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Bioasphalt from Urban Yard Waste Carbonization
A Student Study

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16. Abstract - The project explored the feasibility of producing useful quantities of bitumen from yard waste carbonization. This was evaluated in bench scale reactors designed to yield data on the char, organic byproduct, and aqueous byproduct yields of a wide variety of yard waste components. Variables such as plant type, species, and moisture content were examined. Results indicated that the overall product yield would be approximately 40% biochar and 60% byproduct consisting of roughly 29% aqueous and 31% organic fractions. Of these fractions, approximately 57% were recovered by off gas condensation. Results also indicated that, although preprocessing would probably be required, variations in plant type and moisture content would not have a significant impact on yield.

The results demonstrated that bitumen could be generated from yard waste, and that it is likely that the volume would be sufficient to support the manufacture of asphalt. However, the properties of the resulting product are unknown. Additional research would be required to determine how to best use this material, and to quantify the properties of "green" asphalt made from yard waste derive bitumen.

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1. Introduction

The research project described here was designed to explore the basic feasibility of recovering sufficient bitumen from yard waste carbonization processes to support the production of bioasphalt. If successful, this could produce a non-petroleum-based product of value to the transportation industry that results from a "carbon negative" process that sequesters more CO_2 than it releases. The amount of bitumen that can be produced from yard waste, the physical and chemical properties of this bitumen, the carbonization operating conditions under which the production of this material is optimized, and a host of other unit process and operation details are all unknown, but the potential advantages of this yard waste management strategy are intriguing. The work described here represents groundbreaking research that begins to answer basic questions about the potential of yard waste carbonization (YWC) to produce a practical bitumen product that could be used to produce bioasphalt.

The fundamental approach applied in this research is described in Section 1.7. However, before discussing these project details, it seems prudent to document the context from which the project emerged. Readers will almost certainly observe that carbonizing yard waste is not an obvious approach for yard waste management or the production of useful byproducts. It is, however, plausible and emerged as an option during exploratory research based on a growing interest in carbonization as a "green" technology. Therefore, the following sections present some of the background information that led to this project.

1.1 Recent Interest in Carbonization as a "Green" Technology

Processes based on heating an organic substrate in the absence of oxygen (pyrolysis) and the absence of a bulk liquid phase (anhydrous pyrolysis) predate recorded history. Pyrolysis has been used to produce primary products (char, charcoal, coke) and byproducts (tar, pitch, resin) for thousands of years. Modern applications have led to a wide variety of process innovations (e.g. flash pryrolysis), reactor configurations and target products. Pyrolysis is used to produce fuels and other liquid and gas phase organics, as an analytical method to analyze complex organics, and to manage organic wastes (e.g. pyrolysis of scrap tires). However, until recently, its energy demands and byproduct discharges would probably not have placed it high on the list of "green" technologies. This is changing because of recent interest in "carbonization" which will

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loosely be defined here as pryolysis conducted to produce soil amendment charcoal (also referred to as biochar) and/or desirable byproducts.

"Carbonization" emerged as a technology of renewed interest following the re-discovery of "Terra Preta" or "Terra preto do indio" (Indian dark soil) which refers to dark, unexpectedly fertile, pre-Columbian, anthropogenic soils of the Brazilian Amazon basin (see Fig. 1 and 2). The formations were reported in the 1950's but not documented until "Amazon Soils" (Sombroek, 1966) was published. The formations are noteworthy because they apparently sustained large human populations (c. 450 BC to 950 AD) in areas otherwise characterized by thin unproductive soils believed to be incapable of sustaining agriculture. Similar formations have since been identified in Ecuador, Peru, in western and southern Africa, and in the Far East. It is clear that they are anthropogenic, but it is not known if they were intentionally created or were the byproduct of other activities (the former is considered to be most likely). It is known that their key ingredient is charcoal, which can moderate soil pH, improve moisture retention, enhance mineral availability, and support beneficial microbial activity.

The potential benefits of biochar soil amendments are thought to be substantial. The process sequesters carbon (in soil, charcoal appears to have a half-life of hundreds of years) and may improve crop productivity. This potential has spawned numerous international organizations dedicated to the development of the process (see Table 1). Groups worldwide are conducting field trials to examine crop yield improvements and soil scientists are working to quantify the mechanisms by which biochar improves soil productivity. Equipment manufacturers are also showing interest. Companies in at least 13 nations (Australia, Brazil, Canada, Denmark, Germany, Hungary, India, Korea, the Netherlands, New Zealand, Russia, the United Kingdom, and the USA) (Rasmussen 2009) are producing biochar equipment or running pilot-scale reactors. Commercial scale plants are operating in Australia (ANZBRN 2009), Canada (Reuters 2009), India, Brazil, the Philippines (Australian Biochar 2009) and in the USA (Austin 2009, Gunter 2009).

Fig. 1 – Nutrient Poor Oxisol (left) and Terra Preta Oxisol (right)

Fig. 2 – Terra Preta Formations in Brazil

Numerous agricultural and forestry byproducts have been evaluated as pyrolysis feedstocks (see Table 2 for 50 examples), but it appears that no one has examined the potential benefit of using urban yard waste as the feed stock. This is a mistake! The improved agricultural productivity alone may make yard waste carbonization financially viable. The waste management opportunities alone may make yard waste carbonization financially viable. The CO_2 sequestering and byproduct production (i.e. bitumen) provide additional value and convert an even higher portion of the waste into useful products. Taken together, the merits of yard waste carbonization present exciting new opportunities in solid waste management, agriculture and transportation materials research.

Table 1 – Examples of Organizations Promoting Biochar

Organization	Web Reference
Biochar.org – Balance Carbon and Restore Soil Fertility	http://www.biochar.org/joomla/
International Biochar Initiative	http://www.biochar-international.org/node/648
Biochar Fund	http://biocharfund.org/
The UK Biochar Research Center	http://www.geos.ed.ac.uk/sccs/biochar/
Biokohle.org – Educational Resources of Biochar	http://biokohle.org/
Australia and New Zealand Biochar Research Network	http://www.anzbiochar.org/
Canadian Biochar Initiative	http://www.biochar.ca/
Wiser Earth European Biochar Initiatives	http://www.wiserearth.org/organization/
Outbackbiochar	http://www.outbackbiochar.com/
Biocharinfo (CarboZero Foundation)	http://www.biochar.info/
Biochar Ontario	http://groups.google.com/group/biochar-ontario
Biochar Europe	http://www.biochar-europe.org/
Support Biochar	http://www.supportbiochar.org/

Table 2 – Examples of Feed Stocks That Have Been the Object of Pyrolysis Research

Feed Stock Evaluated	Reference	Feed Stock Evaluated	Reference
Almond shell	Gonzalez et al. 2009	Orange tree prunings	A
Almond tree prunings	Gonzalez et al. 2009	Paulowani wood	Lizhong et al. 2008
Apple tree prunings	A	Peach tree prunings	A
Apricot tree prunings	A	Pear tree prunings	A
Barley straw	B	Pine wood	Butt, 2005
Beech wood	Dupont et al. 2009	Pomegranate seeds	Ucar and Karagoz 2009
CCA-Treated wood	Fu et al. 2008a,b	Poultry DAF skimmings	Smith et al. 2009
Cherry tree prunings	A	Rice husks	Ji-Lu 2007
Chicken manure	Schnitzer et al. 2007	*Rice straw	Chen and Leung 2003
Corn cobs	Worasuwannarak et al. 2007	Scot pine and spruce	Dupont et al. 2009
Corn stover	Green and Feng 2005	*Sewage sludge	Gasco et al. 2005
Cotton stalks	A	Soft wheat straw	A
Doge maize	B	Sunflower seeds	Braadbaart et al. 2006
Elm wood	Lizhong et al. 2008	Sunflower straw	A
Eucalyptus	Guerrero et al. 2005	Swine manure	Godbout et al. 2008
Gavott maize	B	Switchgrass	Boateng et al. 2005
Gray alder sawdust	Zandersons et al. 2009	Textile wastes	Miranda et al. 2007
Japanese cedar	Hosoya et al. 2006	Tobacco stems	A
Lemon tree prunings	A	Toon wood	Lizhong et al. 2008
Linseed seeds	Acikgoz and Kockar 2009	Used ETL poles	Zhurinsh et al. 2005
Oil-palm shells	Lau et al. 2005	Used railway sleepers	Zhurinsh et al. 2005
Olive kernels	A	Vineyard prunings	A
Olive stone (pomace)	Jauhiainen et al. 2004	Walnut shell	Gonzalez et al. 2009
Olive tree prunings	A	*Waste tires (tyres)	Berrueco et al. 2004
Olive-oil residue	Uzun et al. 2007	Wheat straw	B

A- Zabaniotou and Damartzis, 2007 ;   B - Muller-Hagedorn and Brokhorn, 2006;   *- numerous

1.2 Carbonization Research at Case Western Reserve University

   Interest in carbonization at CWRU grew out of interactions with a former graduate student whose family is in the palm oil business. The work originally focused on identifying beneficial uses for harvest byproducts. Efforts examined the production of fiberboard from palm fronds and husks (currently disposed of by open burning), the extraction of chemical products for the palm oil (e.g. β-Carotene), the production of biodiesel and the production of methane from oil processing sludge. Extending this to carbonization to produce useful soil amendments occurred in the progression of ideas.

