

Solid Waste to Energy by Advanced Thermal Technology

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Abstract

Solid waste (SW) outputs of industrial nations, mostly biomass, could fuel much more of their increasing energy needs than they currently do while creating good local jobs and industries. Using U.S. data as an example, 24 types of wasted or underutilized organic solids are identified. Now usually disposal problems, most of these SWs can be converted into useful gas, liquid, and solid (charcoal) fuels via pyrolysis. The non-condensable and condensable pyro-volatiles can be used by direct combustion as a clean source of heat energy or with advanced cleaning, in high-efficiency gas turbines or fuel cells. Pyrolysis processing has some important energy, environmental, economic, and security (EEES) advantages with respect to direct combustion or air or oxygen-blown partial combustion-gasification. An analytical semi-empirical model (ASEM) that points to some order in pyrolysis yields that could be helpful in optimizing the outputs of Solid Waste to Energy by Advanced Thermal Technologies (SWEATT) systems is described. We describe an analytical cost estimation (ACE) model that can be used to relate the cost of electricity for diverse electrical generating technologies including SWEATT systems to capital, operation, environmental control, cost of fuel (COF), and estimated costs of environmental and security externalities (ESE) such as climate change and terror threats. ACE can be useful particularly in estimating the impact of changes in COF and ESE, usually the most uncertain independent variables. The EEES issues related to soil applications of biomass pyrolysis products, i.e., biochar, are outlined. A growing International Biochar Initiative is underway to use biochar to sequester carbon in the soil, thereby mitigating climate change while enhancing soil fertility. High transportation costs due to the low energy densities of biomass/SW, compared to coal or petroleum, imply that siting SWEATT systems close to the SW source would have a number of cost and environmental advantages. The application of SWEATT systems in support of agricultural programs that grow high-yield vegetable oil crops intended for biodiesel production on non-food-producing lands is considered as a means of providing additional revenue streams. Additional SWEATT applications in conjunction with the other forms of the 24 types of SW are to be expected.

SOLID WASTE, SOLID FUELS, AND THEIR PROPERTIES

At this time in our history we are excessively (>60%) reliant on foreign sources for our liquid fuels and are increasingly importing our gaseous fuels (now >15%). Our country is now expending “blood and treasure” in its efforts to stabilize regions of the globe that supply these premium fuels. Yet the United States is well endowed with solid fuels in the form of coal, oil shale, and substantial quantities of renewable but wasted solids. As part of a continuing long search for alternatives to oil,^[1-10] this entry is focused on converting our solid waste to energy by advanced thermal technologies (SWEATTs) while mitigating environmental and economic problems. Table 1 is a list of United States’ abundant supply of solid waste (SW) whose organic matter can be converted into gaseous and liquid fuels as well as charcoal. The value society places on a specific fuel or

energy type is very sensitive to its physical form as indicated in Table 2^[11] which gives prices of various forms of energy in the United States at the beginning of 2010. The large carbon dioxide neutral (neither net producing nor consuming CO₂) plant matter components in Table 1 can help in Greenhouse heating mitigation. The great diversity of physical and chemical characteristics of fuel wastes (feedstock) in Table 1 implies that the world now needs “omnivorous feedstock converters” (OFCs) to change these solid fuels into much more usable liquid or gaseous fuels or better solid fuels. Fig. 1 is a conceptual illustration of an OFC adapted from a number of prior papers^[8-10] in which a SW pyrolyzer-gasifier-liquifier-carbonizer is co-utilized with a natural gas-fired combined cycle (NGCC) system, as will be discussed below.

Table 3 shows major ranks of coals as well as of peat, wood, and cellulose and their ultimate and proximate analyses as measured by industry for over a century. The

Table 1 Potential sources of useful non-conventional fuels.

Waste type	MDT ^a
1. Agricultural residues	1000
2. Forest under-story and forestry residues	400
3. Hurricane debris	40
4. Construction and deconstruction debris	20
5. Refuse-derived fuels	10
6. Urban yard waste	20
7. Food-serving and food-processing waste	80
8. Used newspaper and paper towels	30
9. Used tires	60
10. Energy crops on underutilized lands	50
11. Ethanol production waste	20
12. Anaerobic digestion waste	10
13. Bio-oil production waste	10
14. Waste plastics	40
15. Infested trees (beetles, canker, spores)	20
16. Invasive species (cogon-grass, melaluca, cat-tail)	50
17. Plastics mined when restoring landfills	30
18. Biosolids (dried sewage sludge) ^b	40
19. Poultry and pig farm waste ^b	20
20. Water plant remediators (algae, hydrilla) ^b	10
21. Muck pumped to shore ^b	10
22. Manure from cattle feed lots	10
23. Plants for phyto-remediation of toxic sites	10
24. Treated wood past its useful life	10
Total	2000

^aMDT = million dry tonne.

^bDenote water remediation-related items.

numbers listed in columns labeled C, H, and O (wt% of carbon, hydrogen, and oxygen, respectively) essentially apply to ideal carbon, hydrogen, and oxygen (CHO) materials by correcting measurements to their dry-, ash-, sulfur-, and nitrogen-free (DANSF) form. Then $[C]+[H]+[O]=100$ and any two of the three variables fixes the third. In this work we mostly focus on the variables [O] and [H] which then essentially specifies [C]. The column labeled higher heating values (HHV) gives typical HHV in millions of joules per kilogram (MJ/kg) as measured with standard bomb calorimeters after allowing for the minor components.

Fig. 2a is mainly a plot of [H] (solid diamonds with values read on the left scale) vs. [O] on the top scale for 185 representative DANSF CHO materials taken from ultimate analysis data available in the technical literature. The trend can be represented by $[H]=6(1-\exp([O]/2))$. The bottom scales give conventional coal ranks, some potential names for the biomass region, and some names that might foster more friendly discussions between the coal and biomass sectors. This [H] vs. [O] coalification plot shows that apart from the anthracite region, all natural DANSF feedstock

Table 2 Market and energy prices, December 2010.^[11]

Fossil Fuels	Market Price	\$/MMBtu
Crude oil	\$84.93 \$/Barrel	\$14.64
Gasoline	\$2.865 \$/Gallon	\$22.92
Diesel Fuel	\$3.116 \$/Gallon	\$24.21
Natural gas	\$3.56 \$/MMBtu	\$3.56
Liquid Propane (Gulf)	\$1.11 \$/Gallon	\$12.19
Heating oil	\$2.084 \$/Gallon	\$15.10
Electricity retail, resid.	12.02 ¢/kWh	\$35.23
Coal	\$47.25 \$/ton	\$2.00
Liquid Fuels		
Ethanol (Iowa)	\$2.42 \$/Gallon	\$31.78
biodiesel (Iowa)	\$4.13 \$/Gallon	\$34.96
Soybean oil (Central IL)	51.68 ¢/Lb	\$30.40
No 2, Yellow grease	\$32.88 \$/cwt	\$21.35
Solid Fuels		
Fuel pellets	\$206.60 \$/Ton	\$12.91
Shelled corn	\$5.37 \$/Bushel	\$11.76
Compost	\$25.00 \$/cu. yard	\$3.63
Wheat straw	\$80.00 \$/Ton	\$5.41
Grass hay (1g md bale)	\$50.00 \$/Ton	\$3.33
DDGS	\$156.00 \$/Ton	\$8.30

Source: Adapted from Jenner.^[11]

have [H] values that are close to 6%. The [H] and [O] coordinates of the three main components of all plant matter are lignin-6.1, 32.6, cellulose-6.2, 49.4, and hemi-cellulose-6.7, 53.3. Materials present in SW can depart substantially above and below the coalification curve. For example, the coordinates of polyethylene and polypropylene are 14.2 and 0, respectively.

The [C] vs. [O] data calculated with $[C]=100-[O]-[H]$ for DANSF feedstock are also shown in Fig. 2a. When the smooth [H] vs. [O] formula is used one gets the smooth upper curve in relation to the data. This figure provides strong reasons for regarding peat and biomass simply as lower rank coals. The diagram suggests that coalification is a natural geophysical deoxygenating process. Much of this treatise on SWEATT will be devoted to attempting to bring some order to the confused literature on artificial pyrolysis, deoxygenating or carbonizing processes and their gaseous, liquid, and solid products. For many purposes, natural solid fuels could be ranked simply by [O] to replace the different ranking systems of various countries (a Tower of Babel!). For example, using 34-O for peat, called "turf" in Ireland, might help temper the "turf wars" in fuel sector competitions and in energy vs. environmental confrontations on the use of our available fuels.

HHV of various fuels measured with calorimeters are often reported along with proximate analyses. Representative

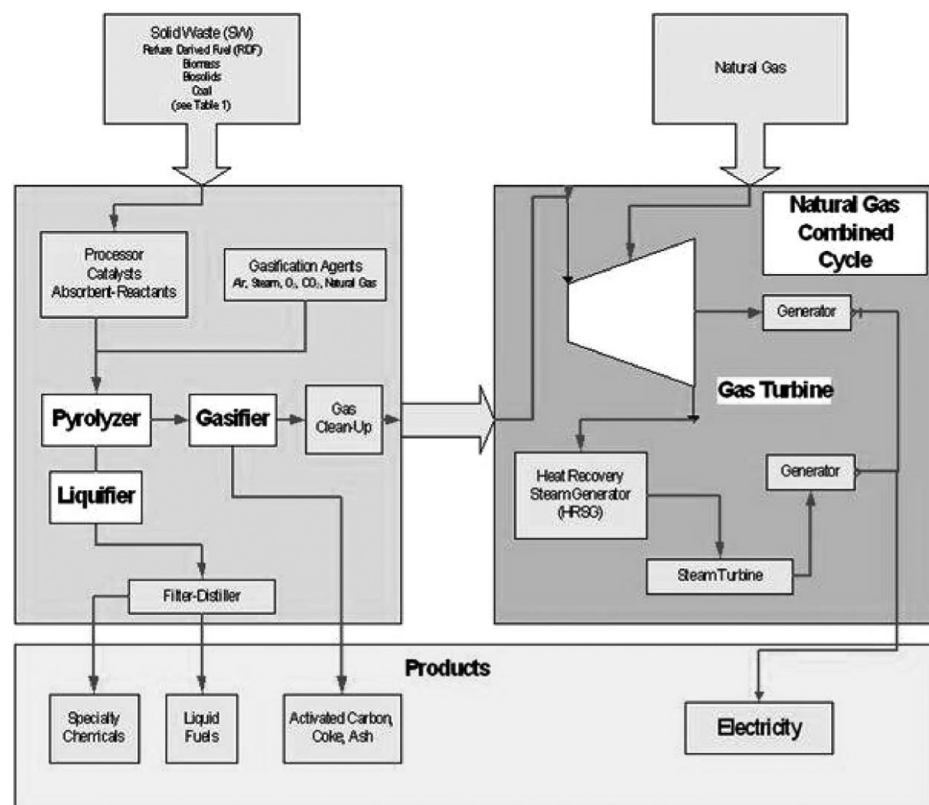


Fig. 1 Diagram of the Omnivorous Feedstock Converter (OFC) illustrating the addition of a solid waste system to an existing NGCC plant to create an effective SWCC system.

