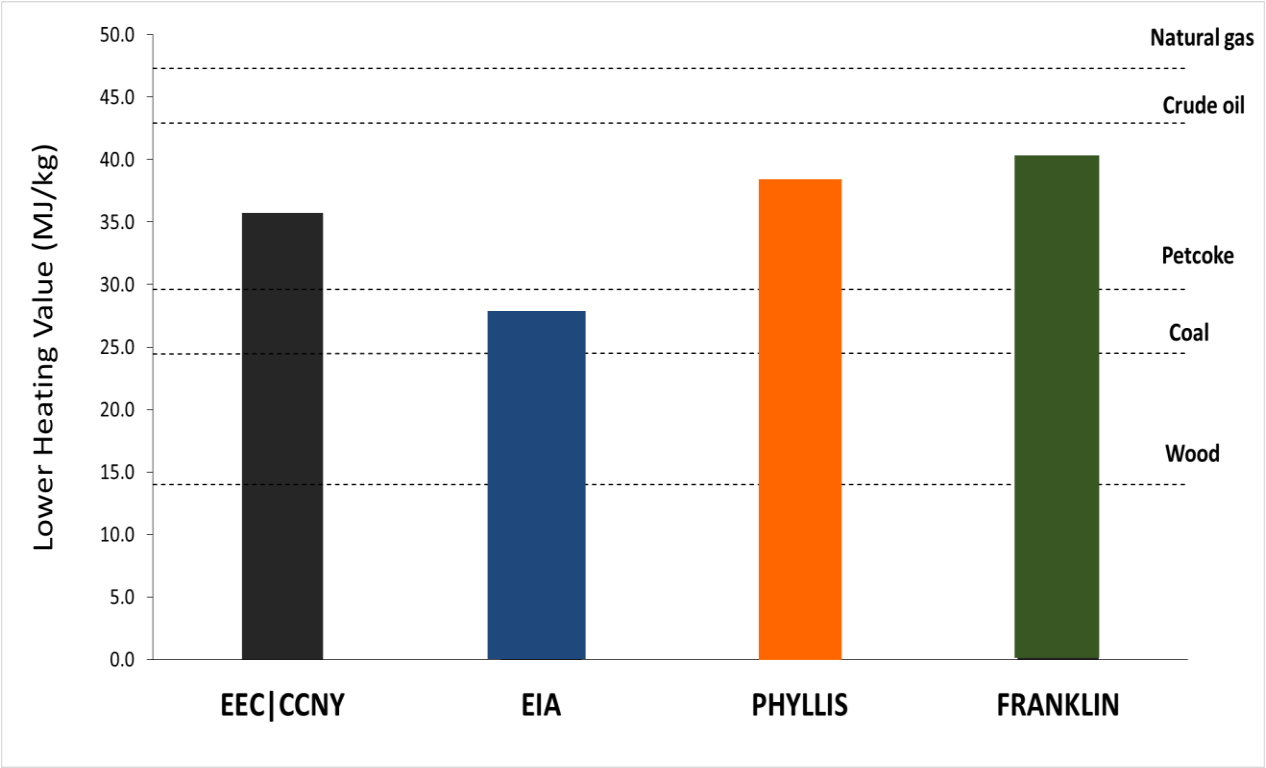


Figure 1: Comparison of EEC|CCNY NRP heating value to literature values and to the LHV of conventional energy sources[1]

KEY FINDINGS

This report contains several key findings. EEC|CCNY's experimental investigation revealed that plastics found in and contaminated by the waste stream retain more of their energy value, and their energy values are closer to virgin resin than originally suspected. Additionally, the impact of contamination and moisture on the energy values of these plastics was also less than expected. EEC|CCNY determined that multi-layered flexible plastic packaging and laminates are well suited for energy recovery since most their mass can be converted to useful energy. As plastics continue to displace other materials in a variety of applications, these findings are important for policymakers tasked with finding post-use solutions for non-recycled plastics as well as abundant, reliable sources of alternative energy.

The detailed technical key findings of this study are as follows:

- **Range of NRP lower heating values determined by EEC|CCNY: 22.9-41.0 MJ/kg (19.7-35.3 MMBtu/ton)**

[1] Excludes #7-Other in average NRP heating value

The range for the LHV for NRP was experimentally determined by EEC|CCNY to be 22.9-41.0 MJ/kg (19.7-35.3 MMBtu/ton). Waste plastics of polypropylene (#5-PP) and low density and linear low-density polyethylene (#4-LDPE and #4-LLDPE, respectively) yielded the highest heating values. Polyethylene terephthalate (#1-PET) and polyvinyl chloride (#3-PVC) yielded the lowest. Table 1 compares the EEC|CCNY NRP heating values to values reported in the literature. It should be noted that the EEC|CCNY reported LHV were calculated based on the experimentally measured higher heating values (HHV). Table 1 demonstrates the variability in the literature values.

Table 1: EEC|CCNY NRP higher and lower heating values compared to values reported in the literature (MJ/kg)

	EEC|CCNY (2015)		**EIA (2012)**	**FRANKLIN**		**PHYLLIS**	
RESIN	**LHV**	**HHV**	**N.R.**	**LHV**	**HHV**	**LHV**	**HHV**
#1-PET	23.8	24.4	23.8	24.7	25.6	21.9	22.8
#2-HDPE	37.1	40.6	22.6	46.5	49.6	43.6	46.7
#3-PVC	22.9	24.4	19.1	18.3	19.3	16.8	17.8
#4-LDPE	40.8	44.1	28.0	46.2	49.3	43.5	46.6
#5-PP	41.0	44.1	44.1	46.4	49.5	44.2	47.3
#6-PS	38.6	40.6	23.8	N.R.	N.R.	44.2	46.0
#7-Other	N/A	40.6	21.0	N.R.	N.R.	N.R	N.R
AVERAGE	**35.7**	**38.4**	**27.9**	**40.2**	**42.8**	**38.4**	**40.9**

Note: Average does not include #7 resin category as it is highly variable and not uniformly characterized

- **NRP heating values are within 15% of virgin resins' heating values.**

  NRP heating values were experimentally determined to be within 15% or less of their corresponding virgin resins. This finding suggests that even after the resin is converted into different products, inserted with fillers and dyes, and contaminated from food and use, 85% of its original energy value can be recovered for energy.