   To examine the potential of palm harvest waste carbonization, two pyrolysis reactors were constructed. There is a wide variety of technical sophistication being applied to pyrolysis research. Several researchers have used sophisticated benchtop reactors to explore the kinetics and thermodynamics of the process. Much of the work noted in Table 2 originates from this effort. However, these reactors use very small samples (a few grams) that have been processed (ground, shredded, pulverized) to small particle sizes. They can produce valuable data, but are not appropriate for "production" carbonization. To produce larger quantities, reactors must accommodate larger volumes of less-processed feedstock. Production reactors range from crude units constructed from steel drums to sophisticated mobile and fixed production plants (Fig. 3).

Fig. 3 – Examples of "Production" Carbonization Reactors

CWRU's carbonization reactors fall in the midrange on this continuum of sophistication. One is a benchtop unit developed by modifying a muffle furnace to house a 1 liter pyrolysis chamber. This is used to study reactor operating conditions and product yields. The second was developed from an industrial annealing oven to house pyrolysis chambers of up to 40 liters and is used for larger volume production. Both can operate at T> 500 ^{o}C, have digital controllers that allow for ramped temperature profiles, and have off gas condensers for byproducts recovery (see Fig. 4).

Fig. 4 - CWRU Bench and Pilot-Scale Carbonization Research Reactors

These reactors are adequate for the production of biochar, and to produce enough material to support plant growth studies conducted in biochar amended soils. However, because of export/import difficulties with oil palm crop residues, researchers began examining other feedstocks. CWRU is adjacent to urban areas with high yard waste generation rates, so researchers began examining yard waste as a carbonization feed stock. This led to the evaluation of yard waste components (see Fig. 5 and Table 3) and to plant growth studies conducted in CWRU's research greenhouse. The growth studies (see Fig. 6 and 7) were not intended to duplicate the worldwide effort to evaluate the agricultural benefits of biochar, but to determine if there was anything unusual about yard waste biochar that would inhibit its use. Results have been promising and show no evidence of growth inhibition. The work proposed here grew out of an observation made during the effort to manufacture sufficient biochar to support growth studies.

Fig. 5 - Example Yard Waste Fractions Before and After Carbonization

Table 3 – Results of Initial Carbonization of Yard Waste Components

Yard Waste Component	% Char.	% Water	% Org.	Yard Waste Component	% Char	% Water	% Org.
Oak (dry leaves)	43.0	19.4	37.6	Beech (green leaves)	55.1	6.7	38.2
Maple Leaves (green)	56.2	11.1	32.7	Beech (green branches)	43.2	26.0	30.9
Mugo Pine (needles)	25.2	53.1	21.7	Cottonwood (branches)	35.2	38.2	26.7
Oak (branches)	38.2	24.5	37.3	Cottonwood (green leaves)	35.5	50.0	14.5
Maple (branches)	34.5	19.0	46.5	Pine Cones (green)	19.5	61.0	19.5
Mugo Pine (branches)	42.7	11.7	45.6	Pine Cones (dry)	36.6	40.3	23.1
Misc. Leaves	53.1	21.2	25.7	Elm (stems/branches)	30.3	39.1	30.6
Maple Leaves (dry)	52.8	11.7	35.5	Black Locust (branches)	32.8	31.7	35.5
Grass Clippings (green)	12.3	68.8	18.9	Magnolia (stems/branches)	41.1	45.6	13.3
Fir (green needles)	30.9	51.8	17.3	Willow (stems/branches)	31.5	42.1	26.4

Fig. 6 - Soybean Plants Growing in Biochar-Amended Soil at CWRU's ValleeVue Farm

Fig. 7 – Corn Growing in Biochar-amended Soil at CWRU's ValleeVue Farm

The results of the growth studies were mixed. For "good" soils (i.e. soils that would be characterized as top soil), no significant improvement in crop yield could be detected and at the highest amendment levels used (50% biochar), yield decreased. However, in soils that would be characterized as poor (sand or glacial till), biochar amendment improved yield by approximately 20 %.

During the carbonization of sufficient biochar to support these growth studies, an operational problem was encountered with both of CWRU's reactors. It was discovered, that once the off gas byproducts leave the reactor, they rapidly cool and can condense and plug the discharge piping. Unchecked, this could become a significant operational problem. However, it was soon realized that this could also be an opportunity. The thick, viscous, tar-like product (bitumen) (see Fig. 8) has several potential applications.

Fig. 8 – Bitumen Generated During the Carbonization of Shredded Yard Waste

Based on this observation, the research team began exploring the potential for using carbonization to produce bitumen of sufficient quantity and quality to be of use in the transportation industry.

1.3 Desirability of Non-petroleum Sources for Asphalt Production

The asphalt industry is faced with increasing prices and decreasing availability of the petroleum used in making conventional asphalt. The U.S. Bureau of Labor Statistics reports that asphalt binder prices have risen by 25% in the last five years and spiked at more than 300% in 2008. Demand for asphalt was expected to reach nearly 40 million tons in 2009 and demand will undoubtedly lead to additional cost increases.

Concerns about the cost, availability and environmental baggage of using petroleum-based materials has led to the evaluation of several alternative materials. Research has examined the use of wood cellulose, wood lignin, bottom and fly ash, waste tires, and coal mine waste as pavement components. Of these wastes, "bio-oil" produced from cellulose and waste tires was thought to represent the most environmentally-friendly, abundant and cost effective opportunity for reducing the amount of petroleum-based materials in asphalt.

Research has shown that lignin and lignin products have potential for use in the asphalt industry (see Table 4). Significant among these studies was the work conducted by Gargulak and Lebo (1999), Sundstrom and Klei (1982) and Sundstrom et al. (1983) who explored uses of lignin–asphalt binders, concrete admixtures, well drilling mud, dust control, vanillin production, and dispersants. Williams et al. (2008) also conducted research that used fast pyrolysis and fractionation to extract lignin and lignin products for organic feed stock. Researchers have also investigated the use of lignin as a biological polymer in retarding the aging (oxidation) of asphalt pavements (Bishara 2005; Dizhbite 2004; McCready 2007; Ouyang 2006). This function of bio-oil serves to prolong asphalt pavement life by reducing aging-related failures such as thermal and fatigue cracking. In the latest research conducted by McCready (2007) and Williams et al. (2008), lignin was found to have a profound effect on widening the performance grade range of asphalt binders. However, as Allen (1980) observed, the properties of bio oils produced are influenced by the source of the biomass, and by the conditions under which they are manufactured. This is especially noteworthy given the wide range of variability in the materials that make up yard waste.

In 2005, the USEPA commissioned an assessment of pavements that included non-petroleum-based asphalts (Cambridge Systematics, Inc., 2005). USEPA's interest stemmed from the potential of these products to reflect more sunlight and reduce heat island effects in urban areas.

The Shell Oil Company has experimented with the use of vegetable oil-based bitumen asphalts on two Norwegian roads (Anderson et al. 2008). They found less emissions than typical petroleum-based binders. Ecopave Australia has also released a bioasphalt (GEO320) made from sugar and molasses (Johnson 2005). Although innovations are being pursued overseas, there is little mention of research on non-petroleum-based asphalts in the National Asphalt Pavement Association (NAPA 2009), the Asphalt Institute (AI 2009), or the National Center on Asphalt Technology at Auburn University (NCAT 2009) web pages. In fact, the Asphalt Institute's mission states that its chief interest is "to promote the use, benefits, and quality performance of petroleum asphalt." It appears that research on non-petroleum-based bitumen for use in asphalt would be on the cutting edge of this emerging technology.

Table 4 – Previous Research Examining the Use of Bio-Oils in Asphalt

Researcher(s)	Key Finding(s)/ Conclusion(s)
Barth (1962)	Bio-oil has structural similarities to resin fractions of asphalt mixtures
Butte et al. (1980)	Pyrolysis - hydrogenation method produces quality bio oil for asphalt paving
Allen (1980)	Composition of bio-oil depends on source, conversion process and reaction conditions
Terrel et al. (1980)	Wood lignin can wholly substitute asphalt binder or serve as extender
Sundstrom et al. (1983)	Lignin and modified lignin-based bio-oil can be used as binder
Marchessault et al. (1982)	Lignin-based bio-oil is water insoluble
Montague (2003)	Ligno-cellulose materials produce 10 to 30% by weight of lignin
Dizhbite (2004) Bishara et al. (2005) Ouyang et al. (2006)	Ligno-based bio-oils act as antioxidants in HMA
Williams et al. (2008)	Switch grass, corn stover and oak wood are excellent sources of bio-oil
McCready and Williams (2007)	Lignin-based bio-oil widens the PG grade range of asphalt binders

1.4 Yard Waste Generation and Management

USEPA reported that 32.9 million tons of yard waste were generated in 2008. This represented 13.2% of the total municipal waste stream. Of the generated yard waste, 21.3 million tons (64.7%) were managed by methods other than direct disposal (USEPA 2009). As of 2006, 23 states had at least a partial ban on landfill disposal of yard waste. For example, Nebraska bans leaves and grass disposal from April 1 to November 30. In Maryland, yard waste collected separately from municipal solid waste (MSW) is banned from landfill disposal (Arsova et al. 2008).

Composting programs are the most prevalent management method for yard waste. As of 2007, there were at least 3,505 active yard waste composting programs. Most of these were operated in the Midwest region of the U.S. (approx. 1,600). The Northeast region is second with approximately 1,100. Another less prevalent management method of yard waste recycling is mixed waste composting (combining yard waste with food waste, paper, and wood). In 2007, there were 16 mixed waste composting facilities, handling approximately 1,500 tons per day (USEPA 2008).