Source: From Pyrolysis in Waste to Energy Conversion (WEC).^[10]

values for the various coal ranks are given in the column labeled HHV in Table 3. The column labeled V_T gives representative “total volatiles,” V_T , as determined by an American Standard Test Measurement Method. A solid sample is heated (pyrolyzed) in a platinum crucible at 950°C for 7 minutes. The weight percent loss due to the escaping volatiles is designated as the total volatile yield (V_T). The balance from 100% then represents the weight percent of the fixed carbon (FC) plus ash. The ash wt%

is the weight percent remaining after combustion in full atmosphere at 750°C for 6 hours.

The columns of Table 3 labeled Dens and E/vol give the physical density (in g/cc) and relative energy density of the various natural solid fuels. These are important factors in determining handling and transportation costs. The column labeled charR gives some relative measures of the reactivity of the chars that are produced by the pyrolysis of these natural feedstock.

Table 3 Properties of fuels along nature’s coalification path.

Name	Ultimate analysis			Proximate analysis			Other properties		
	C	H	O	HHV	V_T	FC	Dens	E/vol	charR
Anthracite	94	3	3	36	7	93	1.6	58	1.5
Bituminous	85	5	10	35	33	67	1.4	49	5
Sub-Bituminous	75	5	20	30	51	49	1.2	36	16
Lignite	70	5	25	27	58	42	1	27	50
Peat	60	6	34	23	69	31	0.8	18	150
Wood	49	7	44	18	81	19	0.6	11	500
Cellulose	44	6	50	10	88	12	0.4	9	1600

C, H, and O are wt% of carbon, hydrogen, and oxygen, HHV = higher heating value (millions of joules per kilogram: MJ/kg), V_T = weight percent volatiles, FC = fixed carbon weight percent, Dens = g cm⁻³, E/vol = relative energy density, charR = relative char reactivity.

Absorbance - Antibiotics

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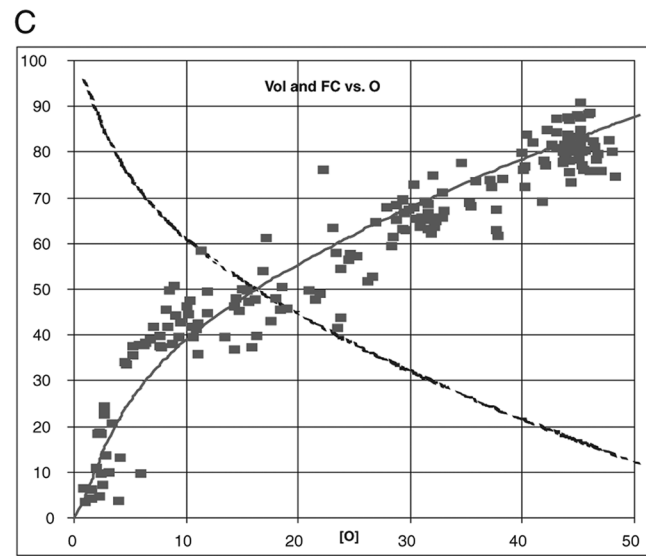
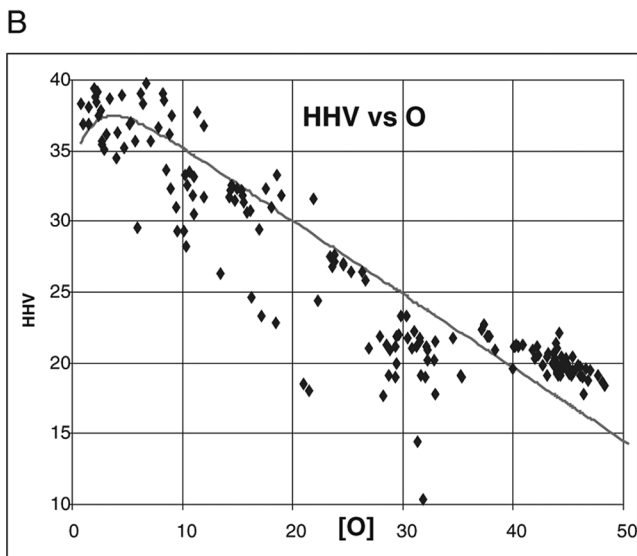
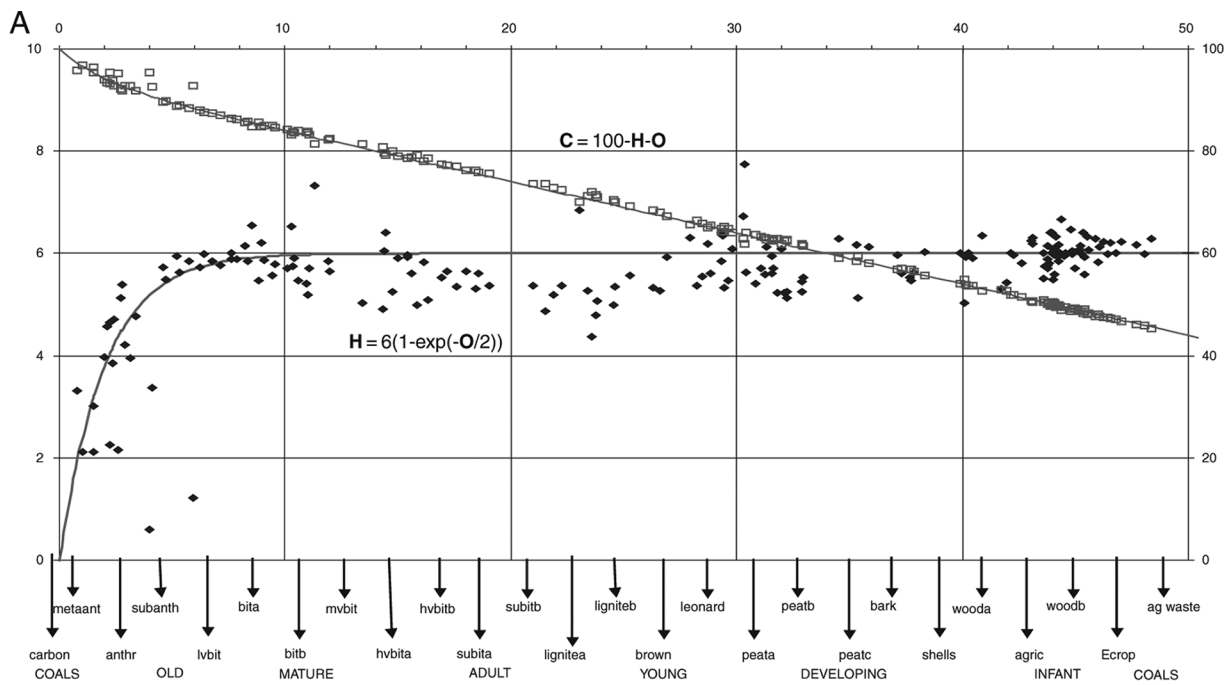


Fig. 2 (A) Weight percentages of hydrogen [H, left] vs. [O, top] for 185 DANSF carbonaceous materials (diamonds) and additional solid waste materials (red circles). Classification labels are given at the bottom axis. (B) Higher heating values (HHV) of 185 carbonaceous materials (corrected to DANSF) vs. [O]. The smoothed curve represents: Eq. 1a when $[H] = 6(1 - \exp([O]/2))$ is used. (C) Total volatile weight percentages (left) vs. [O] for 185 DANSF carbonaceous materials (squares) from proximate analysis. The curve through the data points satisfies: $V_T = 62([H]/6)([O]/25)^{1/2}$. The analytic fixed carbon (FC) vs. [O] is shown as a dashed line. **Source:** From *A Green Alliance of Biomass and Coal (GABC)*.^[4]

Fig. 2b displays HHV data for the compilation of 185 materials after correction to DANSF cases. Most points within this scattered HHV data can be fit within a few percent by a two variable form of Dulong's formula:

$$\text{HHV in MJ/kg} = 34.9 - 0.453[\text{O}] + 0.829[\text{H}] \quad (1a)$$

or

$$\text{HHV in MBtu/lb} = 15.00 - 0.194[\text{O}] + 0.356[\text{H}] \quad (1b)$$

The first form is simplified from the six-variable DuLong formula found by Channiwala and Parikh^[12] who fit a large body of HHV measurements of biomass and other fuels. The smooth curve in Fig. 2b shows the trend of the HHV vs. [O] when $[H] = 6(1 - \exp([O]/2))$ is used. When measured [H] values are used the HHV formula given fits

within a few percent. From a HHV standpoint deoxygenating biomass by pyrolysis endows the char progressively with some properties of the higher ranks of coal except that chars tend to be more porous.

The general trends of total volatiles along nature's coalification curve can be approximately be represented by the empirical formula $V_T = 62([H]/6)([O]/25)^{1/2}$. Note the rapidly increasing trend in V_T from low [O] materials to high [O] materials (Fig. 2c). Because of the large production of volatiles by high [O] materials, pyrolysis of these materials is substantially equivalent to gasification. The [H] dimension is also important and small deviations of [H] from the smooth coalification path have a large impact on the volatile release.

The three diagrams in Fig. 2 all indicate the importance of [O] in determining the fuel and carbonization or pyrolysis properties of organic materials. Coalification might be called nature's carbonization or deoxidation process whereas pyrolysis is an artificial process for carbonization or deoxidation of organic feedstock.

GLOBAL AND U.S. PRIMARY ENERGY SUPPLIES

Fig. 3a presents an overview of the world total primary energy supply (TPES) in 2004 (see International Energy Agency website). Among the major sources of energy, combustible renewables and waste (CRW, mostly biomass) need only be doubled to be competitively with coal and natural gas, and tripled to be competitive with petroleum. Note that the global CRW is currently about twice as large as nuclear. On the other hand, wind and solar must grow by factors of over 100 to become major global energy supplies.