- **Contamination reduced NRP heating value by less than 5%.**

  After long term exposure of NRP in a refuse bag, the original heating value of as-received NRP was reduced by less than 5%. The reduction in heating value could be attributed to increased moisture content of the NRP samples as a result of exposure to the decomposition of organic refuse such as food scraps.

- **Approximately 98.5% of multi-layer NRP can be converted into electricity and heat.**
  Combustion of multi-layer film NRP (i.e., plastic film that has performance additives to preserve food) resulted in a residual that accounted for only 1.5% of the plastic's initial mass. This indicates that 98.5% of multi-layer NRP by mass would be converted to thermal energy if processed in a combustion system for energy recovery.

- **Metals can be recovered from the residue of multi-layer NRP.**
  Approximately 50% of the residual (i.e. 0.75% of the film) of multi-layer film NRP tested was titanium. Qualitative observations of combustion residuals from other NRP samples suggested the presence of aluminum and iron oxides. Such results indicate that the residual material from NRP thermal conversion processes can complement metal recovery initiatives.

Table of Contents

BACKGROUND 2

EXECUTIVE SUMMARY 3

KEY FINDINGS 4

GLOSSARY OF ACRONYMS 8

INTRODUCTION 9

Comparison of EEC|CCNY NRP experimentally determined heating values to the literature 10

METHODOLOGY 13

Sampling Techniques for NRP 13

Virgin resin samples 15

Controlled contamination tests 16

Are multi-layered NRP products suitable for thermal conversion? 17

The Differences between Lower Heating Value and Higher Heating Value 17

RESULTS & DISCUSSION 18

EEC|CCNY heating value range of NRP 18

Does contamination affect the heating value? 19

Impact of contamination on NRP heating value 20

Residuals of NRP after combustion 21

TGA and SEM/EDX analysis of multi-layer film NRP 21

Qualitative observation of NRP residuals after combustion 23

CONCLUSIONS 23

DISCLAIMER 24

CITATIONS 25

APPENDIX 26

GLOSSARY OF ACRONYMS

EEC|CCNY: Earth Engineering Center at City College, City University of New York

EEC-Columbia: Earth Engineering Center at Columbia University

NRP: Non-recycled plastics

MSW: Municipal solid waste

MPW: Municipal plastic waste

LHV: Lower heating value

HHV: Higher heating value

PET: Polyethylene terephthalate

HDPE: High density polyethylene

PVC: Polyvinyl chloride

LDPE: Low density polyethylene

LLDPE: Linear low density polyethylene

PP: Polypropylene

PS: Polystyrene

TGA: Thermogravimetric Analysis

Note: In this report, when references are made "to the literature" it is understood to be various sources of information reported in the public domain ranging from peer-reviewed journal articles to websites.

INTRODUCTION

The U.S. generated approximately 39.33 million tons of post-use plastics in 2011 of which 6.8% (2.66 million tons) was recycled, 0.7% (0.27 million tons) was used as alternative fuel in cement production, and 9.9% (3.88 million tons) was mixed with other non-recycled waste and converted to electricity and steam at waste-to-energy (WTE) facilities. The majority of this post-use plastic, approximately 83% (32.5 million tons), was landfilled. (1)

An attractive resource management option for non-recycled plastics (NRP) is energy recovery. In North America, over 70% of plastic polymers are derived from natural gas (most of the rest are made from oil). Plastics are generally just molecules made up of hydrogen and carbon atoms. Thus, these polymers can be unmade and converted into usable forms of energy and fuels. Most plastics that are thermally converted to energy are currently converted to electricity and heat with other non-recycled waste at WTE facilities. These facilities can greatly reduce the volume of waste that is sent to landfills. Additionally, new processes are being commercialized that can transform NRP into liquid fuels and/or chemical feedstocks. NRP are an attractive feedstock because they are comprised primarily of hydrogen and carbon. Hence, its energy content is generally higher than that of organics and paper found in MSW. Paper and organics often contain oxygen and lower carbon as well as higher levels of moisture compared to plastics. An EEC|CCNY literature search confirmed that the average heating value of NRP exceeds conventional fuel sources such as petroleum coke by 19%, coal by 37%, and wood by 87%. (1)

There is no single representative number for the heating value of NRP because it is a heterogeneous material group. Plastics consist of seven major resin categories identified by numbered resin codes: Polyethylene Terephthalate (#1-PET), High Density Polyethylene (#2-HDPE), Polyvinyl Chloride (#3-PVC), Low Density Polyethylene/Linear Low Density Polyethylene (#4-LDPE/LLDPE), Polypropylene (#5-PP), Polystyrene (#6-PS), and #7-Other. The “Other” category is a miscellaneous category for engineered resins, other plastics that do not fall under resin categories #1-#6, and combinations of resins which may include resins #1-#6. Factors that influence NRP heating value are molecular composition and structure, molding method, additives, and degree of contamination. Although NRP heating value varies with the composition of the plastics, the heating value of the individual plastic resins that make up NRP should be consistent.

A global literature survey conducted by EEC|CCNY revealed that there are discrepancies in the technical literature on the heating value of NRP. Discrepancies were also found where virgin resins were used as a surrogate. The purpose of this EEC|CCNY study was to address the discrepancies in the literature by testing actual non-recycled plastics found in the waste stream to determine their energy content and compare those values to the literature values. Additional objectives of this study included determining the impact of

contamination on NRP heating value and determining the suitability of multi-layered NRP for conversion to energy, heat, and fuels.

Comparison of EEC|CCNY NRP experimentally determined heating values to the literature

Figure 2 compares EEC|CCNY's LHV for resins #1-#6 to those reported in the literature. Based on extensive literature survey, EEC|CCNY concluded that the discrepancies found arose for numerous reasons ranging from errors in reporting to ambiguities in measurement procedure. For example, EIA did not specify the type of heating value (HHV or LHV) that it reports.