There are three main types of yard waste composting operations, which are generally identified by their "mechanical" process design: windrow composting, aerated static pile composting, and in-vessel composting. Windrow composting is the most commonly applied process. Windrow sizing depends on the type of equipment available to construct and till the windrows. Tilling is required to maintain sufficient aeration to accomplish aerobic composting and suppress odors. Typical sizes of windrows are approximately 15 m long by 5 m wide by 2.5 m high (Brewer and Sullivan 2003). Buffer zones around windrows are suggested to be 60 m for purposes of odor control (Komilis and Ham 2004). Depending on feedstock source, windrows generally require 130-170 days to produce a mature compost product (Brewer and Sullivan 2003, Komilis and Ham 2004).

Estimates of total greenhouse gas (GHG) emissions from yard waste composting are unavailable from USEPA, as the biogenic emissions from yard waste composting are not calculated. The USEPA focuses on tracking the extent of anthropogenic GHG emissions. Estimates of GHG emissions from yard waste composting include the collection and transportation of the waste from its source to the composting facility, and the mechanical turning

of the windrows for aeration. The combined emissions amount to 0.01 MTCE/ton of YWC (metric ton carbon equivalent per ton of yard waste compost), but given the estimates of carbon storage using yard waste compost, there is estimated to be a net carbon flux of -0.05 MTCE/ton of YWC (where a negative sign denotes carbon storage) (USEPA 2006). However, this estimate fails to account for the CO_2 that is released as the yard waste becomes compost and as the compost decomposes. The reality is that, although some fraction of the original yard waste organic matter may be incorporated into new plant growth at the point of compost application, the vast majority of the yard waste carbon will ultimately be released as CO_2.

There are also several issues involving potential biological and chemical contamination of yard waste compost since the original feed stock often contains diseased plant matter, animal feces and residuals of yard and garden chemicals. Research investigating the effect of pesticides such as 2,4-Dichlorophenoxyacetic acid (2,4-D) in yard waste composts has been conducted. Michel et al. (1995) found that only 47% of added 2,4-D was mineralized (i.e. experienced complete biodegradation). They also found that less than 1% of added carbon was present in water from the mature compost, signifying a small potential of leaching problems from windrows. This also implies that the chemicals remain in the compost product. However, Muller et al. (1996) found that thermophilic microorganisms are able to degrade many types of pollutants. Typical yard waste composting enters this thermophilic phase once the active respiration of mesophiles raises the internal pile temperature (Fogarty and Tuovinen 1991). The degree to which composting manages biological and chemical yard waste contamination remains an open question.

Another issue surrounding yard waste composting is the establishment of a standard for compost maturity. Yard waste compost maturity is not the same as stability. Stability measures the resistance of further degradation of the compost, and is determined by oxygen uptake rates or carbon dioxide evolution rates. Maturity describes the effectiveness of compost used for a specific function (e.g. mulch for landscaping versus a soil amendment for vegetable crops). The effectiveness of various tests varies depending on the feedstock source and end use of the compost. Tests have been proposed based on C:N ratio, inorganic N concentrations, and cation exchange capacities (Sullivan and Miller 2001, Brewer and Sullivan 2003).

1.5 Pyrolysis and Carbonization

Pyrolysis is a general term for the thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. There are numerous ways in which the process can be configured and run. The version of pyrolysis applied in this research (often referred to as carbonization) involves the heating of biomass in the absence of oxygen for the purpose of recovering a relatively pure carbon. "Fast" carbonization is believed to be most effective for maximizing production of off gas products. "Slow" pyrolysis is believed to be more effective at maximizing the production of char (Williams and Besler 1996). Shredding biomass before pyrolysis often increases the efficiency of the process, as smaller volume particles increase the rate of biomass heating and byproduct release. The type of reactor configuration used also dictates the amount of grinding needed (Demirbas 2007, Bridgwater 2000, 2003).

Fast pyrolysis reactor types include fluid bed, ablative, circulating fluid bed, entrained flow, rotating cone, and transported bed reactors. Slow pyrolysis is undertaken with fixed beds, multiple hearths and rotary kilns (Bridgwater and Peacocke 2000, Williams and Besler 1996) Ablative reactors have the capacity to handle minimally ground yard waste, where fluid bed reactors can require particle sizes of 6 mm. In using these reactors, most experiments have been designed to derive transport fuels from the input biomass, either as additives or as transport fuels on their own (such as biodiesel) (Bridgwater 2003).

1.6 Asphalt Binder Tests

The Asphalt Institute reports that both AASHTO and ASTM test methods are used for evaluation of performance grade (PG) asphalt binders in Ohio. These tests include determination of specific gravity (ASTM D 70), flash point (AASHTO T 48), rotational viscosity (AASHTO T 316), and dynamic shear (AASHTO T 315) on the original binder. Tests are also performed on residues from the rolling thin film oven test (RTFOT) and final pavement (PAV). The Asphalt Institute's required specifications for the state of Ohio (current as of May 2008) have been attached as Appendix A. There are several more sophisticated tests that could (and possibly should) be used (e.g. the SUPERPAVE asphalt binder suite of tests) to characterize the properties of bitumen derived from yard waste. However, they will be of limited value without a detailed basis of comparison. Therefore, it is recommended that the highest priority be given to

implementing the tests for which ODOT already has an inventory of results with which the new data can be compared.

1.7 Fundamental Problem and Research Approach

Urban yard waste poses solid management difficulties for many communities. In many areas, municipal solid waste is disposed of in sanitary landfills. However, the U.S. Environmental Protection Agency strongly discourages this practice and many state, county, and municipal authorities have enacted rules that mandate some other form of disposal. Often communities must collect and dispose of yard waste separately, and with ever-increasing personnel, equipment and fuel costs, separate yard waste collection is an increasing financial burden. Furthermore, there are few waste management alternatives for yard waste. Most communities compost yard waste but this is not an ideal solution:

 i. Composting takes time (months to years), energy, and a large amount of space.

 ii. Yard waste compost is not in high demand as a consumer product.

 iii. Yard waste composting can lead to aesthetic problems such as odor.

 iv. Yard waste composting can lead to concerns about the distribution of plant and animal pathogens that may not be deactivated in compost piles.

 v. Yard waste composting does not destroy the residuals of yard care chemicals such as pesticides and herbicides.

 vi. Composting yard waste releases all of the CO_2 potential of this organic waste.

A project has been initiated at CWRU to evaluate an alternative method of managing yard waste. Research is evaluating the potential of managing yard waste by carbonization. This offers the possibility of allowing for co-collection of yard waste with conventional solid waste (i.e. in one truck instead of two), yard waste management at landfill sites rather than at separate composting facilities, production of soil amendment products that permanently sequester CO_2 (carbon added to soil has been shown to increase crop productivity) and the production of valuable byproducts during the carbonization process.

 The research project described here was formulated specifically to examine the possibility of recovering bioasphalt bitumen from yard waste carbonization processes. This will produce a non-petroleum-based product of value to the transportation industry that results from a "carbon

negative" process that sequesters more CO_2 than it releases. The amount of bitumen that can be produced from yard waste, the physical and chemical properties of the bitumen, and the carbonization operating conditions under which production is optimized are all unknown, but the potential advantages of this yard waste management strategy are compelling. ***The work described here was groundbreaking research conducted to answer fundamental questions about the potential of yard waste carbonization (YWC) to produce a practical bitumen product that could be used to produce bioasphalt.*** It should probably be emphasized that this is not envisioned as a stand-alone technology since it is doubtful that it would be financially viable. The production of yard-waste-derived bitumen is envisioned as one component of a management strategy that reduces the cost of yard waste collection and produces several products (e.g. biochar, bitumen, acetic acid, etc.) that, taken together, result in a financially viable process.

2. Research Objectives

The specific objectives of the project, as outlined in the original proposal, were as follows:

(1) Design reactors that can be optimized to promote the production and collection of bitumen during yard waste carbonization. One will be designed for bench-scale experimentation and one will be designed for use in CWRU's pilot-scale carbonization furnace.

(2) Determine what standard tests should be applied to YWC bitumen to characterize its properties relative to other sources of bituminous materials used in transportation.

(3) Identify professional and manufacturer organizations who may be interested in, and have resources of use to this research project.

(4) Identify and communicate with other Ohio universities interested in research on the properties of asphalt manufactured from yard-waste-derived bitumen.

(5) Using the reactors of (1) and the tests of (2), evaluate the operating conditions under which YWC bitumen production may be optimized.

(6) Evaluate the bitumen mass yield fractions of yard waste components to determine the most appropriate feed stock composition and yard waste collection strategy.

(7) Evaluate the volume and composition of the non-bituminous products produced by the YWC process. The potential value or environmental implications of other YWC products may alter the definition of "optimum" operating conditions.

(8) Apply YWC to a sufficient volume of Cleveland yard waste to produce enough bitumen to support bioasphalt property research to be conducted elsewhere.

(9) Develop a plan for expanding this reconnaissance research project into a pilot-scale project to provide a more rigorous assessment of the practical value of the YWC technology.

(10) Publicize the results of this research.

3. General Description of Research (Materials and Methods)

3.1 Sample Collection

Yard waste samples were collected from the Case Western Reserve campus, or directly from tree lawns in neighborhoods and suburbs surrounding the campus. The majority of samples originated from the Cities of Shaker Heights or Cleveland Heights, Ohio.