This global TPES picture is not representative of the industrial world, particularly the United States today. Fig. 3b shows the percentage subdivisions of the US TPES in 2007 when the total consumption was over 101.5 quads, (quadrillion British thermal units (Btu)/annum or quads). It is seen that about 39% of our energy consumption is in the form of petroleum that is mainly consumed in our transportation sector. As Fig. 3c illustrates renewables now only constitute 7% of the US TPES. The percentage subdivisions of these in 2007 are shown in the figure, and it is seen that biomass was 53% of the 7%. The major thrust of this work is that the solid wastes listed in Table 1, consisting mostly of biomass, now only a minor component (~3.5%) of the U.S. annual TPES, could in the near term become a major component comparable to coal and natural gas, both now at about 23%. The more popular renewables, geothermal wind and solar have much further to go than solid waste before becoming a major primary energy source in the United States. Since SWEATT is based on locally available solid waste, it would also create good non-exportable local industries and jobs while mitigating

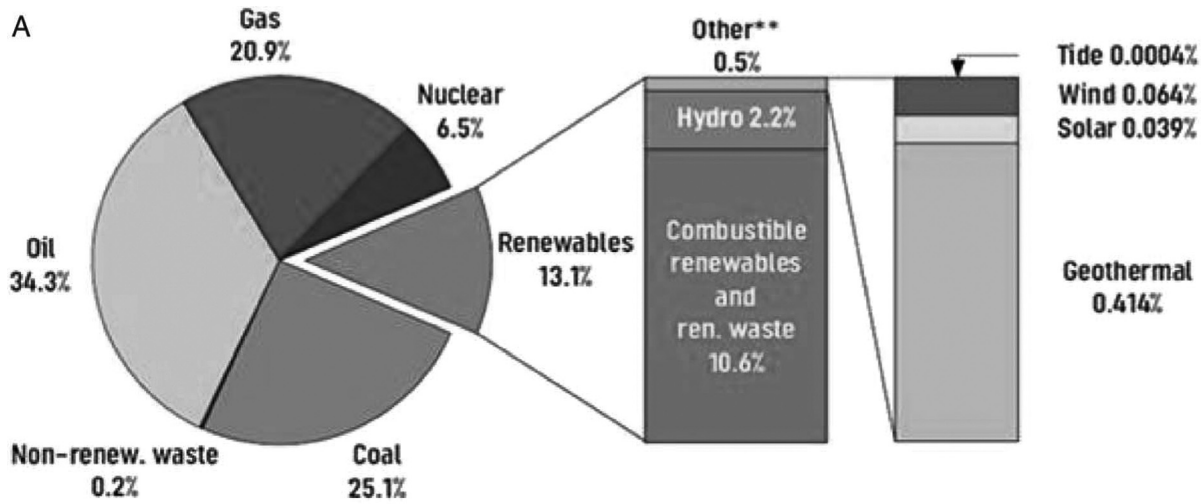
serious U.S. energy import and waste disposal problems. An Oak Ridge National Laboratory study^[13] estimates the sustainable supply of the first few biomass categories in Table 1 at about 1.4 billion dry tons. The remaining categories should readily bring the total sustainable U.S. solid waste available to over 2 billion dry tons. Assuming a conservative HHV of 7500 Btu/lb, a simple calculation shows that with SWEATT technologies similar to those that are now in place in Japan, U.S. solid waste contribution to its primary energy supply could reach the 25% level.

Without doubt, the biggest energy problem faced by the United States today is the need to find alternatives to oil.^[1-3] In the 70s and early 80s, the United States focused heavily on alternatives to oil in the utility sector. The alternatives first were pulverized coal plants and in the late 80s and 90s, on NGCC systems. At this time, the U.S. focus should, in part, be on the developing alternatives to natural gas for electricity generation via the use of advanced thermal technologies (ATTs).

It is important to differentiate secondary energy supplies (SESs) from the primary energy supplies (PESs) shown in Fig. 3. Secondary energy supplies include steam, syngas, reactive chemicals, hydrogen, charges in batteries, fuel cells, and other energy sources that draw their energy from PESs. If a SES is converted to another type of energy, say mechanical energy via a steam turbine, the mechanical energy becomes a tertiary energy supply (TES). This TES can be converted to electrical energy using magnetic generators in which case the electricity is a quaternary (QES) supply. In the case of electricity, the many conversions are usually justified since electricity can readily be distributed by wire and has so many uses as a source of energy for highly efficient electric motors, illumination systems, home appliances, computers, etc. Table 2 points to the high cost/value placed on electricity and on liquid fuels.

In many communities debates are underway as to whether increasing electricity needs should be met with the solid fuel coal, MSW, biomass via conventional steam and steam turbine generator systems, or via conversion to a gaseous fuel and using integrated gasifier combined cycle (IGCC) systems. Granting that the steam turbine route has had many advances over the last century, converting the solid fuel to gaseous fuel is increasingly being accepted as the ATT route of the future. The ATT route is not only driven by environmentally acceptable waste disposal needs and increased needs for electricity, but also by the need for liquid and gaseous fuels. A number of petroleum resource experts have recently advanced the date that the globe's supply of oil and natural gas will run out. The prices of oil and to a lesser extent natural gas now reflect this drawdown and are already high enough that conversion of organic matter in solid waste to liquid and gaseous fuels makes economic sense. We should recognize, however, that for the most part, cartels govern fuel prices not free markets. Thus we should not abandon alternative fuels efforts whenever cartels, for their interests, lower prices.

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* TPES is calculated using the IEA conventions (physical energy content methodology). It includes international marine bunkers and excludes electricity/heat trade. The figures include both commercial and non-commercial energy.
 ** Geothermal, solar, wind, tide/wave/ocean.
 Totals in graph might not add up due to rounding.
 Source: IEA Energy Statistics

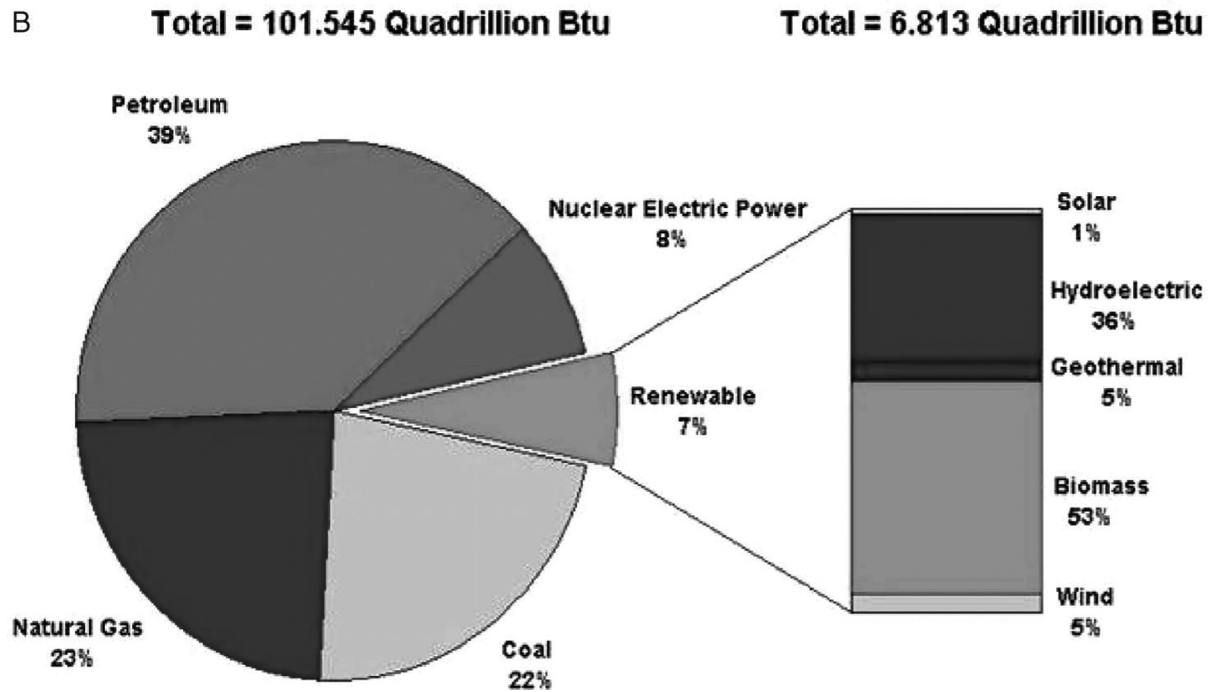


Fig. 3 (A) Total primary energy supply (TPES) for the globe at 2004 (IEA Website). (b) TPES for the United States in 2007 (EIA Website). *TPES is calculated using the IEA conventions (physical energy content methodology). It includes international marine bunkers and excludes electricity/heat trade. The figures include both commercial and non-commercial energy. **Geothermal, solar, wind, tide/wave/ocean. Totals in graph might not add up due to rounding.
 Source: From IEA Energy Statistics.

ADVANCED THERMAL TECHNOLOGIES

The largest solid waste to energy systems in operation today are direct combustion municipal solid waste (MSW) incinerators with capacities in the range of 1000–3000 tons SW per day. In such mass burn systems, the organic constituents of the solid waste are combusted into the gaseous products CO_2 and H_2O . These have no fuel value but can be carriers of the heat of combustion as in coal and biomass boiler-furnace systems. Along with the flame radiation, these gases may be used to transfer heat to pressurized water to produce pressurized steam that drives a steam turbine-driven electric generator. The steam can also serve as a valuable SES to distribute heat for heating buildings, industrial processes, etc. The production and use of steam, along with the steam engine, launched the industrial age.

Instead of using the heat released to raise steam, in SWEATT systems the solid waste is first converted into gaseous or liquid fuels and, in pyrolysis systems, partly to char. The volatiles, gases, and vaporized liquids fuel then serve as a SES that can be used in efficient internal combustion engines (ICEs), combustion turbines or, in the future, in fuel cells, none of which can directly use solid fuels. Over the past century automotive and aircraft developments have pushed ICEs and gas turbines (GT) to very high levels of efficiency. Furthermore, with the use of modern high temperature GTs in NGCC systems, the heat of the exhaust gases can be used with a heat recovery steam generator (HRSG) to drive a steam turbine. Alternatively, the HRSG can provide steam for heating buildings or industrial applications of steam. These combined heat and power (CHP) system at this time make the most efficient use of the original solid fuel energy.

If one considers the United States' heavy dependence on foreign sources of liquid and gaseous fuels, the most challenging technical problem facing the United States today should be recognized as the development and implementation of efficient ways of converting our abundant domestic solid fuels into more useful liquid and gaseous fuels. In view of the diversity of feedstock represented in agricultural, municipal, or institutional solid waste, the United States and the world need an omnivorous feedstock converter such as is illustrated in Fig. 1. Here, the right block represents a typical NGCC system, whereas the left block represents a conceptual Omnivorous Conversion System that can convert any organic material into a gaseous or liquid fuel.