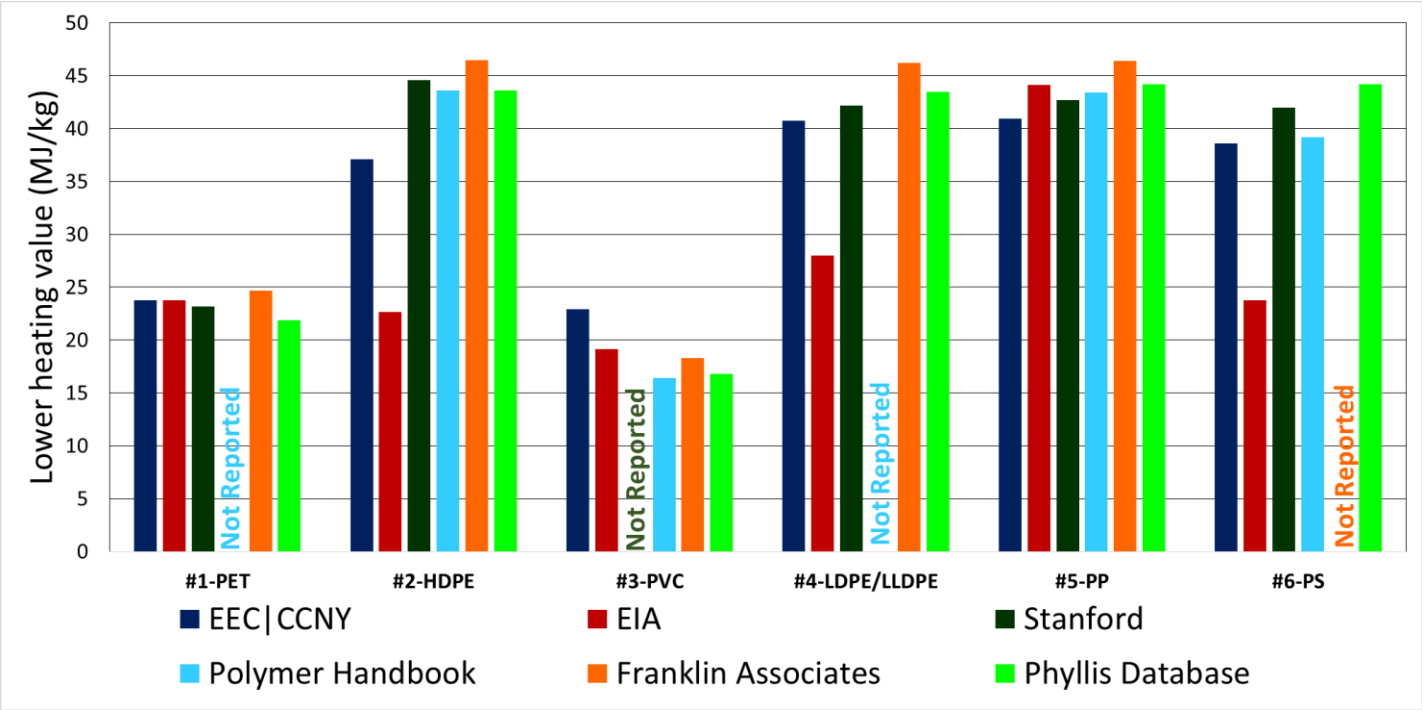


Figure 2: Comparison of EEC|CCNY NRP resin heating values to literature values[2] (MJ/kg)

Figure 2 clearly shows that EIA's heating values for HDPE, LDPE/LLDPE, and PS were significantly lower than those reported by other sources. EIA's heating values for HDPE, LDPE/LLDPE, and PS were 49%, 38%, and 48% lower, respectively, than EEC|CCNY's LHV for those same resins. EEC|CCNY conducted a literature survey of EIA publications on NRP heating values to understand these discrepancies. Table 2 shows the NRP heating values reported in EIA's publications and the references cited by EIA of where those values were obtained.

[2] Excludes #7-Other in average NRP heating value

Table 2: Typical heating values of waste plastics reported by EIA (MMBtu/ton)

Resin Type	EIA[1] (2007)	EIA[2] (2012)	Penn State[3]	Utah State University[4]	Percent Difference between EIA 2007 and EIA 2012
#1-PET	20.5	20.5	18.7	22.2	0.0
#2-HDPE	38	19.5	38	19.0	-64.3%
#3-PVC	16.5	16.5	16.5	N.R.	0.0
#4-LDPE/LLDPE	24.1	24.1	N.R.	24.1[5]	0.0
#5-PP	38	38	38	N.R.	0.0
#6-PS	35.6	20.5	35.6	N.R.	-53.8%
#7-Other	20.5	18.1	N.R.	N.R.	-12.4%

1: US EIA/DOE, Office of Nuclear, Electric, and Alternate Fuels. *Methodology for Allocating Municipal Solid Waste to Biogenic and Non-Biogenic Energy.* 2007. http://www.eia.gov/totalenergy/data/monthly/pdf/historical/msw.pdf
2: US EIA/DOE. *More Recycling Raises Average Energy Content of Waste Used to Generate Electricity.* 2012. http://www.eia.gov/todayinenergy/detail.cfm?id=8010
3: Garthe, James W. *Resource Recovery: Turning Waste into Energy.* Penn State.
4: *FAQ: USU Recycling Center.* Utah State University, 2010. http://www.usu.edu/recycle/faq/
5: Heating value reported in this source is only for #4-LDPE.

The yellow highlighted entries (HDPE and PS) in Table 2 indicate discrepancies in EIA reported values with its cited sources or with other EIA publications. The most recent EIA publication from 2012 does not indicate where values were obtained (i.e., source references) yet most of the heating values are similar to EIA's 2007 publication. The exceptions are HDPE and PS. Some of these discrepancies were unexpected and significant, suggesting a mistake in the reporting or calculation errors.