The City of Cleveland Heights (population =50,000, size = 8.1 mi^2), collects yard waste weekly, but only from the tree lawn. Yard waste must be bagged or bundled for collection.

The City of Shaker Heights (population = 30,000, size = 6.3 mi^2) collects bagged yard waste (May 1 – Oct. 15) from behind homes on an ''on demand'' basis from homes displaying a yellow door hang tag, but also collects yard waste from tree lawns from April 1 to April 30, and yard waste plus leaves from tree lawns from Oct. 15 to Dec. 15. Most yard waste is hauled to a commercial composting facility, although the city also provides free wood chips to its residents.

In both of these communities, residential lots are large and the landscaping is mature. Both communities use a combination of standard collection vehicles, vacuum trucks, front end loaders, and street sweepers to manage yard waste.

Samples of compost were also taken from piles in the Cuyahoga County communities of Shaker Heights, Beachwood, and from Boyas Excavating, Inc. in Valley View. Samples from 2008 were acquired in late June through mid-July. Samples from 2009 and 2010 were acquired in late summer, from mid-July to mid-August. Different types of yard waste were collected as much as possible in this project because of the inevitable variability in yard waste stream composition (residents will not always be discarding waste from the same plants, trees, etc.). Testing a range of samples would help to isolate any potential types or components of yard waste that would be best for bitumen collection, or for char production.

In the summer, yard waste was deposited on tree lawns for pickup in three forms: wastes were placed in biodegradable bags, in piles of mixed waste, or in piles of waste from one specific

origin type (see examples in Fig. 9 through 11). Some waste was bundled, but most was not. The volumes of deposited yard waste varied greatly. Piles could range from only a pair of biodegradable bags to ten or more, or from a few branches from one type of tree to large piles of trimmings stretching 20 feet or more along the curb. In autumn, most yard wastes were from fallen leaves, and were not bagged. Piles of a mix of leaves were concentrated on the tree lawn or spilled out into the street slightly.

Samples were typically collected only if there was an appreciable amount of both leaves and branches for moisture and organics testing, and only if the origin of the waste (i.e. type of plant) could be identified. On some occasions, only selected components such as fruits or seeds were collected for testing (e.g. pine cones, buckeyes). Collected samples were preserved as collected in 5 gal. plastic buckets, or 20 gal. lidded plastic bins. Some bins were vented to allow the yard waste to dry.

Fig. 9 - Yard Waste in Lawn and Leaf Bags Staged for Collection

Fig. 10 -Yard Waste Brush Pile (Oak Branches)

Fig. 11- Yard Waste Log Pile

3.2 Sample Preparation

In preparation for testing, samples were separated into their components (i.e. leaves/needles, branches and/or stems, and fruit). They were reduced to a manageable size with either garden clippers or by hand. Such separation was not needed with single component samples such as acorns or pine cones. Once prepared, samples were split into two aliquots. One of these was used to measure moisture content. The other was subjected to carbonization to measure organics content and for collection of bituminous off-products. Preparation of yard waste samples for both the drying and carbonization processes were identical, but drying experiments made use of smaller sample sizes. Prepared samples for carbonization are shown in Fig. 12 and 13.

Fig. 12 - Rhododendron Leaves Prepared for Carbonization

Fig. 13 - Oak Branches Prepared for Carbonization

3.3 Testing Methods

Drying - To measure the moisture content of each yard waste component, specimens of known mass were left to dry in crucibles (of known mass) overnight (approx. 18-20 hr.) in a drying oven at a temperature of 97°C. The mass of the crucible (m_r), mass of the crucible with yard waste before drying (m_{r+yw}), and the mass of the crucible with yard waste after drying (m_{r+dyw}) were measured with a Denver Instrument Company A-250 balance. The yard waste moisture content (MC) was then calculated as follows.

$$MC(\%) = 100 * \left[1 - \frac{m_{r+dyw} - m_r}{m_{r+yw} - m_r} \right]$$
(Eq. 1)

The results of these calculations for each component are included in the **Results** section of this report. Figures 14 and 15 show two examples of samples after the drying process.

Fig. 14 - Dried Willow Branches

Fig. 15 - Black Locust Leaves After Drying

Carbonization - The carbonization process required a reactor that prevented sample exposure to oxygen as the yard waste was heated. The principal part of the reactor used was a 0.95 1 (1 U.S. quart) steel vessel, modified with an off gas discharge port that could be piped out of the muffle furnace heat source and into a off gas management system (see Fig. 16). This reactor was designed with an emergency blowoff lid that would prevent the generation of excessive pressure in the reactor if the discharge piping became plugged.

After it was filled with a sample of yard waste and sealed, the carbonization reactor was set in a Fischer Scientific Isotemp Programmable Muffle Furnace (see Fig. 16). The reactor was attached to copper discharge piping, directing off-gases into a 250 ml collection flask on top of the muffle furnace. Adjustable electric BriskHeat XTremeFLEX heating tape was wrapped around the copper discharge piping to maintain an off gas temperature consistent with the heating setting of the muffle furnace. The temperature of the pipe was monitored by thermocouples, installed underneath the heating tape. The first thermocouple monitored the temperature at the end of the copper pipe, where a second (added in later trials) monitored the beginning of the pipe. The off gases entered the collection flask through a glass fitting that was connected with high temperature silicone sealing tape from Nashua Tape Products. This fitting

24
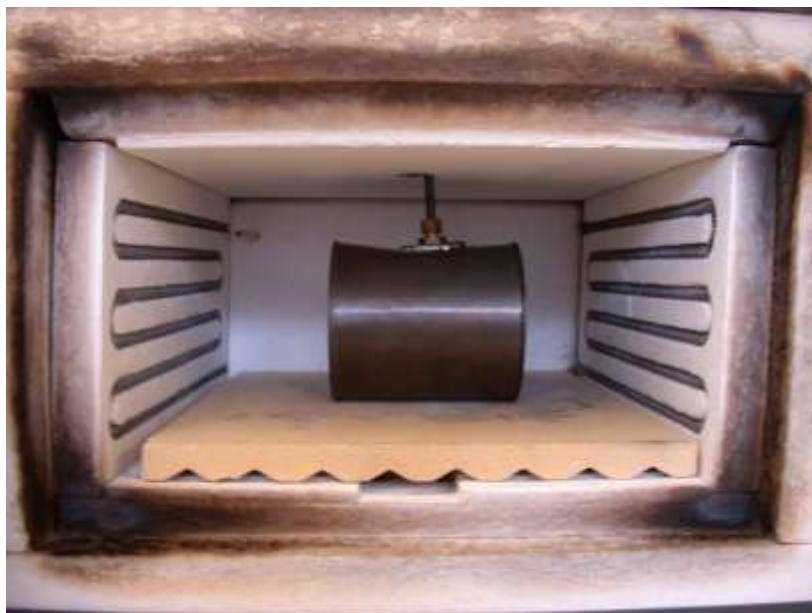
Fig. 16 - Sealed Carbonization Reactor Attached to Off Gas Discharge Piping

directed the gas flow downward, leading to condensation of denser products. Products staying in gas form could continue to flow up through a second fitting and towards a second 1000 ml collection flask. The open top of the second glass fitting was covered with a screw-on test tube cap to avoid the loss of off-gases. Figure 17 shows the setup of the pipe, heating tape, thermocouples and first collection flask on top of the muffle furnace.

Fig. 17 - Heated Off Gas Piping and Thermocouples to Regulate Discharge Temperature

The second 1000 ml collection flask was attached to the first by plastic tubing. The second flask was also attached to a series of water-cooled condensers. This was configured to allow condensate to drain back into the collection flask. Any gaseous byproducts that did not condense were discharged through the exhaust of a laboratory hood (see Fig. 18).

In early trials of the carbonization process (i.e. with samples from 2008), unheated discharge piping directed the off gas directly to the 1000 ml flask and the water-cooled condensers. This led to more bituminous products condensing and concentrating within the discharge pipe, which required constant clearing to maintain adequate flow. To avoid this problem and to increase actual collection of off-products, the configuration with the 250 ml collection flask was used. The impact of these collection system modification are discussed in the **Results** section.

Fig. 18 - Secondary Collection Flask with Water-Cooled Condenser

Once the setup and all connections were made between the reactor, pipe, flasks, and tube, the muffle furnace was closed and set to a temperature of 250° C for approximately 45 min. After this initial period of heating, the furnace would be raised and set to 350° C. While some off gassing occurred during the first heating setting (mostly steam), much more significant off gassing (a dense white smoke) would begin to travel through the collection system after the

interior temperature of the furnace would reach 350° C (see Fig. 19). The duration of carbonization at 350° C was variable (depending on the rate of off gas discharge) , and the furnace was shut off once significant off-gassing into the first collection flask concluded. After the furnace had cooled, the reactor was detached from the collection system and the carbonized yard waste was removed. Figures 20 through 23 show two examples of yard waste both before and after the carbonization process.

Fig. 19 - Secondary Collection Flask Filled with Dense Off Gas
During the Initial Steps of Carbonization

Fig. 20 - Maple Branches Before Carbonization

Fig. 21 - Maple Branches After Carbonization

Fig. 22 - Maple Samaras Before Carbonization

Fig. 23 - Maple Samaras After Carbonization

The two collection flasks containing the byproducts were consolidated in a glass bottle after measurements were taken. The byproducts were a mixture of water, organics, and small suspended particles of yard waste char. The transfer of all these byproducts into the bottle was never 100% efficient. In early trials, a portion of off gases escaped from around the cap on top of

the glass fittings. In all trials, some bitumen would solidify within the small glass fittings, within the plastic tubing between the flasks, or in the water-cooled condensers (bitumen collecting within the glass fittings is visible in Fig. 24). After transferring the products to the bottle, a fraction of bitumen would be left within the collection flasks as it was too viscous to flow into the bottle. This required an acetone wash of the collection flasks and glass fittings after each carbonization trial. The waste acetone from these washes were consolidated and dewatered for increased bitumen collection.