We will first consider the gross nature of the output gas from biomass or cellulosic type material, the major organic components of most solid waste streams. Apart from minor constituents such as sulfur and nitrogen, the cellulosic feed types are complex combinations of carbon, hydrogen, and oxygen such as $(\text{C}_6\text{H}_{10}\text{O}_5)$ that might serve as the representative cellulosic monomer.

ATT systems used to produce output can be divided into 1) air blown partial combustion (ABPC) gasifiers; 2) oxygen blown partial combustion (OBPC) gasifiers; and 3) pyrolysis (PYRO) systems. The three types of systems for converting waste into a gaseous fuel have many separate technical forms depending upon the detailed arrangements for applying heat to the incoming feed and the source of heat used to change the solid into a gas or liquid fuel. We use “producer gas” as a generic name for gases developed by partial combustion of the feedstock with air as in many traditional ABPC gasifiers that go back to Clayton's coal gasifier of 1694. We will use “syngas” for gases developed by partial combustion of the feedstock with oxygen as in OBPC gasifiers, which are mainly a development of the twentieth century. We will use “pyrogas” for gases produced by oxygen-free heating of the feedstock such as in indirectly heated (pyro)gasifiers. The objective is to replace the natural gas, that is, fossil fuel gas, that has a HHV, ~ 1000 Btu/cft = 1 MBtu/cft (with Btu $M = 1000$) with a biomass-generated fuel gas having similar energy and combustion qualities.

When an ABPC gasifier is used with cellulosic materials (cardboard, paper, wood chips, bagasse, etc.), the HHV of biomass producer gas is very low, 100–200 Btu/cft. Essentially, the useful product of partial combustion of biomass is CO that only has a HHV of 322 Btu/cft. Unfortunately, considerable CO_2 and H_2O are produced during partial combustion and together with the air–nitrogen these inerts substantially dilute the output gas. The “syngas” obtained from biomass with OBPC gasifiers is better, ~ 320 Btu/cft, since it is not diluted by the atmospheric nitrogen. However, because of the partial combustion it is still somewhat lower than the energy contained within the feedstock molecules. Additionally, the oxygen separator is a major capital cost component of an OBPC gasifier. With a Pyro system, the original cellulosic polymer is broken by the applied indirect heat to its monomers and then to the major pyro-products CO , CO_2 , and H_2O as well as hundreds of hydrocarbons (HCs) and carbohydrates (HCOs), each with yields that depend upon the applied temperature, heating time, and particular processing arrangement. Cellulosic pyrogas can have heating values in excess of 400 Btu/cft.

Among the pyro-volatiles coming from pyrolysis systems are the paraffins (CH_4 , C_2H_6 , C_3H_8 , . . .), olefins (C_2H_4 , C_3H_6 , . . .), acetylenes (C_2H_2 , C_3H_2 , . . .), and various carbohydrates, carbonyls, alcohols, ethers, aldehydes and phenols, and other oxygen-containing gaseous products. Attempting to find some patterns or regularities in the literature on products of pyrolysis from various natural and man-made fuels has been the goal of multiyear effort.^[14–26] Table 4 is a list of the families of molecules that have been detected in pyrolysis volatiles and the rules that connect the family member, labeled by $j = 1, 2, 3, \dots$ (see Section “The ASEM and Organization of Pyrolysis Products”).

Table 4 Organization of functional groups by families.

Families	a	b	c
Paraffins	j	$2a + 2$	0
Olefins	$j + 1$	$2a$	0
Acetylenes	$j + 1$	$2a - 2$	0
Aromatics	$5 + j$	$4 + 2j$	0
Polynuclear	$6 + 4j$	$6 + 2j$	0
Aldehydes	$j + 1$	$2a$	1
Carbonyls	j	$2a$	1
Alcohols	j	$2a + 2$	1
Ethers	$j + 1$	$2a + 2$	1
Phenols	$5 + j$	$4 + 2j$	1
Formic acids	j	$2a$	2
Guaiacols	$6 + j$	$6 + 2j$	2
Syringols 1	$7 + j$	$8 + 2j$	3
Syringols 2	$8 + j$	$10 + 2j$	4
Sugars 1	$4 + j$	10	5
Sugars 2	$5 + j$	$10 + 2j$	5

a , b , and c are the subscripts in $C_aH_bO_c$, $j = 1, 2, 3, \dots$

HC plastics such as polyethylene and polyolefins are heavily represented in many solid waste streams. Thus one might use (C_2H_4) as representative of the monomers in the plastic component of MSW or refuse-derived fuels (RDFs). Polyethylene pyrolysis products are dominated by C2–C4 olefins, acetylenes, and other HCs and at higher temperatures by H_2 as well as aromatics (Ar) and polynuclear aromatics (PNAs) identified in Table 4. On a per unit weight basis, all but H_2 have gross heating values in the range 18–23 MBtu/lb, similar to oil, whereas H_2 has a gross heating value of 61 MBtu/lb. On a per unit volume basis, polyethylene pyrolysis products have gross heating value ranging from 1 to 5 MBtu/cft whereas H_2 is 0.325 MBtu/cft = 325 Btu/cft. Because natural gas is typically about 1 MBtu/cft, we would expect the pyrogas from polyethylene to have a gross heating value comparable or greater than that of natural gas and much greater than cellulosic pyrogas.

In summary since cellulosic feedstock is already oxygenated compared with pure HC plastics, its pyrogas, syngas, and producer gas will all have considerably lower heating values than the corresponding gases from HC feedstock. From the viewpoint of maximizing the HHV of SW-derived gas, Pyro gasification scores better than OBPC gasification, both of which score much better than ABPC gasification. Pyrolysis also leaves more of a solid residue in char-ash form than ABPC gasification or OBPC gasification. Fig. 4 illustrates a typical pattern of evolution of the solid in an indirectly heated slow pyrolysis system.^[27] For DASNF materials the asymptote of the solid (char) curve would represent the FC and the balance from 100% would represent the total volatiles. Fig. 4 also shows a typical pat-

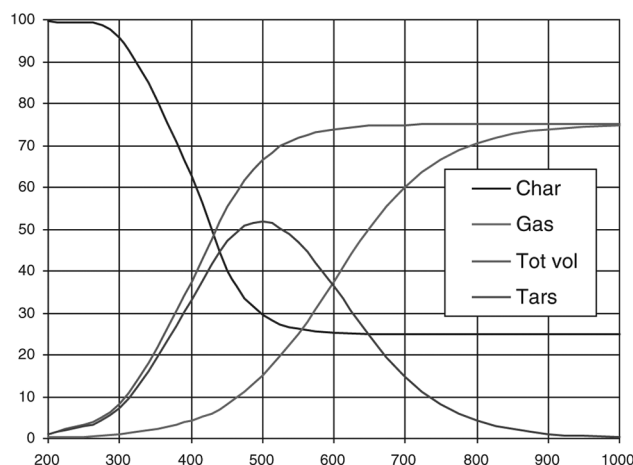


Fig. 4 Typical pattern of evolution of char, tar, and gas from wood feedstock as temperature is raised at a slowly ($10^\circ\text{C}/\text{min}$).

tern of evolution of the tar and gas from wood feedstock in the pyrolysis of a small particle of wood when its temperature is raised at a slow rate such as $10^\circ\text{C}/\text{min}$. These curves are representative of results from the analytical semiempirical model (ASEM).

Studies of the evolution of chars, tars (volatiles condensable at standard temperature), gas (not condensable at standard temperature), and total volatiles have been carried out at heating rates (r) from $1^\circ\text{C}/\text{min}$ to $1000^\circ\text{C}/\text{sec}$. Usually the heat rate is coupled to the temperature via a linear relationship such as $T = rt + T_0$ (where t is time and T_0 is an initial temperature). The dependence of these products upon temperature then changes dramatically from that shown in Fig. 4 in ways that are difficult to track via standard kinetic modeling. However, they can be relatively easily represented via formulas used in the ASEM by letting the parameters of the model be simply dependent upon the heating rate. This approach is often dismissed as “just curve fitting” in academic circles where the search for models that depend upon fundamentals physical variables has become traditional. Unfortunately, in pyrolysis studies, because of the complexity of products released at various temperatures, this quest is still far from realization. Accordingly, it appears to some investigators that after the experimental assembly of reproducible scientific data (the first step of the scientific method), organizing the results in some robust analytical form (the usual second step of the scientific method) cannot only be useful for applications, but could help in achieving a fundamental model.

THE ASEM AND ORGANIZATION OF PYROLYSIS PRODUCTS

Proximate analyses of coal and biomass measured for over a century provide extensive data on total volatile content. However, quantitative data as to the molecular constituents

in these volatiles have only been reported in recent years and a predictive method for identifying these molecules is still not available. This despite the fact that such knowledge could provide a more fundamental understanding of humankind's oldest technology (the use of fire). For control and application of a pyrolysis system it would be useful to have at least an engineering-type knowledge of the expected yields of the main products from various feedstock subjected to oxygen-free thermal treatment (pyrolysis).

In most attempts to describe the systematic of pyrolysis yields of organic materials such as coal and biomass, including the initial CCTL studies,^[14–19] it has been customary to characterize the feedstock by its atomic ratios $y = H/C$ and $x = O/C$. In recent studies,^[20–26] it has been found more advantageous to work with the weight percentages [C], [H], and [O] of the feedstock after correcting to DASNF conditions (i.e., pure CHO materials). Focusing on weight percentages appears to facilitate easier connections between the great complexity of compounds that evolve from pyrolysis and the gas, liquid (tar), and solid products of pyrolysis.

The ASEM is a phenomenological attempt to find some underlying order in the pyrolysis yields of any product $C_aH_bO_c$ vs. the [O] and [H] of the DASNF feedstock and the temperature (T) and time (t) of exposure. The ASEM was developed so as to be useful for a number of applications of pyrolysis.^[18–26] Some progress has been made in including the time dimension but much more work remains on that front. When the time dimension is not an important factor, as in many cases of slow pyrolysis, the yield $Y(T)$ as a function of temperature of each product for slow pyrolysis (or fast pyrolysis at a fixed time) is represented by

$$Y(T) = W[L(T : T_0, D)]^p [F(T : T_0, D)]^q \quad (2)$$

where

$$L(T : T_0, D) = \frac{1}{1 + \exp((T - T_0)/D)} \quad (3)$$

and

$$F(T : T_0, D) = 1 - L(T) = \frac{1}{1 + \exp((T - T_0)/D)} \quad (4)$$

Here $L(T)$, is the well-known logistic function that is often called the “learning curve.” Its complement, $F(T) = 1 - L(T)$ thus might be called the “forgetting curve.” For engineering applications this “curve fitting” approach provides a more robust and convenient means for organizing pyrolysis data than traditional methods that use conventional Arrhenius reaction rate formulas.^[27] In the ASEM each product is assigned five parameters (W, T_0, D_0, p, q) to represent its yield vs. temperature profile. The objective has been to find how these parameters depend on the [H] and [O] of the feedstock and the a, b, c of the $C_aH_bO_c$ products for the data from particular types of pyrolyzers.