EIA's 2012 heating value for HDPE is 49% lower than its 2007 report. Inconsistencies were also noted in the cited sources for the EIA's 2007 publication. Specifically, EIA's 2007 publication reports a different value than its cited source from Utah State University. The EIA 2007 HDPE value seems like it is actually based on a Penn State source. However that source has inconsistencies as well because it cites two different values for HDPE. EIA's 2007 HDPE heating value of 38 MMBtu/ton is within the LHV range of 32-40 MMBtu/ton found in other literature sources. However, EIA's 2012 HDPE value was reduced to 19.5 MMBtu/ton.

EIA's 2012 heating value for PS was 42% lower than EIA's 2007 PS heating value. EIA's 2007 PS heating value of 35.6 MMBtu/ton was within the other literature sources' PS LHV range of 33-38 MMBtu/ton. It was also in the range experimentally determined by EEC|CCNY. The significant reduction in heating values for both HDPE and PS resins was not explained by EIA.

The heating value of LDPE/LLDPE reported by EIA in 2007 and 2012 was 24.1 MMBtu/ton. This is approximately 44% less than the average LHV for LDPE of 38 MMBtu/ton reported in the other literature sources. EEC|CCNY's LHV for LDPE/LLDPE was 35.1 MMBtu/ton. This is another confusing finding since LDPE and HDPE are both polyethylene molecules. EIA's 12% variation in the "Other" heating value between 2007 and 2012 can be attributed to the heterogeneity of this miscellaneous resin category.

Figure 3 compares EEC|CCNY's LHV for NRP, resins #1-#6, to LHVs reported in the literature. Figure 3 also compares the LHV of NRP to the LHV of conventional fuel sources. All the LHV's of NRP presented in Figure 3 are a weighted average of individual resin heating values based on NRP composition provided in the 2014 EEC-Columbia study. The average excludes #7- Other due to the wide variation of heating values in this miscellaneous resin category. The difference between the average heating values for NRP that included the #7 category versus excluding #7 was approximately 1% based on EEC|CCNY values and approximately 6% for EIA values.

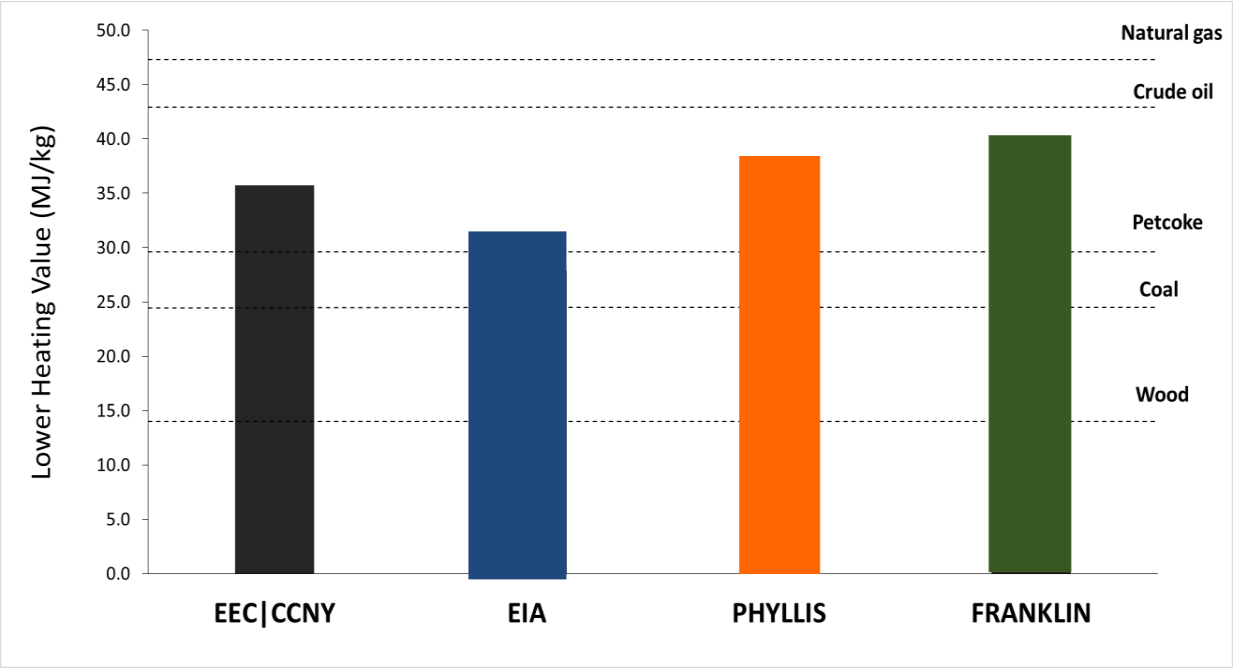


Figure 3: Comparison of EEC|CCNY NRP heating value to literature values and to LHV of conventional energy sources[3]

[3] Excludes #7-Other in average NRP heating value

METHODOLOGY

EEC|CCNY conducted its own experimental analysis of NRP found in the waste stream. The purpose was to create another data set to compare to the heating values of EIA and to other literature. EEC|CCNY also compared the NRP to virgin resin samples and studied how contamination might reduce the heating value of the NRP.

Sampling techniques for NRP

The higher heating values (HHVs) of virgin resins #1-#6 and of NRP samples were measured in a standard Parr 1341 oxygen bomb calorimeter. The NRP samples consisted of plastics in rigid, flexible, film, and foam forms. No provisions were taken to alter or identify contamination found on the NRP samples. Lower heating values (LHVs) were calculated from the HHVs using the standard conversion factor associated with the hydrogen content (obtained using the Phyllis 2 Database) of the plastic resins found in waste. HHV includes the energy obtained from condensing the water vapor produced during combustion. LHV reports just the energy obtained with water remaining as a vapor.

EEC|CCNY reviewed standardized sampling techniques to develop the sample collection for this study. The sampling technique chosen was EN14899, which is the European Norms (EN) that specifies an accepted method to obtain representative samples. A test matrix was designed to control the type and amount of contamination that could be found with as-received NRP. Random grab samples were procured from the waste stream to provide insight on possible variation.