Fig. 24 - Off Products Collecting in Glass Fittings Above the First Collection Flask

3.4 Data Analysis

In order to calculate the organic content, the mass of the reactor (m_r), mass of the reactor with yard waste (m_{r+yw}) and the mass of the reactor with carbonized yard waste (m_{r+cyw}) were measured with a Denver Instrument Company XL-1810 balance. The organic content (OC) by mass percentage was given by the equation.

$$OC(\%) = 100 * \left[\frac{m_{r+yw} - m_{r+cyw} - \frac{MC(\%)}{100}(m_{r+yw} - m_r)}{(m_{r+yw} - m_r)} \right] \quad \text{(Eq. 2)}$$

The results of these calculations for each component are included in the next section of this report.

The efficiency of byproduct collection was calculated as follows. The masses of the empty collection flasks ($m_{f1,1}$ and $m_{f2,1}$), and the masses of the collection flasks with off-products ($m_{f1,2}$ and $m_{f2,2}$) were measured gravimetrically. The collection efficiency (E_F) was then given by the following equation. The results of these calculations for each component are included in the next section of this report.

$$E_F(\%) = 100 * \left[\frac{(m_{f1,2} - m_{f1,1}) + (m_{f2,2} - m_{f2,1})}{m_{r+yw} - m_{r+cyw}} \right] \quad \text{(Eq. 3)}$$

next section of this report.

The char content of each yard waste component was calculated with three masses: the mass of the carbonization reactor (m_r), the mass of the reactor with prepared yard waste (m_{r+yw}), and the mass of the reactor with carbonized yard waste (m_{r+cyw}). Equation 4 was used to calculate this char content (CC).

$$CC(\%) = 100 * \left[\frac{m_{r+cyw} - m_r}{m_{r+yw} - m_r} \right] \quad \text{(Eq. 4)}$$

4. Results

During the course of this research, nearly 50 distinct components of yard waste were examined. The moisture content, organic composition and char yield of each sample were measured and where possible, the byproduct recovery efficiency was determined. The results of these analyses are summarized in Table 5.

Table 5 - Moisture, Organic and Char Content, and Byproduct Collection Efficiency

Year	Yard Waste Type	Component	Moisture (%)	Organics (%)	Char (%)	Byproduct Collection Efficiency (%)
2008	Beech	Branches	25.98	30.87	43.16	
2008	Beech	Leaves	6.67	38.22	55.11	
2008	Compost	Boyas Mix	39.46	3.89	56.65	
2008	Compost	Mature Mix	57.92	13.87	28.21	
2008	Cottonwood	Branches	38.18	26.66	35.17	
2008	Cottonwood	Leaves	50.00	14.48	35.52	
2008	Grass	Clippings	68.77	18.93	12.30	
2008	Leaves	Assorted	21.24	25.69	53.07	
2008	Maple	Branches	19.00	46.50	34.51	
2008	Maple	Leaves	11.11	32.68	56.21	
2008	Maple - dead	Leaves	11.66	35.50	52.85	
2008	Mugo Pine	Branches	11.70	45.57	42.73	
2008	Mugo Pine	Leaves	53.10	21.65	25.25	
2008	Oak	Branches	24.50	37.27	38.23	
2008	Oak	Leaves	19.36	37.60	43.04	
2008	Pear	Branches	41.15	27.31	31.54	
2008	Pear	Leaves	8.29	37.01	54.70	
2008	Pine Cones	New	68.39	13.63	17.98	
2008	Pine Cones	New - Brown	40.26	23.11	36.62	
2008	Pine Cones	New - Green	61.03	19.46	19.51	
2008	Pine Cones	Old	52.27	11.13	36.60	
2008	Fir	Branches	45.41	8.82	45.78	
2008	Fir	Leaves	51.75	17.35	30.90	
2009	Acorns	Immature	12.92	47.80	39.28	70.9
2009	Acorns	Mature	9.89	48.58	41.53	68.7
2009	American Elm	Dried Branches	0.00	62.99	37.01	22.2
2009	American Elm	Leaves	10.64	38.07	51.29	59.1
2009	American Elm	Branches	39.12	30.65	30.23	74.1
2009	Birch	Leaves	8.30	40.79	50.91	61.9
2009	Black Locust	Branches	31.74	35.47	32.79	85.0
2009	Black Locust	Leaves	8.90	37.94	53.16	61.9

2009	Buckeye	Fruit	10.37	51.64	37.99	23.5
2009	Buckeye	Husks	9.49	45.79	44.72	46.9
2009	Juniper	Leaves	7.42	43.76	48.82	57.9
2009	Magnolia	Leaves	10.57	36.95	52.48	51.2
2009	Magnolia	Branches	45.56	13.26	41.18	17.7
2009	Rhododendron	Leaves	9.60	34.23	56.17	57.4
2009	Sycamore	Branches	8.08	50.88	41.04	54.3
2009	Sycamore	Leaves	9.31	37.56	53.13	46.5
2009	Willow	Branches	42.14	28.11	29.75	31.2
2009	Willow	Leaves	10.59	37.96	51.45	58.3
2010	Maple	Branches	37.68	35.64	26.68	79.0
2010	Maple	Leaves	13.03	37.61	49.36	58.9
2010	Maple	Samaras	36.82	31.31	31.87	74.0
2010	Oak	Branches	34.39	37.72	27.89	42.7
2010	Oak	Leaves	46.30	14.03	39.67	64.3
2010	Rhododendron	Branches	45.83	30.17	24.00	81.0
2010	Rhododendron	Leaves	57.36	18.94	23.70	73.2
AVERAGE			**28.82**	**31.56**	**39.62**	**56.9**
STANDARD DEVIATION			**19.58**	**12.91**	**11.45**	**18.4**

One of the goals of the research was to determine if there were significant performance differences between distinct components of yard waste. If there were significant performance differences, this information could help collection efforts concentrate on components of yard waste that would be most beneficial for bitumen production. The most common types of yard wastes in the samples tested were branches and leaves. The yields of these two components are summarized in Tables 5, 6 and 7. Although it is not obvious, results indicated that branches have higher average moisture content (30.6%) than leaves (21.3%). The reason is apparently that leaves dry more rapidly than bulkier plant tissues once they have been harvested. Branches also have higher average organic content (34.2% versus 32.2% for leaves). Leaves have higher average byproduct yield and collection efficiencies (58.2% versus 54.1% for branches). The implication is that branches would be modestly more effective as a feed stock for yard waste carbonization if the goal is bitumen production. However, it is difficult to envision a collection system that could easily separate leaves from branches and leaves are nearly as effective at producing bitumen. In addition, the economic viability of the overall process will depend on the beneficial uses of the bio-char and possibly other off gas products in addition to the bitumen. Therefore, the overall optimum operating strategy may require optimization for the production of some other component.

Table 6 - Types of Branches Carbonized

Year	Yard Waste Type	Component	Moisture (%)	Organics (%)	Byproduct Collection Efficiency (%)
2009	American Elm	Branches	0	62.99	22.24
2009	American Elm	Branches	39.12	30.65	74.14
2008	Beech	Branches	25.98	30.87	
2009	Black Locust	Branches	31.74	35.47	85.04
2008	Cottonwood	Branches	38.18	26.66	
2008	Fir	Branches	45.41	8.82	
2009	Magnolia	Branches	45.56	13.26	17.66
2008	Maple	Branches	19.00	46.50	
2010	Maple	Branches	37.68	35.64	79.01
2008	Mugo Pine	Branches	11.70	45.57	
2008	Oak	Branches	24.50	37.27	
2010	Oak	Branches	34.39	37.72	42.68
2008	Pear	Branches	41.15	27.31	
2010	Rhododendron	Branches	45.83	30.17	81.05
2009	Sycamore	Branches	8.08	50.88	54.30
2009	Willow	Branches	42.14	28.11	31.23
	Average		**30.65**	**34.24**	**54.15**
	Standard Deviation		**14.40**	**13.36**	**26.70**

Table 7 - Leaf Components Carbonized

Year	Yard Waste Type	Component	Moisture (%)	Organics (%)	Byproduct Collection Efficiency (%)
2009	American Elm	Leaves	10.64	38.07	59.12
2008	Beech	Leaves	6.67	38.22	
2009	Birch	Leaves	8.30	40.79	61.94
2009	Black Locust	Leaves	8.90	37.94	61.94
2008	Cottonwood	Leaves	50.00	14.48	
2008	Fir	Leaves	51.75	17.35	
2009	Juniper	Leaves	7.42	43.76	57.94
2009	Magnolia	Leaves	10.57	36.95	51.25
2010	Maple	Leaves	13.03	37.61	58.88
2008	Maple - dead	Leaves	11.66	35.50	
2008	Maple - live	Leaves	11.11	32.68	
2008	Mugo Pine	Leaves	53.10	21.65	
2008	Oak	Leaves	19.36	37.60	
2010	Oak	Leaves	46.30	14.03	64.32
2008	Pear	Leaves	8.29	37.01	
2009	Rhododendron	Leaves	9.60	34.23	57.39

|					
2010	Rhododendron	Leaves	57.36	18.94	73.21
2009	Sycamore	Leaves	9.31	37.56	46.54
2009	Willow	Leaves	10.59	37.96	58.34
	Average		**21.26**	**32.23**	**59.17**
	Standard Deviation		**18.97**	**9.56**	**6.83**

Another goal of the project was to investigate if drying yard waste feed stock before carbonization significantly increased yields of byproducts. A drying step would not be difficult to implement, but would add additional area and cost requirements to the carbonization process. The basic concept is that, if yard waste had less moisture to expel, off-products might have higher organic concentrations, and might favor higher molecular weight products.