Studies by Xu and Tomita (XT)^[28] that gave data on 15 products from 17 coals at 6 temperatures have been particularly helpful in revealing trends of the parameters with [O] and [H]. In applying the ASEM to the CCTL data collection, the XT collection, and several other collections, a reasonable working formula was found for the yield of any abc product for any [O], [H] feedstock given by

$$Y(C_aH_bO_c) = W_{abc} z^\alpha h^\beta x^\gamma [L(T : T_0, D)]^p [F(T : T_0, D)]^q \quad (5)$$

where $z = [C]/69$, $h = [H]/6$, and $x = [O]/25$ and the parameters α, β, γ , and δ . T_0, D, p , and q were found to have simple relationships to the feedstock and product defining parameters [H], [O], a, b , and c . The final ASEM formulas that fit the data could then be used to extrapolate or interpolate the XT results to any [H], [O] feedstock and temperature. Fig. 5 gives an overview of the interpolated and extrapolated outputs $Y(T)$ for a selection of products for six representative feedstock along nature's coalification path.

Several hundreds, even thousands, of organic products of pyrolysis have been identified in the literature. Thus, to bring order from chaos will require some comprehensive organization of these products. Toward this goal, the ASEM approach groups products into the families as summarized in Table 4, which gives rules for the a, b, c 's that connect these groups. This list can be subdivided into pure HCs, i.e., (C_aH_b) , and the oxygenates ($C_aH_bO, C_aH_bO_2, C_aH_bO_3, \dots$, etc.). Isomers (groups with identical a, b , and c) can differ in detailed pyrolysis properties and hence parameters. We use $j = 1, 2, 3, \dots$ to denote the first, second, third, etc., members of each group or the carbon number (n). In the most recent ASEM studies^[20–26] of specific feedstock, pyrolysis formulas have been proposed and tested for the dependence of the W, T_0, D_0, p , and q parameters upon the carbon number of the product within each group. This makes it possible to compact a very large body of data with simple formulas and a table of parameters.

The case of polyethylene is an example of such a study. It is not shown on Fig. 2a, as it is far removed from the coalification curve having the position [H] = 14.2 on the [O] = 0 axis. Without oxygen in the feedstock, the pyrolysis products are much fewer and the ASEM is much simpler to use than with carbohydrates. Thus, only the first 6 rows of Table 4 are needed to cover the main functional groups involved in organizing the pyrolysis products of polyethylene. Fig. 6 gives an ASEM-type summary of the product yields vs. temperature for polyethylene based on fits to the experimental data of Mastral et al.^[29,30] at five temperatures that were constrained to approximately satisfy mass, [C], and [H] balances. Once the parameter systematic is identified, the ASEM representation can be used to estimate the pyrolysis product of polyethylene pyrolysis at any intermediate temperature or at reasonable extrapolated temperatures. The experimental data was only available up to 850°C but the extrapolations to 1000°C were

Absorbance - Antibiotics

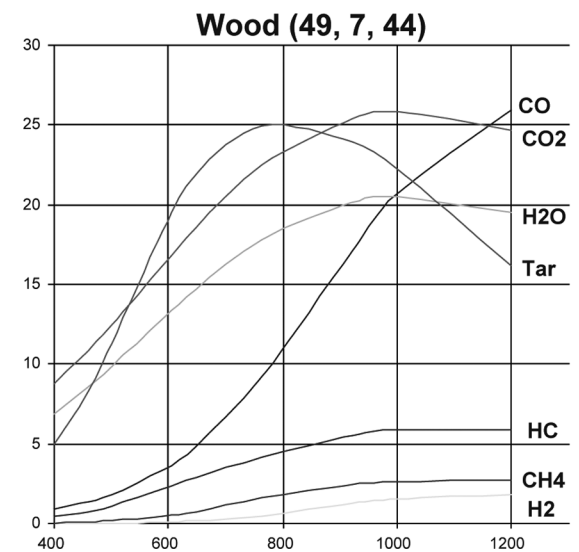
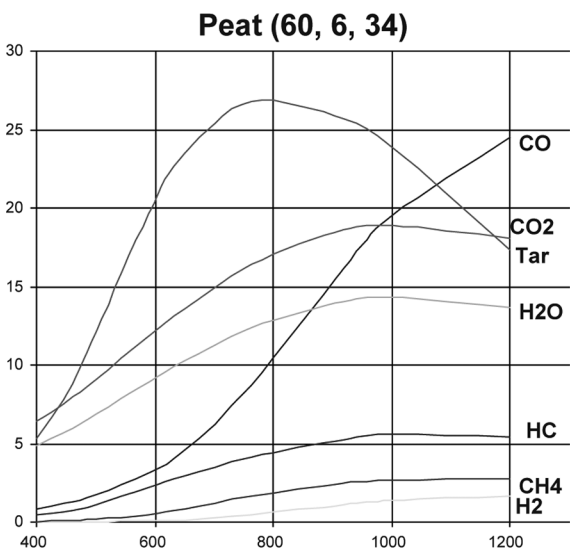
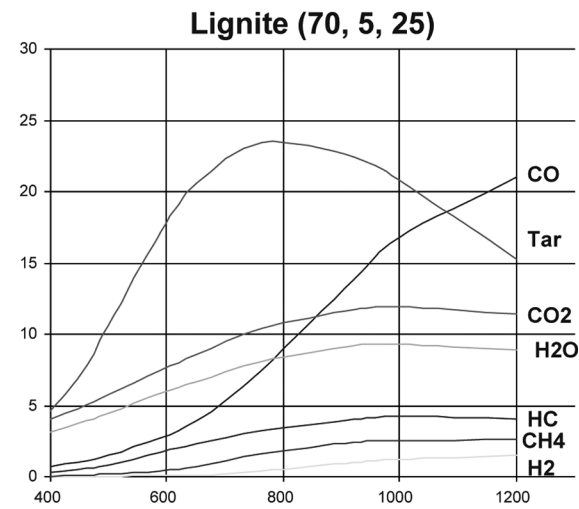
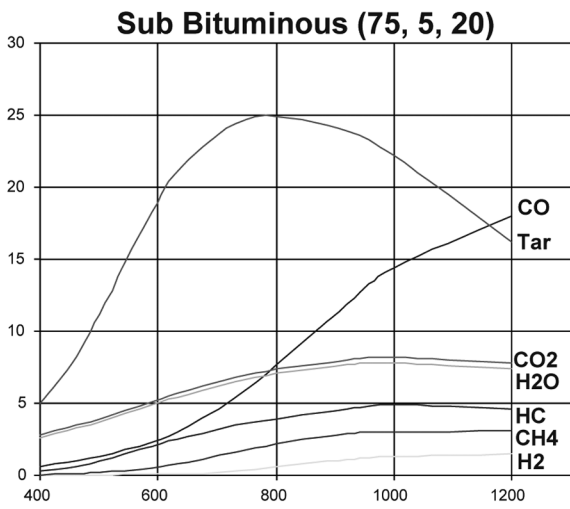
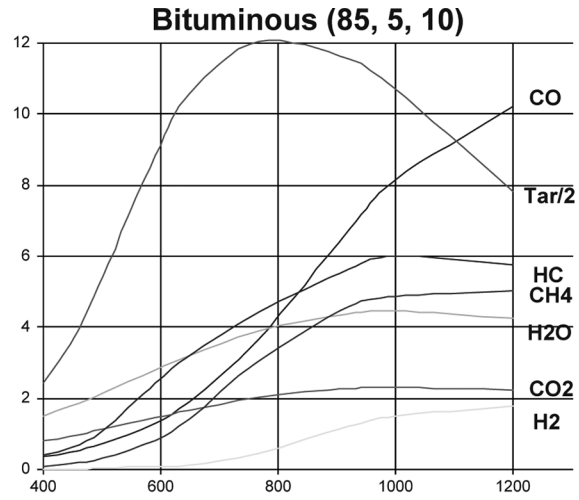
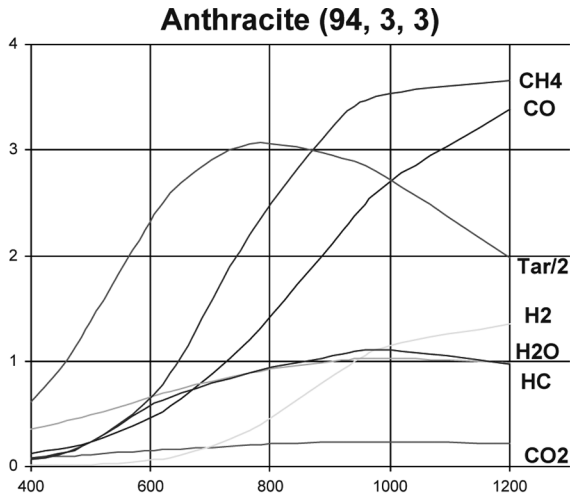


Fig. 5 Weight percent yields (left axis) vs. temperature (in °C, bottom axis) of pyrolysis products of anthracite, bituminous coal, subbituminous coal, lignite, peat, and wood of ([C], [H], [O]) composition as shown. HC represents C2 and C3 gasses and aromatics. **Source:** From Pyrolysis in Waste to Energy Conversion (WEC).^[10]

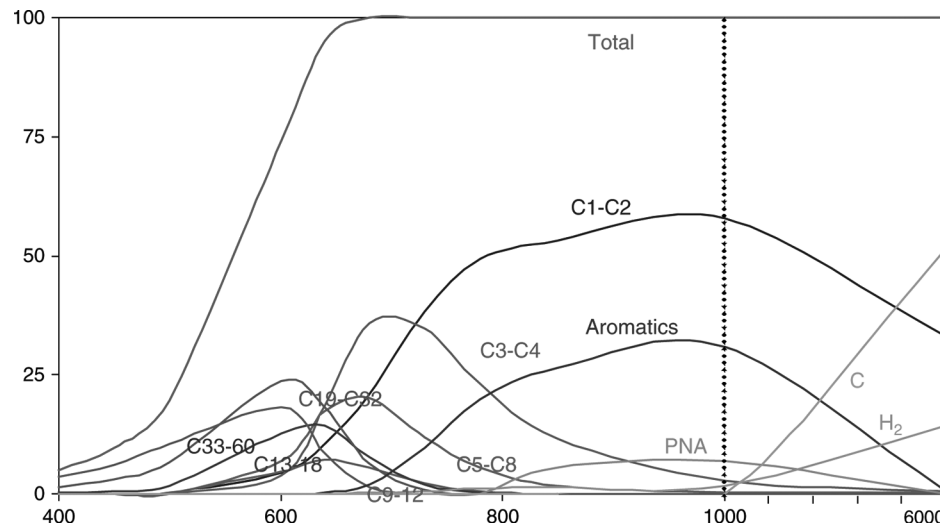


Fig. 6 Weight percent yields (left axis) vs. temperature (in °C, bottom axis) of pyrolysis products of polyethylene in various hydrocarbon groups.