Grab samples of NRP of Resin #1-#7 were collected from municipal solid waste (MSW). Grab samples are considered one-time collection from the MSW stream. EEC|CCNY obtained four garbage bags from the CCNY custodial staff during their daily garbage collection. The bags were brought to the laboratory, opened and examined to recover and separate NRP from the MSW. Once all the NRP components were collected and aggregated a random sample of each resin was taken. The grab samples included rigid, film, and foam plastics and varied in degree of contamination. Approximately 3 samples were collected for each resin type. Table 3 lists the NRP samples that were tested in this study and Figure 4 contains photographs of the samples.

Table 3: NRP grab samples by resin

Resin Code	Resin	Sample Type	Sample Item
#1	PET	Rigid	Salad dressing lid
		Rigid	Cookie tray
		Rigid	Peanut butter jar
#2	HDPE	Rigid	Cereal snack container
		Flexible	French fries freezer bag
		Film	Shopping bag
#3	PVC	Flexible	Blister pack
#4	LDPE	Rigid	Cereal snack container lid
		Foam	Laptop packaging
#4	LLDPE	Film	Grocery bag
		Film	Drycleaner bag
#5	PP	Rigid	Bottle cap
		Rigid	Fast food soda cup
		Rigid	Peanut butter jar lid
#6	PS	Foam	Egg carton
		Rigid	Salad dressing cup
		Rigid	Deli container lid
#7	Other	Flexible	Bunny food packaging

Figure 4: Examples of NRP samples tested in EEC|CCNY study

Virgin resin samples

EEC|CCNY obtained virgin resin samples from Braskem America Inc., Chevron Phillips Chemical Company LP, the Vinyl Institute, and Total Petrochemicals & Refining USA, Inc. These samples were used to compare the heating value of non-recycled plastic products to their virgin resin sources. The same calorimeter was used to determine the HHVs of both virgin resins and NRP grab samples. The virgin resins and their common applications are listed in Table 4.

Table 4: Virgin resin samples

Resin Code	Virgin Resin	Applications
#1	PET	--
#2	HDPE-5502BN	Household food, pharma and chemical rigid containers
	HDPE-9656	Cereal box liners, trash liners
#3	PVC	--
#4	LDPE - 4517	Plastic coated paper, multilayer food packaging
	LDPE - 5628	Shrink film, bulk beverage packaging overwrap
	LLDPE- D143	Trash liners, multilayer packaging
#5	PP: Inspire 6025	Deli containers, pudding/gelatin snack containers, storage containers, yogurt containers
#6	PS - 585B	Foam products (i.e. egg cartons)
	HIPS - 825E	Cups and lids

Controlled contamination tests

The impact of contamination on the heating value of NRP was also examined. Contamination can reduce the heating value of waste because it increases the waste's moisture content. This increased moisture content absorbs some of the heat released and consequently reduces the heat available for processes such as heating or power generation. To test the impact of contamination, selected NRP grab samples were placed in a trash bag filled with refuse. The trash bag was procured from the custodial staff of CCNY's Grove School of Engineering. The trash bag containing the NRP samples and refuse was sealed and left stationary in a room at ambient temperatures for approximately 3 months. The NRP samples were tested in the calorimeter at the end of the contamination exposure period. None of the samples were cleaned or modified prior to testing. EEC|CCNY compared the heating values of the as-received NRP samples prior to and immediately following the three month contamination exposure period.

Figure 5 shows the trash bag that was used for the contamination test. It contains a typical MSW mixture. EEC|CCNY tested this exposure, because during the three month exposure period, organic matter decomposed. As a result, the rendered volatiles and free water typically becomes more mobile (i.e., would flow due to gravity and attach to the NRP samples thus impacting the heating value. The rate of impact depends on the amount and type of contamination.

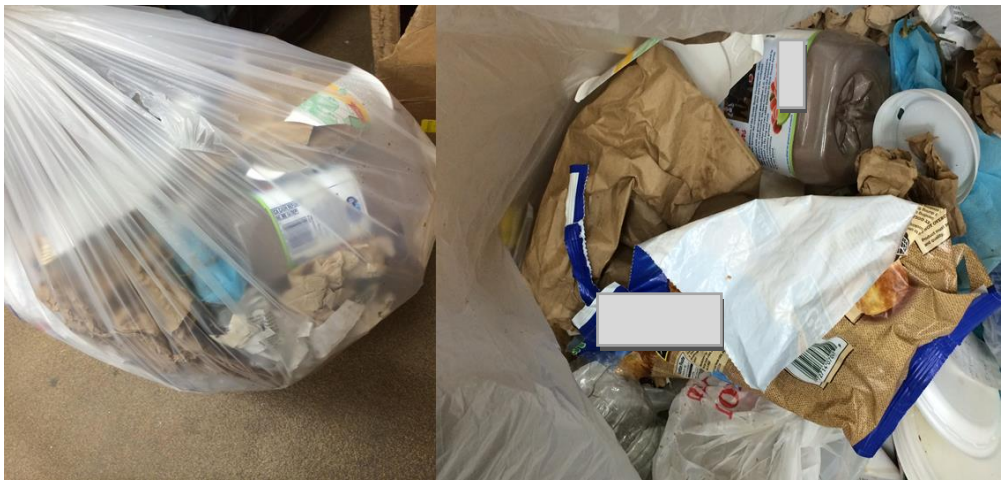


Figure 5: Refuse environment for controlled contamination test

Are multi-layered NRP products suitable for thermal conversion?

Calorimetry and thermogravimetric analysis (TGA) were conducted on a waste plastic candy bar wrapper to determine its heating value and non-combustible fraction, respectively. The candy bar wrapper is classified as a multi-layer film sample. The wrapper was analyzed in a Netzsch Luxx TGA (Model 409PC) in a combustion environment of 10% oxygen by volume and a constant heat rate of 10˚C per minute up to 1000˚C. This oxygen percent is representative of the amount found in a typical combustion environment experienced by parts of the waste. The residue from combustion was analyzed via SEM/EDX to determine its elemental composition.