Two comparisons between dried and "wet" yard waste are included in Table 5 and are emphasized in Table 8. In both cases, although the dried samples had a smaller moisture content and larger organic content than"wet" samples, the collection of byproducts was less efficient when the yard waste was dried before carbonization. Figure 25 illustrates the relationship between moisture content and collection efficiency.

Table 8 - Comparison of the Yield from Un-dried and Dried Carbonization Feed Stock

| Year	Yard Waste Type	Component	Moisture (%)	Organics (%)	Byproduct Collection Efficiency (%)
2009	American Elm	Branches (dried)	0	62.99	22.2
2009	American Elm	Branches	39.12	30.65	74.1
2009	Rhododendron	Leaves	9.60	34.23	57.4
2010	Rhododendron	Leaves	57.36	18.94	73.2

After applying linear regression analysis, the results of Fig. 25 illustrate that, although there is a models correlation that seems to favor higher moisture content, the correlation is not sufficient to conclude that pre-drying is advantageous. If anything, the data indicate that the presence of more moisture assists in the formation of organic byproducts.
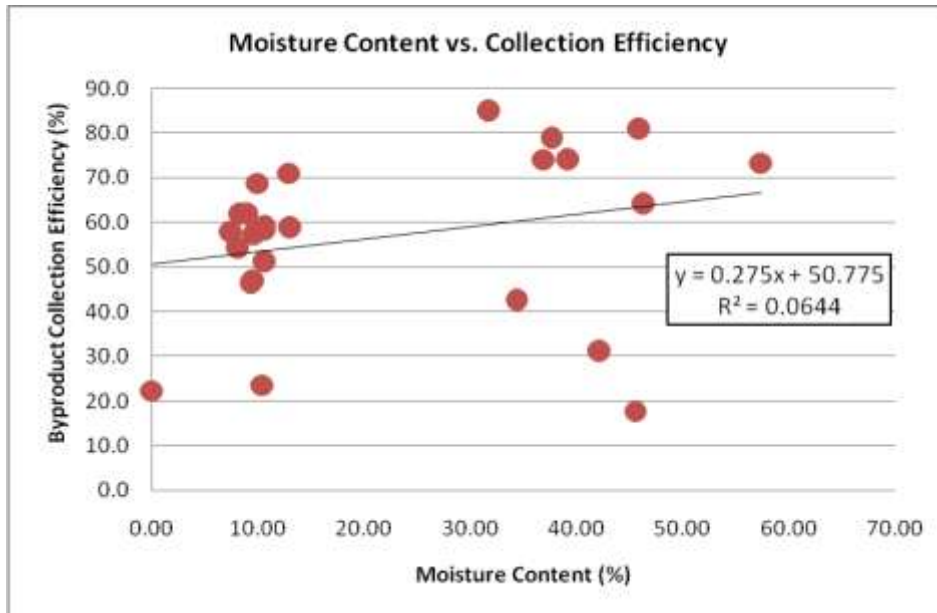
**Fig. 25 – The Impact of Moisture Content On Byproduct Collection Efficiency**

Another research task was to evaluate the effectiveness of carbonization process design modifications. After experimenting with alternative reactor designs, the efforts of this project concentrated on improving the performance of discharge piping. The thought was that if temperatures in the discharge piping were more carefully controlled, the bituminous materials could be "encouraged" to condense and be removed at a desirable location rather than becoming an operational problem elsewhere in the discharge piping.

Figure 26 illustrates the collection efficiency in the designated collection vessel as a function of time as efforts were made to "tune" production and collection. With the exception of a couple of uncharacteristic results achieved early in the experimental program, the results demonstrate that these efforts were able to make a significant improvement in the dependability and a modest improvement in the magnitude of collection.
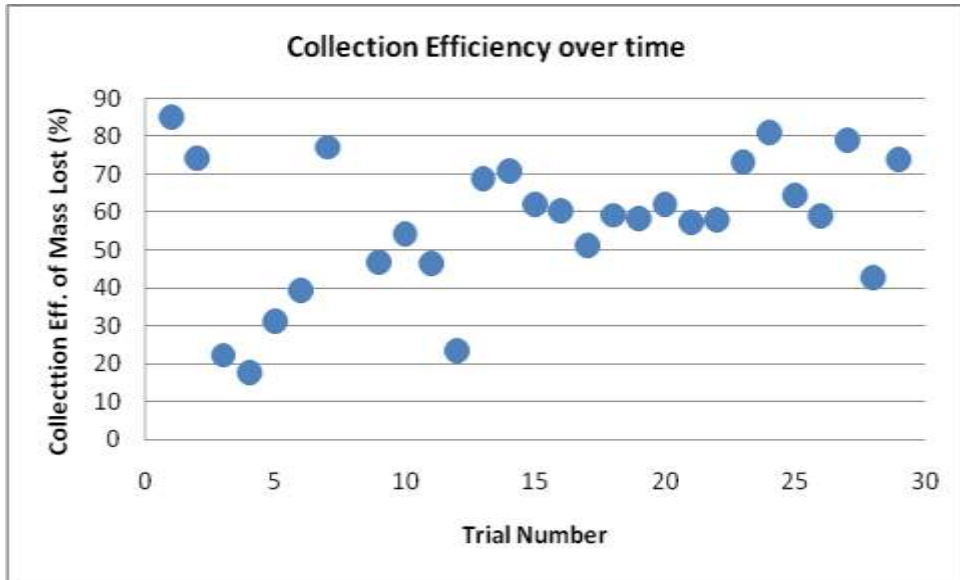
Fig. 26 – Improvement of Byproduct Collection Efficiency Over the Course of the Project

Figure 27 illustrates the organic content of the major species of deciduous and coniferous tree species tested. One might assume that the conifers would yield and higher organic content, but this did not appear to be the case. From the data available, one would have to conclude that there was probably no significant difference. The degree to which these would yield equivalent amounts of bitumen is unknown.
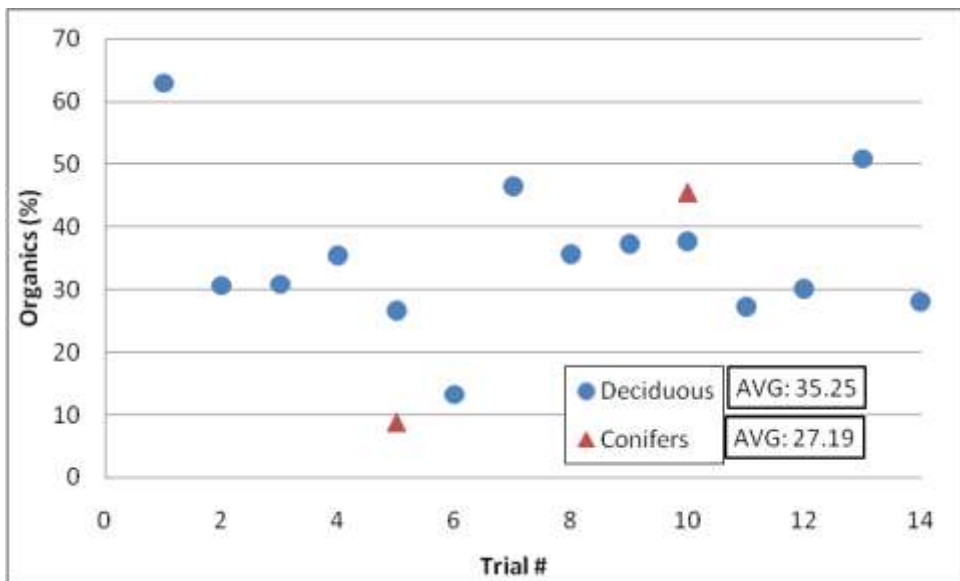
Fig. 27 - Comparison of Organic Content in Deciduous and Conifer Branch Samples

Based on the overall results of Table 5, the average bio-char production was 39.6 %. The remainder of the mass (60.4%) was given off as byproducts. Of these byproducts, the average collection efficiency (i.e. the recovery rate) was 56.9%. The remainder of the byproducts (mostly smoke and water vapor) was discharged into the ventilation system. To put these numbers in perspective, if a yard waste carbonization process with these properties was applied to the whole of yard waste generation in Cuyahoga County, the production of total bio-char and byproduct production would be as follows.

Annual U.S. Yard Waste Production Estimate -   32.9 million ton/yr (USEPA 2009)
U.S. Population Estimate -   307,006,550 (USCB 2009a),
Cuyahoga County Population Estimate -   1,275,709 (USCB 2009b).

Total Biochar - $32.9*10^6$ ton/yr * $(307,006,550 \text{ c})^{-1}$ * 1,275,709 c * .396 = 54,160 ton/yr.

Total Byproduct - $32.9*10^6$ ton/yr * $(307,006,550 \text{ c})^{-1}$ * 1,275,709 c * .604 = 82,550 ton/yr.