Source: From Analytical representations of experimental polyethylene pyrolysis yields, in *J. Anal. Appl. Pyrolysis*.^[23]

constrained in detail to conform to mass, [C], and [H] balances. Fig. 6 also shows extrapolations to 6000°C that might be of interest if one goes to very high temperatures, for example, by plasma torch heating. Here we incorporate a conjecture that at the highest temperatures H₂ and C emerge among the products at the expense of the C1-C2 compounds as well as Ar and PNA components. While we have already found that an ASEM can begin to bring some order into pyrolysis yields, clearly there is a long way to go. When the time dimension is important, the overall search is for a reasonable function of seven variables [H], [O], a , b , c , T , and t . In comparison, Einstein's special theory of relativity only dealt with four variables x , y , z , and t .

ANALYTICAL COST ESTIMATION AND SW-IGCC VS. NGCC

Before World War II (WWII) almost every town had its own gas works, mainly using coal as a feedstock. After WWII, cheap natural gas became available and became a major PES for home heating and cooking as well as for industrial purposes. In the 1980s, factory-produced natural gas combined cycle (NGCC) systems became available and natural gas became a base load fuel source for many electric utilities hastening the drawdown of U.S. domestic supplies. In the last 4 years, natural gas prices have risen to some 3–10 times greater than they were when most of these NGCC facilities were built. Thus, pursuing SWEATT has become very timely. For most biomass and plastic feedstock, pyrolysis is substantially equivalent to gasification.

Most comparative economic analyses use detailed life cycle analysis (LCA) or other forms of cost–benefit (C/B) approaches. However, it must be recognized that in recent

years fuel costs, an important component of LCA, or C/B approaches have become so volatile that long-term projections based on assumed fuel cost can be grossly inaccurate. Fortunately, the economic feasibility of using a gasifier in front of a gas-fired system can be examined with simple arithmetic and algebra using an analytical cost estimation (ACE) method.^[8–10] ACE takes advantage of the almost linear relationship between the cost of electricity (COE = Y) vs. cost of fuel (COF = X) observed in utility practice and in many LCA for many technologies, i.e.,

$$Y(X) = K + SX \quad (6)$$

In Eq. 6, Y is in ct/kWh (cents per kilowatt hour), X is in \$/MMBtu, and S is the slope of the $Y(X)$ line in ct/kWh/\$/MMBtu or 10,000 Btu/kWh. S relates to the net plant heat rate (NPHR, see Chapter 37 in^[31]) via

$$S = \frac{\text{NPHR}}{10,000} \text{ or efficiency via } S = \frac{34.12}{\text{Eff}} \quad (7)$$

A slope $S_{\text{ng}} = 0.7$ is now a reasonable assignment for a NGCC system reflecting the high efficiency of recent gas and steam turbines.

In Eq. 6 the parameter K is obviously the COE if the fuel comes to the utility without cost (i.e., $X = 0$). In previous studies,^[8–10] $K_{\text{ng}} = 2$ was used as a reasonable zero fuel cost parameter for a 100-MW NGCC system.^[32,33] This low number reflects the low capital costs of factory-produced gas and steam turbines in NGCC systems. In addition the contribution to the intercept K from operations and maintenance costs are reasonable. The K_{sw} for a solid waste-integrated gasification-combined cycle (SW-IGCC) system is higher than K_{ng} because the capital costs and

operating cost must include the gasifier and gas cleanup system. The value of S_{sw} is also higher than S_{ng} because we must first make a SES producer gas, syngas, or pyrogas which involves conversion losses. A study of the literature^[33–37] suggests that $S_{sw} = 1$ is a reasonable estimated slope for a SW-IGCC system. The X_{sw} for a SW-IPGCC system that would compete with a NGCC system at various X_{ng} thus must satisfy

$$K_{sw} + X_{sw}S_{sw} = K_{ng} + X_{ng}S_{ng} \quad (8)$$

It follows that the solid waste fuel cost X_{sw} that would enable a SWCC system to deliver electricity at the same cost as a NGCC system paying X_{ng} is given by

$$X_{sw} = \frac{K_{ng} - K_{sw}}{S_{sw}} + X_{ng} \left(\frac{S_{ng}}{S_{sw}} \right) \quad (9)$$

In the following, all X numbers are in \$/MMBtu and all Y and K numbers are in ct/kWh. Let us use Eq. 9 with $K_{ng} = 2$, $S_{ng} = 0.7$, $S_{sw} = 1$, and $K_{sw} = 4$ as reasonable estimates based on several SWCC analyses.^[6–10] Then the first term in Eq. 9 is -2 . Now when the $X_{ng} = 2$ to generate SWCC electricity at the same cost the solid waste provider must deliver the fuel at a negative price, i.e., pay the tipping fee of -0.7 . However, if X_{ng} is near 6 as it has been several times between 2004 and 2010 the SWCC utility could pay up to 2.4 for the SW fuel. If the X_{ng} is at 12, the SWCC facility could pay 7.1 to the SW supplier. This X_{sw} price is much higher than that of coal whose delivered price (X_c) these days usually is in the 2 range. It is also much higher than a pulp and paper mill would pay for waste wood. This simple cost comparison is illustrated in Fig. 7 that shows

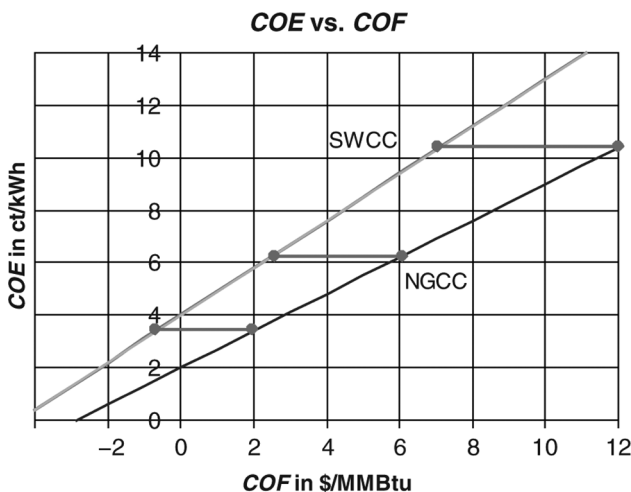


Fig. 7 Cost of electricity (COE) vs. the cost of fuel (COF) for an integrated pyrolyzer combined cycle (IPCC) and for a natural gas combined cycle (NGCC) system. COF comparisons of 2, 6, 12 \$/ MMBtu are indicated in red lines.

Source: From Pyrolysis in Waste to Energy Conversion (WEC).^[10]

the opportunities for SWCC systems when natural gas prices are above say \$5/MMBtu. The results are slightly less favorable if the K_{sw} were higher say at $K = 5$. However, the conclusions that at high natural gas prices SWCC electricity becomes competitive with NGCC electricity would be similar. It is conceivable that K_{sw} could be held as low as 2 ct/kWh by retrofitting a NGCC system stranded by high natural gas prices. In this case the first term in Eq. 9 vanishes and the competitive $K_{sw} = (S_{ng}/S_{sw})X_{ng}$. This illustrates the main point that at high natural gas prices, with an ATT system, SW can be a valuable PES. Indeed, this simple algebraic–arithmetic exercise establishes the feasibility of a new paradigm in which solid waste (mostly biomass) can become potentially valuable marketable assets.

As described above, the values of K and S are the key factors in determining the COF_{sw} that can be used in a SW-integrated pyrolysis combine cycle (IPCC) to have the COE equal or less than the COE with a NGCC system at the available COF_{ng} . The ACE method can be extended to the use of SW or biomass with other technologies if we can identify the K and S for each technology. Where actual facilities have been built and placed in operation, the K s and S s can be assigned on the basis of actual plant experience which is the case for many fossil fuel technologies. However, for new technologies proposed for the renewable age, some accepted form of C/B analysis is needed to provide COE vs. COF relationships. The ACE method cannot serve in this role. However, if a detailed C/B analysis or LCA is available at a particular power level, its $Y(X)$ results can generally be cast into the Eq. 6 form which is generally more useful and transparent than tables of numbers. A major advantage of doing so is the possibility of then making reasonable $Y(X,P)$ extrapolation to other power levels (P) on the basis of many years of economy of scale experience with a wide range of technologies.

The ACE method has been applied to reformulations of a large body of COE vs. COF calculations on biomass use presented in an Antares Group Inc. report (AGIR)^[34] for a number of technologies. The technologies investigated in the AGIR were for systems in which 100 tons per day forest thinning were available in wild land–urban interface areas. This assumption limited the power level (P) for that technology quite severely. The technologies in the AGIR included a biomass-integrated gasifier combined cycle (B-IGCC) system, a B-IG simple cycle (B-IGSC) system, a B-IG internal combustion (B-IGIC) system, a biomass–gasification–coal co-firing B-IGCC system, a direct co-firing of biomass and coal in a coal-steam boiler BCoSt, a direct use of biomass in a feed water heat recovery arrangement (FWHR), direct use of biomass in a Stoker fire boiler steam turbine (SFST) system, and direct firing in a CHP plant (CHP) with a steam market at \$6/MMBtu. For each technology, it was possible to approximately represent the tabulated COE vs. COF results of their detailed economic analysis by Eq. 6 and to evaluate K and S for that technology at that power level.

The most interesting result of this ACE digest of the massive tables of the AGIR was that by slight extrapolations to higher power levels.^[9] The competitive results in several important cases were opposite to those for the power levels limited by the 100 tons biomass per day assumption.