The differences between Lower Heating Value (LHV) and Higher Heating Value (HHV)

Calorimetry measures the higher heating value (HHV) and uses the following procedure. It fully combusts the plastic sample using pure oxygen and then produces carbon dioxide and water. The water is initially produced as a vapor. However, once the entire sample is combusted (i.e., the test is complete) the water vapor condenses. This condensation process releases additional heat. Technically this additional heat is latent heat from the conversion of water from a vapor to a liquid phase. The combination of the heat released during the combustion of the sample and the subsequent heat released during the conversion of water vapor to liquid provides the maximum heat that can be obtained. This is known as HHV.

If the process maintains the water produced in the vapor state then the latent heat is not recovered. This is known as the lower heating value (LHV). The LHV is only the heat of combustion and does not include the

heat released during condensation of the water vapor. LHV is the key measurement for most combustion systems that convert heat to power or energy. The presence of condensed water in a system can cause problems.

Since the calorimeter yields the HHV, it is necessary to calculate the LHV. The LHVs were calculated using the following equation that subtracts the energy required to maintain the water produced during combustion in the vapor phase from the HHV:

$$\Delta h^{l}_{c} = \Delta h^{u}_{c} - 0.2196 \times [\%H]$$ *Source: Babrauskas*

Where Δh_c^l is LHV in MJ/kg, Δh_c^u is the HHV in MJ/kg, 0.2196 is the conversion factor for heat of condensation of water, and [%H] is the mass percent of hydrogen in the fuel. The hydrogen content of NRP was provided by the Phyllis database which contains an extensive information set. The equation above shows that the mass percent of hydrogen in the fuel sample must be known. Therefore, the molecular formula or chemical composition of the sample must be identified to determine the exact number of hydrogen atoms relative to the carbon, oxygen and other atoms. Reports in the technical literature typically publish LHV and HHV to enable the reader to choose the required value without adding the risk of assuming or using incorrect mass percent hydrogen.

EEC|CCNY provided both LHV and HHV in order to make comparisons to values reported in the literature. If a report contained both LHV and HHV, EEC|CCNY chose HHV because it was directly measured in the tests of this study. EEC|CCNY only compared LHV to LHV or HHV to HHV if a report only contained one value (either LHV or HHV)

RESULTS & DISCUSSION

EEC|CCNY heating value range of NRP

EEC|CCNY experimentally determined that the HHV range of NRP was 24.7 - 44.1 MJ/kg (20.6-38.0 MMBtu/ton). All NRP resins, except PET and PVC, had an average HHV within the range of 40-46 MJ/kg. PP had the highest measured HHV at 44.1 MJ/kg (38.0 MMBtu/ton). The HHV of LDPE/LLDPE was a close second at 43.9 MJ/kg (37.8 MMBtu/ton). The heating value of LDPE differed significantly from the EIA number which is 24.1 MJ/kg. PET and PVC yielded the lowest heating values at approximately 24.7 MJ/kg (21.3 MMBtu/ton) and 23.9 MJ/kg (20.6 MMBtu/ton). Plastic products being in rigid, flexible or foam form did not seem to impact heating values. Therefore, it can be estimated that the amount of energy captured per unit mass from a non-recycled film plastic compared to a non-recycled rigid plastic would be similar if the plastics

are the same resin. Table 5 lists EEC|CCNY's HHVs and calculated LHVs for NRP resins. Please refer to the Appendix for a detailed tabulation of the NRP samples' heating values.

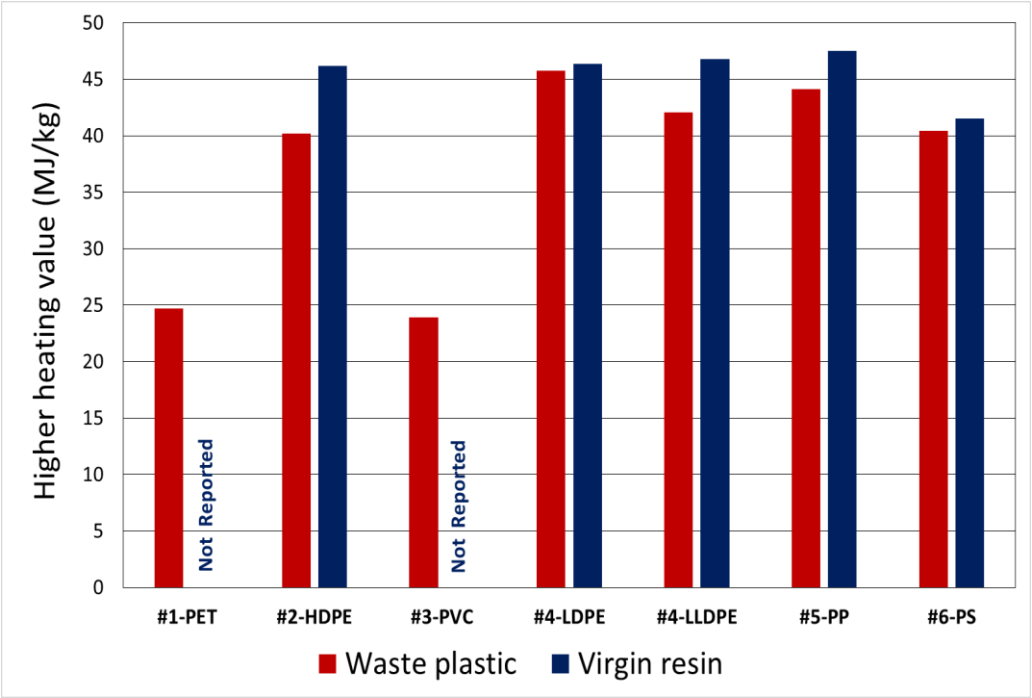
Table 5: EEC|CCNY heating values of NRP

Resin	Measured HHV (MJ/kg)	Calculated LHV (MJ/kg)
#1-PET	24.7	23.8
#2-HDPE	40.2	37.1
#3-PVC	23.9	22.9
#4-LDPE	45.7	42.6
#4-LLDPE	42.0	38.9
#5-PP	44.1	41.0
#6-PS	40.4	38.6
#7-OTHER	40.7	N/A
AVERAGE HEATING VALUE OF NRP[1]	**38.4**	**35.7**

1: Excludes #7-Other heating value in average; based on weight percent resin breakdown of NRP provided in 2014 EEC-Columbia report

Does contamination affect the heating value?