In producing this, a portion of the byproduct will be aqueous. Using the average moisture content measured for all samples of yard waste, this fraction would be as follows.

Aqueous Byproduct - $32.9*10^6$ ton/yr * $(307,006,550 \text{ c})^{-1}$ * 1,275,709 c *.288 = 39,400 ton/yr

The remainder of the byproduct would be organic materials.

Organic Byproduct - $32.9*10^6$ ton/yr * $(307,006,550 \text{ c})^{-1}$ * 1,275,709 c *.316 = 43,100 ton/yr

However, it should be noted that not all of the organic fraction was actually collected in liquid phase. Some of this escapes in the gaseous discharge. The overall collection efficiency of this fraction was 57%. Obviously, these estimates assume that all yard waste is collected and successfully carbonized, but the production potential seems adequate to generate a material and revenue stream that would help offset the cost of the carbonization operation.

One task of the research project was to generate a sufficient volume of yard-waste-derived bitumen to support future physical characterizations studies. This has been accomplished. The carbonization efforts described here resulted in approximately 3 liters of bio-oil and bitumen.

One consideration that has not yet been addressed is that carbonization also yields an aqueous byproduct. This may be released as steam, but doing so would substantially reduce the recovery of the organic fraction, and could lead to serious air pollution control compliance issues. Generally, it is preferable to condense the off gas into a liquid phase and then separate the organic phase from the aqueous phase. However, as the image of Fig. 28 illustrates, there can be a great deal of variability in the nature of the aqueous phase depending on the type of yard waste feed stock. Table 9 presents a preliminary chemical characterization of off gas condensate. Note that these solutions are dominated by organic acids (high COD, low pH, high % volatile solids). Additional analysis should be conducted to determine to what extent valuable byproducts can be extracted from this byproduct fraction, and to what extent the management of this as wastewater will lead to additional costs.

Fig. 28 – Liquid Phase Carbonization Byproducts

Table 9 – Preliminary Chemical Characterization of Yard Waste Carbonization Off Gas Condensate

Sample	COD (mg/L)	pH	Specific Conductance (mMhos)	Total Solids (g/L)	Total Volatile Solids(g/L)	Volatile Solids (%)
Blue Spruce Branches	256,000	2.43	1.41	72.26	69.24	95.8
Blue Spruce Leaves/Needles	140,000	3.38	2.18	31.65	30.75	97.2
Conifer Branches	145,000	2.58	1.21	32.97	30.91	93.8
Conifer Leaves/Needles	78,000	3.85	3.85	19.40	18.52	95.5
Norwegian Pine Branches	140,000	2.62	1.29	30.59	30.06	98.3
Norwegian Pine Leaves/Needles	91,000	3.85	3.22	23.56	23.20	98.5
Average	142,000	3.1	2.2	35.1	33.8	96.5

One task of the research was to identify other organizations that may be interested in, and have resources useful to research in the area of this project. Tables 10 through 15 present lists of such organizations. Table 10-13 list organizations, institutes and manufacturers with obvious interests in asphalt technology. Table 14 lists tree care companies that, although not directly involved in the asphalt business, are responsible for generating a great deal of wood waste that could serve as a feed stock to the process. These companies might also be interested in implementing carbonization at their facilities for the purposes of generating both bitumen and soil-amendment carbon. Table 15 lists composting facilities and organizations. All of these are in the business of collecting what could be a viable feed stock for the carbonization process investigated here and might be interested in diversifying their businesses to include this process. Table 16 lists communities with explicit yard waste collection programs. Again, these are organizations that generate a potential feed stock for carbonization, and public programs might find additional motivation in the carbon sequestering aspect of the technology.

Table 10 – National Asphalt Organizations

Name	Internet Address	City
Asphalt Institute	http://www.asphaltinstitute.org	Lexington, KY
Asphalt Pavement Alliance	http://asphaltroads.org	Lanham, MD
Asphalt Recycling & Reclaiming Association	http://www.arra.org	Annapolis, MD
Association for Modified Asphalt Producers	http://modifiedasphalt.org	St. Louis, MO
National Asphalt Pavement Association	http://www.hotmix.org	Lanham, MD

Table 11 - State-Wide Asphalt Organizations

Name	Internet Address	City
Asphalt Pavement Association of Indiana	http://www.asphaltindiana.org	Indianapolis, IN
Asphalt Paving Association of Iowa	http://www.apai.net	Ames, IA
Flexible Pavements of Ohio	http://www.flexiblepavements.org	Dublin, OH

Table 12 - Institutes with Possible Interest in or Experience with Bioasphalt or Biochar

Name	Internet Address	City
BioCentury Research Farm at Iowa State U.	http://www.biocenturyresearchfarm.iastate.edu	Boone, IA
Bioeconomy Institute, Iowa State U.	http://www.biorenew.iastate.edu	Ames, IA
Center for Sustainable Environmental Technologies at Iowa State U.	http://www.cset.iastate.edu	Ames, IA
Institute for Transportation at Iowa State U.	http://www.intrans.iastate.edu	Ames, IA
Ohio Research Institute for Transportation and Environment at Ohio U.	http://www.ohio.edu/orite/index.cfm	Athens, OH

Table 13 - Asphalt Manufacturers

Name	Internet Address	City
Barrett Paving Materials, Inc.	http://www.barrettpaving.com	Dayton, OH
BP Asphalt USA	http://www.bp.com/modularhome.do?categoryId-=4860&contentId=7017042	Chicago, IL
Central Allied Enterprises	http://www.central-allied.com	Canton, OH
Erie Blacktop, Inc.	http://www.erieblacktop.com	Sandusky, OH
Gerken Paving, Inc.	http://www.gerkencompanies.com/gpi.html	Napoleon, OH
Kokosing Construction Co. Inc.	http://www.kokosing.biz	Frekericktown, OH
Meshberger Brothers Stone Corp.	http://www.meshbergerbros.com	Bluffton, IN
Milestone Contractors, LP	http://www.milestonelp.com	Indianapolis, IN
Rose Paving Co.	http://www.rosepaving.com	Bridgeview, IL
Shell Bitumen	http://www.shell.com/home/content/bitumen/	
Shelly & Sands, Inc.	http://www.shellyandsands.com	Zanesville, OH
The Shelly Company	http://www.shellyco.com	Thornville, OH
Unique Paving Materials Corporation	http://www.uniquepavingmaterials.com	Cleveland, OH
Valley Asphalt Corp.	http://www.jrjnet.calls.net/asphalt/	Cincinnati, OH

Table 14 - Tree Care Companies and Associations

Name	Internet Address	City
Asplundh Tree Expert Company	http://www.asplundh.com	Willow Grove, PA
Davey Tree Company	http://www.davey.com	Kent, OH
Utility Arborist Association	http://www.utilityarborist.org	Champaign, IL
Wright Tree Service	http://www.wrighttree.com	Des Moines, IA

Table 15 - Composting Organizations and Companies with Composting Facilities

Name	Internet Address	City
Barnes Nursery, Inc.	http://www.barnesnursery.com	Huron, OH
Biodegradable Products Institute	http://www.bpiworld.org	New York City, NY
Earth 'n Wood Landscape Supply	http://earthnwood.com	North Canton, OH
Garick LLC	http://www.garick.com	Cleveland, OH
Hope Timber Companies	http://hopetimber.com	Granville, OH
Kurtz Bros., Inc.	http://www.kurtz-bros.com	Independence, OH
Mid-Atlantic Composting Association	http://www.midatlanticcompost.org	
North East Biosolids and Residuals Association	http://www.nebiosolids.org	Tamworth, NH
Northwest Biosolids Management	http://www.nwbiosolids.org	Seattle, WA
Organics Recycling Association of Ohio, Inc.	http://www.ohiocompost.org	Medina, OH
Paradise Composting Company	http://www.paradiselawncareinc.com	Smithville, OH
Rosby Resource Recycling	http://www.rosbycompanies.com	Brooklyn Heights, OH
Sagamore Soils	http://sagamoresoils.com	Hudson, OH
The U.S. Composting Council	http://compostingcouncil.org	Ronkonkoma, NY

Table 16 – Example State Municipalities with Yard Waste Collection Programs

Name	Internet Address
Shaker Heights, OH	http://www.shakeronline.com/services/collection
Beachwood, OH	http://www.beachwoodohio.com/publicservice.html
Cleveland Heights, OH	http://www.clevelandheights.com/citydept_works_refuse_waste.asp
Columbus, OH	http://publicservice.columbus.gov/yardwaste
Dublin, OH	http://www.dublin.oh.us/services/yardwaste.php
Gahanna, OH	http://www.gahanna.gov/departments/service/refuse.aspx
Grove City, OH	http://service.grovecityohio.gov/collection/
Lakewood, OH	http://onelakewood.com/PublicWorks/Refuse_Recycling/
Oxford, OH	http://www.cityofoxford.org/Page.asp?NavID=308
Upper Arlington, OH	http://www.uaoh.net/publicservices/division.php?fDD=48-275

5. Conclusions and Recommendations

This study was designed to evaluate the fundamental feasibility of producing useful quantities of bitumen from yard waste carbonization. To accomplish this, the research evaluated the moisture, organic, and char content of nearly 50 distinct yard waste components, and evaluate the recovery efficiencies of the bio-char and byproducts. The overall average byproduct generation rate was 60.4% (28.8 % aqueous and 31.6 % organic). Of this, approximately 57% was recovered by the collection system used in this project.