Several other detailed economic COE vs. COF analyses have been used to refine ACE and generalize the ACE methodology. In particular, K has been broken into components $K = K_c + K_{om} + K_{en}$, where c stands for capital costs, om for operating and maintenance costs, and en for environmental costs. Establishing the magnitudes of these components for various technologies and power levels is still at the cutting edge of utility economic analyses, and there are large disagreements particularly on K_{en} . In one generalized component form of ACE (CACE) Eq. 6 is replaced by

$$Y(X, P) = K_{cr} \left(\frac{P_r}{P} \right)^\alpha + K_{omr} \left(\frac{P_r}{P} \right)^\beta + K_{er} \left(\frac{P_r}{P} \right)^\gamma + X S_r \left(\frac{P_r}{P} \right)^\delta \quad (10)$$

where K_{cr} , K_{omr} , K_{er} , and S_r are established on the basis of a detailed analysis at a reference power level P_r and α , β , and γ are scaling parameters intended to reflect the tendency of per energy unit cost to go down as the power goes up (economy of scale). Table 5 lists CACE parameters extracted from a detailed analysis "Options for Meeting the Electrical Supply Needs of Gainesville" prepared by ICF Consulting.^[35] Here the final COE is given in 2003 ct/kWh. The third and fourth cases NGCCc have been added to better reflect the high volatility of natural gas prices that have ranged from \$1/MMBtu to \$16/MMBtu over the past 25 years.

The final column shows that at the reference power levels without the NGCCc case the IGCC scores the lowest COE as was concluded in the ICF report (ICFR). The value of the ACE analysis is that with a bit of algebra anyone can easily consider other fuel cost projections and other power levels (with the assigned values of α , β , γ and δ). Based

on prior exploratory work and economy of scale investigations it was estimated that for costly field erected facilities $\alpha = \beta = 0.3$ are reasonable choices. However, with factory fabrication of gas and steam turbines these parameters might not follow the usual economy of scale pattern and that their α may be somewhat smaller in magnitude. Assigning a value for γ is a wide open question since environmental costs and methods of incorporating them into the COE are still highly debated issues.^[36] Reasonable values for δ are also somewhat difficult to find. For NGCCs the author tentatively assigns close to zero or a very small value (~ 0.1) perhaps because the development of highly efficient aero-derivative turbines has proceeded on a wide range of power levels.

A somewhat simpler generalized formula for $Y(X, P)$ has been developed in the form^[37]

$$Y(X, P) = \alpha C_{cr} \left\{ \left(\frac{P_r}{P} \right)^\gamma \right\} (1 + f_{om}) + SX(1 + f_e) \quad (11)$$

Here, $\alpha C_{cr} = K_{cr}$ at a reference power level where C_{cr} is the specific capital cost for that facility in \$ per watt (\$/W or \$1000/kW) for that technology at the reference power level. Based on tabular data contained in the RA report a value $\alpha = 1.34$ was identified as the coefficient that approximately relates specific capital costs (in \$/W) to K_{cr} (in ct/kWh). This essentially is the COE when the fuel cost is free and OM can be ignored. As for economies of scale, based on an extensive literature survey, Green et al.^[37] found the different technologies had scaling parameters in the range $0.13 < \gamma < 0.33$. When no information is available one might use some intermediate gamma between these extremes or let $\gamma = 0$.

Typical dimensionless values for f_{om} can be identified for various technologies from the Antares report on 6 technologies, ICFR on 5 technologies, and the RA study of 14 widely ranging technologies. In most cases they are less than unity and can be assigned within reasonable bounds on the basis of experience.

In Eq. 11 f_e is an added dimensionless "correction" to the delivered COF that reflects environmental costs not

Table 5 Analytical cost estimation (ACE) results from ICFR for five technologies. Four natural gas prices are assumed for the NGCC technology.

Technology	P_r	K_o	K_{om}	K_{en}	S_o	COF	COE
NGCC-a	220	0.598	0.234	-0.17	0.68	11.34	8.37
NGCC-b	220	0.598	0.234	-0.17	0.68	6.1	4.81
NGCC-c	220	0.598	0.234	-0.17	0.68	5	4.06
NGCC-d	220	0.598	0.234	-0.17	0.68	4	3.38
SCPC	800	1.491	0.299	0.714	0.93	1.91	4.28
CFB-CB	220	2.531	0.261	0.618	1.05	1.41	4.89
CFB-B	75	2.845	0.261	0.039	1.39	1.67	5.47
IGCC	220	2.2	0.196	0.407	0.86	1.41	4.02

COE = cost of electricity, COF = cost of fuel.

included in the cost charged by the utility but paid for by the public in other ways (reduced visibility, added coughs, higher cancer rates, etc.). The landmark RA^[36] study that incorporated externalities into a levelized cost of energy analysis for 14 electric generating plants provided a basis for estimating the dimensionless externality correction f_e to the price of fuel. Table 6 translates RA's results for the 14 utilities using their minimum externality cost estimates into the generalized analytic cost estimation (GACE) analytical form of Eq. 11. As one sees these f_e are substantially larger than 1 for fossil fuel technologies but small (0.15) for a biomass system. Wind turbines, photo voltaic, and landfill gas systems do not have a fuel cost hence f_e cannot be assigned. However, these technologies are directly assigned externality C_{ex} by RA. The major uncertainty in the future COE is probably represented by the variable X , the externality parameter f_e , and possibly the power level of the facility. Having an explicit formula with these variables and parameters can help in bringing transparency to important policy decisions.

The GACE approach to reaching decisions in the face of large uncertainties might be viewed as application of the operations analysis methods used by one of the authors in WWII.^[38] It will be interesting to compare this approach with recent European Union operations analysis effort for incorporating externalities in electricity-generating technology evaluations.^[39]

Going back to the 2007 SWEATT study it mainly considered the competition between NG-fueled technologies and coal-steam-generated electricity. These included supercritical coal-burning units that reached efficiencies as high as 40%. However, when coal-steam turbine's expensive scrubber costs are included in the K_c and environ-

mental costs in their K_{en} this technology did not compete compared with the IGCC. Thus a major conclusion of the 2007 SWEATT study was that the age of making gas has returned. At the same time the most favorable EEE position of natural gas among the fossil fuels is recognized.

It should be noted that in an effort to minimize a major environmental externality, global warming, the U.S. Department of Energy is now investing a \$4 billion plus effort in carbon capture and storage (CCS) technologies that first starts with oxygen-blown coal gasification. DOE funds will be matched by about \$7 billion from the coal and utility industry. This effort could bring up to ten commercial demonstration projects online by 2016. The goal of the program is to provide the information needed to evaluate whether such CCS technologies are commercially deployable.

Mercury emission control has recently become mandatory for coal fired plants. Injecting activated carbon as a sorbent to capture flue gas mercury has shown the most promise as a near-term mercury control technology. The process is still in its early stages and its effectiveness under varied conditions (e.g., fuel properties, flue gas temperatures, and trace-gas constituents) is still being investigated.

BIOENERGY AND BIOCHAR

During the first decade of the 21st century, the most widely pursued sources of renewable biofuels were fermentation of corn or corn stover leading to ethanol, anaerobic digestion of animal waste yielding methane, and compression of plant seeds to extract bio-oil. Since this Solid Waste to

Table 6 Roth-Amb's Externality impacts on cost of electricity for 14 technologies using low RA estimates, impacts, and derived GACE parameters.

Technology	C/W	K_c	f_{om}	S	C_{of}	C_{ex}	f_e	COE	COE _e
Coal Boiler	1.80	2.81	0.36	0.995	1.06	4.45	4.20	4.86	9.29
Adv Fld Bed	2.20	3.52	0.49	0.975	1.04	2.86	2.75	6.26	9.05
IGCC (coal)	2.10	3.28	0.28	0.889	0.95	2.64	2.78	5.05	7.40
Oil Boiler	1.30	2.15	0.19	0.943	3.22	6.03	1.87	5.59	11.27
Gas Turb SC	0.70	10.1	0.12	1.15	3.47	4.62	1.33	15.28	20.59
Gas T Adv	0.40	0.82	0.51	1.09	3.29	4.45	1.35	4.83	9.68
NGCC	0.60	0.91	0.34	0.683	2.11	3.46	1.64	2.66	5.02
MSW Inc.	5.70	9.63	0.44	1.687	5.16	7.7	1.49	22.55	35.54
LFG	1.50	3.3	0.3	1.215	0	0.7		4.29	5.14
SOFC	1.60	2.42	2.71	0.758	2.29	2.75	1.20	10.71	12.79
Wind Turb	1.00	5.74	0.29	0	0	0.7		7.40	7.40
PV Utility	4.70	49.5	0.02	0	0	0.25		50.53	50.53
Hybred solar	3.70	20.3	0.15	0.346	1.07	2.38	2.22	23.64	24.46
Biomass	2.40	3.54	0.73	1.431	2.75	0.41	0.15	10.07	10.65

COE_e are Roth-Amb's total COE with low externalities.

Energy by Advanced Thermal Technologies (SWEATT) work is focused on advanced thermal technologies (ATTs), we refer the reader to the literature on these non-thermal conversion methods. This section is largely devoted to the economic, environmental, and energy (EEE) impacts on SWEATT that the production of “pyro-char” or “black carbon” may have. These terms can be used to include many solid pyrolysis products that might serve as charcoal, bio-char, or activated carbon. Charcoal and activated carbon are well documented in the technical literature. However, the literature on biochar is just developing. Biochar applications have recently inspired an International Biochar Initiative, a community of scientists and enthusiasts that envision large-scale conversion of waste biomass into bio-char while generating energy at the same time.^[40,41] This biochar can be applied to soils, both enhancing soil fertility and mitigating climate change by sequestering CO₂ drawn from the atmosphere.

Charcoal was used as early as 5000 BCE in the smelting of copper, and 2000 yr later, it became commonplace in the smelting of iron and bronze. Charcoal was burned to produce temperatures in excess of 1000°C that are needed to produce these alloys. Other uses include blacksmith forges and household cooking, in which maximal heat with minimal smoke is desirable, and the filtering and removal of impurities such as in the spirit or sugar processing industries. Charcoal was commonly made in covered conical piles of wood, sometimes covered with earth, constructed so as to exclude air, thus attaining greater yields of charcoal. Its large-scale production is presumed to have led to widespread deforestation of Europe and Eastern North America in the 18th century, until coal supplanted charcoal as an industrial fuel.

In an extensive review, Antal and Gronli^[42] have summarized knowledge of the production and properties of charcoal that has been accumulated over the past 38,000 yr. They point out that biomass carbonization can be carried out, leading to high char yields (~30%) by the manipulation of pressure, moisture content, and gas flow involved in the process. The review also provides a good summary of measurements of the heat of pyrolysis from various plant feedstock that range from +0.7 MJ/kg (exothermic) to -0.3 MJ/kg (endothermic). When viewed in the light of the fact that the higher heating value (HHV) for most DASNFBiomass are about 17 MJ/kg and pure carbon is 32 MJ/kg, it should be clear that, in any case, the heat cost of pyrolysis is small compared to the heat content of the feedstock. However, in various practical biomass pyrolysis arrangements, component system losses need to be kept as small as possible so that acceptable conversion efficiencies from the feedstock to the desired form of energy are achieved.