The impact of contamination on NRP heating value was determined by comparing the NRP grab samples to virgin resin samples. The virgin samples were provided by several resin manufacturers. Figure 6 shows a comparison of EEC|CCNY's HHVs for NRP and virgin resins. The adjacent table shows the percent difference between the NRP and virgin resin heating values for each resin. Samples of PET and PVC virgin resins were not provided for testing and are listed as "Not Reported" in Figure 6. The category "Other" is excluded from this comparison because it is a miscellaneous category and has no corresponding virgin resin. Please refer to the Appendix for a detailed tabulation of waste plastic and virgin resin heating values.



Resin Type	% difference (NRP : virgin resin)
#1-PET	N/A
#2-HDPE	14
#3-PVC	N/A
#4-LDPE	1
#4-LLDPE	11
#5-PP	7
#6-PS	3
AVERAGE	**7**

Figure 6: Higher heating value of NRP and virgin resins

Figure 6 shows that the heating value of NRP is consistently lower than its corresponding virgin resin. It varies approximately 15% or less with an average of 7%. However, since the differences remain small, estimating the heating value of NRP using virgin resin values would result in a remarkably accurate value.

Impact of contamination on NRP heating value

The quantified impact of contamination on NRP heating value was determined via a controlled contamination test. Two NRP samples were kept in a trash bag filled with refuse representative of typical MSW for approximately three months. The heating value of the samples was measured before and after exposure. The results of the controlled contamination test are shown in Table 6.

Table 6: HHV of as-received NRP and NRP exposed to contamination for a controlled period of time (MJ/kg)

Resin Code	Sample Type	Sample	As-received NRP (MJ/kg)	NRP after 3 month Exposure to Contamination (MJ/kg)	Percent Difference (%)
#4 - LLDPE	Film	Grocery bag	38.3	37.0	3.7
#6 - PS	Foam	Egg carton	41.0	38.9	5.2

NRP heating value was only slightly reduced after controlled exposure to contamination. EEC|CCNY found it was within approximately 5% of the as-received NRP heating value. The small reduction of the heating value could be attributed to increased moisture of the NRP samples. The moisture was a result of exposure to decomposed organics in the trash bag. Organics, such as food scraps, generally have high moisture content. Moisture reduces the heating value of waste items because part of the thermal energy generated during combustion is used to evaporate the water. EEC|CCNY determined that the heating value of the foam egg carton sample had a larger decrease from controlled contamination than that of the grocery bag. One possible explanation for this is that foam absorbs more moisture than film.

From this test, it was concluded that contamination, specifically moisture, reduced the heating value of NRP. However it is a small reduction give that it's within 5% of the original heating value of the as-received NRP.

Residuals of NRP after combustion

TGA and SEM/EDX analysis of multi-layer film NRP

Multi-layer plastics are one of the more difficult materials to recycle because they contain a complex mixture of constituents, including metal coatings. The purpose of the TGA was to determine how much residual mass remains if multi-layer NRP were to be processed in a combustion unit for energy recovery. The multi-layer film waste plastic analyzed was a used candy bar wrapper and the results of its calorimetry and TGA analyses are shown in Table 7 and Figure 7.

Table 7: Calorimetry and TGA results for multi-layer film NRP

HHV (MJ/kg)	Mass Conversion (%)	Residual (wt%)
41	98.5	1.5

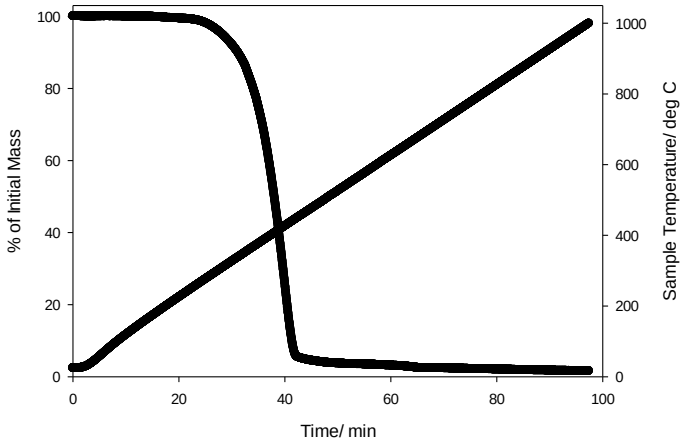


Figure 7: Mass conversion of multi-layer film NRP in TGA

Most of the multi-layer plastic wrapper was converted during combustion and the residual accounted for only 1.5% of the initial mass of the wrapper. This indicates that most of the mass of this specific multi-layer waste plastic package could be converted to thermal energy if processed in a combustion system or converted to petroleum products via pyrolysis. Calorimetry determined that the energy available in the multi-layer film NRP sample was approximately 41 MJ/kg.

The residual in waste-to-energy facilities can be reused in different applications based on its physical, thermal, and chemical properties. Figure 8 shows the elemental composition of the residual of the multi-layer film NRP sample based on SEM/EDX analysis. Based on these results, recovery of metals, such as titanium, from the residual of multi-layer film NRP could be considered as a source of additional revenue to a waste-to-energy facility processing multi-layer film NRP of this type. For example if a facility recovers 35% of the non-ferrous metal and 49% is titanium, historical pricing ($0.75/lb for titanium) shows it could generate approximately $60,000 per year.