The variability of moisture content, organic content, and byproduct collection were grouped by type of yard waste. This was done to investigate whether any typical yard waste component would be more beneficial for bitumen production. In the comparison between branches and leaves, neither type has a significantly higher organic fraction (0.34 and 0.32, respectively). This fact is relevant in that, if collecting bitumen from yard waste carbonization was implemented at a larger scale, extensive feedstock separation would not be necessary.

The benefit of drying feedstock prior to carbonization was also investigated. In comparing byproduct collection of unaltered samples and pre-dried samples, pre-drying decreased the total byproduct collection. This was partly due to the increased viscosity of the off-products after drying. In looking at the same relationship between byproduct collection and moisture content over all samples tested, a sample's moisture content seemed to have little impact on byproduct production.

In retrospect, the laboratory apparatus used was more effective at accomplishing the carbonization process (i.e. the basic pyrolysis step) than managing the recovery and separation of byproducts. Improvements were made during the course of the project by installing heating elements to control gas discharge temperatures in strategic sections of the discharge piping, and these helped stabilize and improve recovery. However, the off gas management system should be further improved. Such improvements would increase the production of the organic fraction and could help reduce the potential air discharge complications of the process.

The difficulties arising from transferring bitumen from collection flasks to storage containers or bottles also warrant more attention. Although in an aqueous solution, a portion of higher viscosity bitumen in the flasks could not be transferred to separate containers without an acetone wash. Of those bitumen samples that were transferred to separate containers, they were eventually consolidated for the creation of a larger sample. They were easily transferred as they

had a significant aqueous fraction. After consolidation of these aqueous bitumen products, dewatering was necessary to increase the organic concentration. As the dewatered samples in this study had various viscosities, further exploration and standardization of this dewatering process could help deliver a bitumen product with uniform properties. Further research should probably make use of a rotary evaporator to help implement the separation and concentration of the organic fraction.

The physical properties of yard waste bitumen and asphalt made from this bitumen should be explored in detail. This project demonstrated that bitumen could be generated from yard waste, and that it is likely that the volume would be sufficient to support the manufacture of asphalt. However, the properties of the resulting product are unknown. A considerable amount of additional research would be required to determine how to best use this material, and to quantify the properties of the products produced.

Experience has also demonstrated that some of the byproducts of carbonization may represent significant aesthetic or environmental problems. The gas phase discharges can be malodorous and may lead to air pollution compliance obligations. Likewise, the aqueous phase discharges will probably require treatment. The properties of these discharges should be quantified and both liquid and gas treatment systems should be examined to ensure that both discharges can be successfully treated.

Finally, it is important to keep in mind that yard waste carbonization is desirable for several reasons. It will yield bitumen, but this is probably not sufficiently valuable to justify the process. The process also sequesters carbon, allows for yard waste collection efficiencies, produces a bio-char soil amendment of potential value to agriculture and may yield other by-products of commercial value. A successful implementation of yard waste carbonization will require the success of many elements of the process that were not evaluated in the work described here.

6. Implementation Plan

Yard waste carbonization for the purpose of bitumen production is not a process that is currently ready for implementation. Substantially more laboratory research, economic analysis and field performance testing will be required before this process is ready for full-scale implementation. The next step should be the generation of bitumen in sufficient quantity to support the production of several asphalt mixes, and the testing of these mixes a potential

flexible pavement materials. Without examining the qualities of the pavements that can be made from yard-waste-derived-bitumen, if would be premature to invest in significantly larger carbonization facilities.

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Appendix A - The Asphalt Institute's Specifications for Ohio Asphalt Testing

State: OHIO	Materials: Re: Section 908 - Bituminous Materials
Date Last Reviewed: 05/21/08	Web Address: www.dot.state.oh.us
Materials Engineer: Dave Powers	Contact Info: david.powers@dot.state.oh.us

ASPHALT BINDER:

Section 908	Description:	The PG Binder shall be homogenous, free from water and deleterious materials, and shall not foam when heated to 350°F (175°C). The asphalt binder (before modification or after modification if liquid modified used) shall be proven fully compatible with a negative result by means of the Spot Test per AASHTO T 102 using standard naphtha solvent. If standard naphtha shows a positive results, a retest using 35% Xylene/65% Heptane (volume) may be used. The PG Binder shall be at least 99% soluble as determined by ASTM D 5546 or D 2042. Any insoluble component shall be substantially free of fibers and have discrete particles less than 75um. Flash Point shall be 500°F (260°C) min. Mass Loss on RTFOT of final PG grade binder shall be 0.5% max. PG 58-28 shall have a minimum Viscosity (ASTM D 2171 @ 60°C) of 800 Poise and PG 64-22 shall have a Penetration (ASTM D 5) between 55 & 75. Direct Tension testing is not required, unless otherwise required in this specification.
	PMA's:	A PGM Binder shall meet the requirements of Table A and shall be obtained through modification of a non-oxidized, neat asphalt binder by using a styrene butadiene latex rubber compound (SBR polymer) or a styrene butadiene styrene polymer block copolymer (SBS polymer).
	Exclusions:	Air Blown Asphalts for PMA's

PROPERTY		Test Method AASHTO or Other	Requirements by Performance Grade, PG (Common Grade)					
			58-28	64-22	64-28	64-28PM	70-22PM*	76-22PM*
ORIGINAL:								
Specific Gravity	15.6°C	ASTM D 70	Report					
Flash Point, °C		T 48	260 min.					
Rotational Viscosity, Pa Xs	135°C	T 316	3.0 max.					
Dynamic Shear, kPa (G* / sin δ, 10 rad./sec)	At grade temperature	T 315	1.0 min.					
RTFOT RESIDUE:								
Mass Loss, %		T 240	0.5 max.					
Dynamic Shear, kPa (G* / sin δ, 10 rad./sec)	At grade temperature	T 315	2.2 min.					
PAV RESIDUE:		R 28	100°C; 20hrs; 300 psi					
Dynamic Shear, kPa (G* · sin δ, 10 rad./sec)	At test temperature	T 315	5,000 max.					
			19°C	25°C	22°C	22°C	28°C	31°C
Creep Stiffness	At test temperature	T 313	Stiffness 300 max. MPa & m Value 0.300 min.					
			-18°C	-12°C	-18°C		-12°C	
Direct Tension, (1mm/min.), % Strain		T 314	No Requirement					
PG PLUS REQUIREMENTS: YES								
Penetration,100g, 5 sec, dmm	25°C	ASTM D 5	--	55-75	--	--		--
Dynamic Shear, Phase Angle, °	At grade temperature	T 315	--			80	80	76
Separation[a], Softening Point Difference, °F		--	--			10 max.		
Homogeneity[b], lumps nor particles on 50 mesh		--	--			None		
RTFOT RESIDUE:								
Elastic Recovery[c], 10 cm, %	25°C	ASTM D 6084	--			65 min.		75 min.
NOTES:								

a. Separation: (340°F, 48 hours)
b. Homogeneity: 400g, 177°C, 2.5 hrs
c. Elastic Recovery: 10 cm elongation @ 77C, hold 5 min. before cutting, RTFO residue
* Required to report actual high and low pass temperature, shall not grade out to -28°C grade. (PG 70-22PM test @ 70 & 76, -12 & -18°C, PG 76-22PM test @ 76 & 82, -12 & -18°C)

OH Page 1 of 2

Table A Material Requirements for PGM Binder					
Test / Requirement		**SBR Polymer**		**SBS Polymer**		**Notes**

Test / Requirement		SBR Polymer		SBS Polymer		Notes
Final PG Binder Grade		70-22 (a)	70-22 (b)	70-22 (a)	76-22 (a)	c
Actual Pass Temperatures		Report				i
RTFOT Mass Loss, %		0.5 max.				d
Phase Angle, °	At grade temperature	76 max.		80 max.	76 max.	d
Elastic Recovery, %	25°C	--		65 min.	75 min.	e
Toughness, in-lbs	25°C	118 min.		-----		f, d
Tenacity, in-lbs		68 min.				f, d
Elongation	25°C	20 min.		----		f, d
Ductility	25°C	28 min.		-----		j, d
Separation, °F		10 max.	--	10 max.		g
Homogeneity		--		None Visible		h, d

NOTES:

a. Pre-blended PGM binder with a base binder of at least -22 grade or stiffer.
b. Post blended PGM binder make from neat Supplement 1032 certified or pre-approved standard PG binder grade and rubber solids amount equal to or above 3.5 percent by weight of total binder to achieve the PG binder grade.
c. As required by 906.052.
d. PGM binder.
e. ASTM D 113, 10 cm @ 25°C on RTFO material.
f. ASTM D 5801, 50 cm/min. @ 25°C.
g. Softening Point difference of top and bottom of frozen sealed aluminum tube conditioned at 340°F for 48 hours. Compatibility of polymer and neat binder is sole responsibility of supplier. PGM binder shall be formulated to retain dispersion for 3 days minimum. Failure in the field to retain dispersion for this time will mean automatic removal from Supplement 1032 certification.
h. Heat a minimum 400 gram sample at 177°C for 2.5 -3.0 hours. Pour entire sample over a hot No. 50 (300 um) sieve at 340°F. Look for retained polymer lumps.
i. Actual high and low temperature achieved by PGM binder beyond required grade, but shall not grade out to the next standard PG binder grade for low temperature.
j. ASTM D 113 @ 4°C, 1 cm/min.

PRI   Disclaimer: "To ensure the most accurate and current information, the specific agency should be contacted."

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