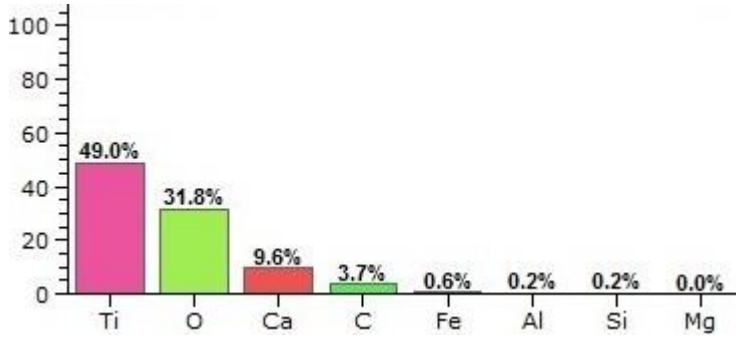


Figure 8: Elemental composition of residual from multi-layer film waste plastic (mass percent)

Qualitative observation of NRP residuals after combustion

Residual of NRP samples were observed in the crucible after each calorimetry run. The mass was measured to determine a rough estimate of the mass composition of residual in the sample. It was observed that most NRP with color produced white residues with some reddish tint as is pictured in Figure 9. This may indicate the presence of aluminum and iron oxides. EEC|CCNY recognizes that it is difficult to make sweeping conclusions about the conversion of multi-layered flexible plastic packaging via one product and one test. Additional testing of different types of commonly used multi-layered flexible packaging is currently being performed and will be released in a supplemental report.

Figure 9: Example of residual from #4-LLDPE NRP after calorimetry

CONCLUSIONS

This study confirmed that post-use, non-recycled plastics are more energy dense than conventionally used energy resources such as coal, petroleum coke, and wood. Furthermore, it concluded that plastics found in the waste stream retain most of their energy value even when contaminated with moisture and other substances found in waste. Since not all plastics can be recycled via commercial markets, these plastics represent a good source of alternative energy that could displace some forms of conventional energy. Lastly, this study confirmed that while some sources undervalue the energy contained in NRP, CCNY's experimentally determined values are closer to several other sources found in its literature search.

DISCLAIMER

This Report, titled, *Determining a More Accurate Heating value of Non-Recycled Plastics (NRP)* has been prepared to provide information to parties interested in the recycling and recovery of plastics and other materials. This report is not designed or intended to define or create legal rights or obligations. ACC does not make any warranty or representation, either express or implied, with respect to the accuracy or completeness of the information contained in this report; nor does ACC assume any liability of any kind whatsoever resulting from the use of or reliance upon any information, conclusion, or options contained herein. The American Chemistry Council sponsored this report. This work is protected by copyright. The American Chemistry Council, which is the owner of the copyright, hereby grants a nonexclusive royalty-free license to reproduce and distribute this work, subject to the following limitations: (1) the work must be reproduced in its entirety, without alterations; and (2) copies of the work may not be sold.

CITATIONS

(1) Themelis, Nickolas and Mussche, Charles. *2014 Energy and Economic Value of Municipal Solid Waste (MSW), Including Non-Recycled Plastics (NRP), Currently Landfilled in the Fifty States.* New York: Columbia University, 2014.

(2) Themelis et. Al. *Energy and Economic Value of Non-Recycled Plastics (NRP) and Municipal Solid Wastes (MSW) that are Currently Landfilled in the Fifty States.* New York: Columbia University, 2011.

(3) Shin, Dolly. *Generation and Disposition of Municipal Solid Waste (MSW) in the United States – A National Survey*. New York, Columbia University, 2014.

(4) US EIA/DOE, Office of Nuclear, Electric, and Alternate Fuels. *Methodology for Allocating Municipal Solid Waste to Biogenic and Non-Biogenic Energy*. 2007. Available at: http://www.eia.gov/totalenergy/data/monthly/pdf/historical/msw.pdf

(5) US EIA/DOE. *More Recycling Raises Average Energy Content of Waste Used to Generate Electricity.* 2012. Available at: http://www.eia.gov/todayinenergy/detail.cfm?id=8010

(6) Garthe, James W. *Resource Recovery: Turning Waste into Energy.* Penn State.

(7) *FAQ: USU Recycling Center*. Utah State University, 2010. Available at: http://www.usu.edu/recycle/faq/

(8) Babrauskas, Vytenis. *Related Quantities: (a) Heat of Combustion and Potential Heat.* *http://fire.nist.gov/bfrlpubs/fire92/PDF/f92030.pdf*

APPENDIX

Resin Code	Resin Type	Sample	Measured HHV (MJ/kg)
#1	PET	Salad dressing lid	24
		Cookie tray	25
		Peanut butter jar	25
		AVERAGE	**25**
#2	HDPE	Cereal container bottle	46
		French fries freezer bag	46
		Shopping bag	29
		AVERAGE	**40**
#3	PVC	Blister pack	24
#4	LDPE	Cereal container lid	47
		Laptop packaging	45
		AVERAGE	**46**
#4	LLDPE	Grocery bag	38
		Drycleaner bag	46
		AVERAGE	**42**
#5	PP	Bottle cap	46
		Soda cup	41
		Peanut butter lid	45
		AVERAGE	**44**
#6	PS	Styrofoam egg carton	41
		Salad dressing cup	38
		Deli container lid	42
		AVERAGE	**40**
#7	Other	Bunny food packaging	41
AVERAGE HHV OF WASTE PLASTICS (MJ/KG)			**38**

Resin Code	Resin Type	Sample	Measured HHV (MJ/kg)
#1	**PET**	--	--
#2	**HDPE**	HDPE-5502BN	47
		HDPE-9656	46
		AVERAGE	**46**
#3	**PVC**	--	--
#4	**LDPE**	LDPE - 4517	47
		LDPE - 5628	46
		AVERAGE	**46**
#4	**LLDPE**	LLDPE- D143	47
#5	**PP**	Inspire 6025	48
#6	**PS**	PS - 585B	41
		HIPS - 825E	42
		AVERAGE	**42**

Resin Type	Average measured HHV of waste plastic (MJ/kg)	Average measured HHV of virgin resin (MJ/kg)	% difference
#1-PET	25	--	--
#2-HDPE	40	46	14
#3-PVC	24	--	--
#4-LDPE	46	46	1
#4-LLDPE	42	47	11
#5-PP	44	48	7
#6-PS	40	42	3
#7-OTHER	41	--	--
AVERAGE*	**38**	**46**	