Conventional combustion technologies, or even advanced combustion systems, when applied to biomass/solid waste (SW), leave little carbon in the fly or bottom ash. Thus, it might be difficult to adapt these technologies to the useful production of pyro-char products. Air-blown

partial combustion and oxygen-blown partial combustion systems might be adapted since they essentially take advantage of substoichiometric combustion to produce CO fuel rather than CO₂ and, depending upon the oxygen content of the feedstock, could leave a substantial carbon residue. The solid char residues produced during forest fires is an example of natural combustion under limited oxygen conditions. The charred woods and plastics remaining after building fires are further examples of limited oxygen combustion. An extensive technical literature is available on Fire and Fire Protection technology that could be drawn upon if carbonization again becomes a widespread technology. Pyro-char or black carbon, when produced intentionally in partial combustion gasifiers or more efficiently in indirectly heated pyrolyzers, is now being referred to as “biochar.” Some uses of biochar are quite ancient, while others are quite recent.^[40-47]

It is only fairly recently that another ancient use of biochar has come to the wider attention of environmental scientists. *Terra preta* are small plots (20 ha, on average) of highly fertile Amazonian soils, enriched in organic carbon and nutrients, that are surrounded by Oxisols, typical of tropical soils, that are extremely depleted in nutrients and organic matter. Because *terra preta* are associated with high concentrations of charcoal and ceramic fragments, and can be dated to have formed between 800 BCE and 500 ACE, they are presumed to be anthropogenic, made either intentionally by some method of slash and char forestry for agricultural purposes or accidentally through the dumping of kitchen fire wastes over long time periods.^[41] This discovery has inspired the current “biochar movement” and interest in identifying optimum methods of producing and using biochar. It is recognized that the optimum characteristics of biochar are still uncertain and are the subject of research.

The unique properties of some biochar, particularly its high adsorption capacity, can be attributed to its high surface-specific surface area (SA) as well as its surficial functional group content. Although charcoal can be “activated,” that is, altered with physical or chemical treatment or by “carbonization,” heating above 800°C, to produce extremely high SAs or oxidized surfaces, even non-activated biochars can possess some of these features. Biochar SA tends to increase with pyrolysis temperature but starting biomass type and pyrolysis atmosphere and duration of heating will also play a role. For example, Zimmerman^[48] has reported N₂-BET SA of less than 13 m²/g for a variety of biomass types pyrolyzed at 400°C (3 hr), including grasses as well as softwoods and hardwoods. At 525°C, SA ranged from 31 to 501 m²/g, and at 650°C, 220–550 m²/g. Between 800°C and 1000°C, SA of between 400 and 1000 m²/g are commonly recorded by Downie et al.^[44] These measurements, however, include only pores larger than a few nanometers (nm) in diameter. Surface present within micropores (pores smaller than about 1.5 nm in diameter), measured using CO₂ sorptometry, have yielded SA in the

Q1

range of 160 to 650 m²/g and have been found to be more strongly related to the ability of a biochar to sorb low molecular weight organic compounds and cations.^[49,50]

One can envision a number of possible ways in which the sorbent properties of biochar could be utilized. First, much as activated carbons have been used for many centuries in a wide variety of industrial process that require the adsorption of noxious, odorous, or colored substances from gases or liquids, biochar could be used as a low-cost alternative, especially in circumstances where large volumes of material are required. Much like activated carbon,^[51] biochar can be powdered to increase SA or granulated for use in fixed bed filtration systems. Although somewhat lower in SA and, thus, sorption capacity compared to activated carbons, its characteristics can be tuned via production conditions, for sorption of specific components. For example, biochar made from anaerobically digested bagasse has been shown to be a superior sorbent metal including of lead.^[52] Its most cost-effective industrial use is likely to be in the areas of primary or secondary water treatment or in contaminant remediation as reactive media for surficial or subsurface permeable barriers such as trenches, wall barriers, funnels and gates, or landfill bottom linings. In all these cases, both the biochar C and the adsorbed C may be sequestered from the atmosphere and, thus, may be considered an additional C sink, or at least an avoided C source.

Q2
Q3 With new EPA (Environmental Protection Agency) limitations on mercury emissions from coal plants and municipal waste incinerators, one might anticipate a large market increase for mercury-adsorbing activated or non-activated carbons.

Much as black-carbon-enriched soil such as *terra preta* in the Amazon has been prized for centuries for its ability to produce sustained enhanced crop yields, it is presumed that biochar amendments to soil, if carried out properly, can increase soil fertility in both the United States and perhaps more critically in the third world where soil depletion is reaching critical levels. Some biochars have high cation exchange capacity, lending it the ability to adsorb and retain such essential plant nutrients as nitrate, ammonium, calcium, and potassium.^[43,46] Biochars have also been shown to adsorb the critical anionic nutrient phosphate, though the chemical mechanism for this is unclear. Other positive agricultural effects may include better soil moisture retention and the encouragement of unique microbial populations that may be beneficial to plant growth.^[53] Thus, while not yet shown on a large-scale basis, biochars amendment may reduce a farmer's costs for fertilizer and irrigation, while reducing runoff of environmentally damaging nutrients into surrounding surface waters and groundwaters (cultural eutrophication) and reliance on inorganic fertilizers made using energy from fossil fuels (another CO₂ source).

A recent life-cycle assessment (LCA) study assessed the energy and carbon impacts of four biochar-cropping systems.^[47] They found that, for late and early corn stover,

switch grass, and yard waste as biomass feedstock sources, the net energy generated was +4116, +3044, +4899, and +4043 MJ t⁻¹ dry feedstock, respectively. Most of the energy consumed was in either agrochemicals or feedstock drying, and most of the energy yield was in syngas heat. Net greenhouse gas emissions were negative for both stover types and yard waste, with the majority of the total reductions, 62–66%, realized from C sequestration by the biochar. For switch grass, however, land use change and field emissions were high enough to drive net emissions to positive. The main conclusion of this LCA analysis was that the energy and carbon impact of small-scale use of pyrolysis systems using yard waste is the most economically favorable at this time. However, many numbers used in these calculations were, by necessity, broad estimates. Much more research is required to improve the inputs to these types of models.

Because of biochar's environmental stability, conversion of biomass to biochar represents a long-term transfer from a C pool rapidly cycling between biomass and the atmosphere to a pool held sequestered within soils or even aquatic sediments. Conversion of 1% of all biomass to biochar each year could reduce the atmosphere CO₂ by 10% in only 14 yr (assuming 50% conversion efficiency and no biochar C degradation). These figures are certain not realistic, however. First, it has been shown that biochars degrade abiotically as well as microbially at rates ranging from C half-lives of a few 100 yr (for lower-temperature chars, particularly those made from grasses) to 10⁵ yr for higher-temperature chars with additional losses to be expected from leaching. Second, the amount of biomass that could be reasonably used as feedstock without using major quantities of fossil fuels in the process of gathering and transportation, and without endangering soil stocks, habitat, or human food resource security (i.e., without land-use conversion), is likely in the range of 2.27 Pg C yr⁻¹.^[55] Aside from C sequestration and enhanced crop growth, further reduction in greenhouse gas concentration and associated climate change may be obtained via reductions in methane (CH₄) production associated with waste land filling and suppression of nitrous oxide (N₂O) production when biochar is added to soils^[43,46] and energy extraction. Using this estimate of maximum sustainable feedstock generation and accounting for all possible benefits, biochar production could potentially offset a maximum of 12% of current anthropogenic CO₂-C equivalent emissions each year.^[54] Another interesting finding of this study was that the greatest environmental benefits are to be had by the biochar approach in regions of infertile soils or where water resources are scarce. However, where soils are already fertile, and particularly in regions where coal emissions can be offset, bioenergy (see next section) may be a better approach.

It is hoped that production of biochars or application of biochar to soils may soon qualify as a "carbon offset" or be traded on the open market should a "C cap and trade"

policy be implemented. The biochar concept has received formal political support in the U.S. and globally. The U.S. 2008 Farm Bill established the first federal-level policy in support of biochar production and utilization programs nationally and biochar has been included in the United Nations Framework Convention on Climate Change (UNFCCC in Dec. 2009).

BIO-LIQUID FUELS

Intensive use of liquid petroleum products, particularly diesel and gasoline, by automobiles, trucks, airplanes, trains, and ships in the 20th century drew down national and global reserves to the point that energy security has become a major concern of the United States, other industrial countries, and the globe in general. During this same period, CO₂, the major product of hydrocarbon combustion, has further increased from its preindustrial level of 280 ppm to its current level of 385 ppm. Global warming is now emerging as the biggest environmental problem of the 21st century and “What to do about CO₂” is the biggest environmental question.^[56–59]

Producing liquid fuels from plants could potentially mitigate both security and environmental problems in countries that have land available that is not in food production. Plants use the sun’s energy, the atmosphere’s CO₂, and the soil’s H₂O to make carbohydrates such as cellulosic matter and lignin. When biomass, or a converted form of it, is combusted (oxidized), the CO₂ is returned to the atmosphere as a part of a short-term cycle that can be considered *carbon neutral*. On the other hand, combustion of coal and petroleum fossil fuels adds CO₂ that had been extracted by plants from ancient atmospheres to today’s atmosphere.

In contrast to solid and gaseous fuels, the convenience of energy storage and transfer makes liquid fuels much more useful in the transportation sector. Because ethanol, pyrolysis oil, vegetable oil, and biodiesel are biomass-derived liquid fuels that are closer to carbon neutral, they are now under rapidly increasing consideration as replacements of or supplements to conventional diesel and gasoline. The high energy value of liquid fuels is illustrated in Table 2. Table 7 lists typical properties of these liquid fuels.

Technologies to convert plant simple sugars to ethanol go back to the beginnings of the wine, beer, and liquor

industries thousands of years ago. In recent years, genetic manipulation^[60] has led to microbes that can convert cellulose to ethanol as well. We refer the reader to the extensive biochemical literature for such recent developments. As compared to ethanol, the oils listed in Table 7 have about twice the energy per unit volume, an important consideration in transportation applications, particularly aeronautical.

The properties of pyrolysis oils vary over wide ranges depending upon the feedstock, the rate of heating, the temperature reached, catalysts used if any, the speed of quenching after the polymeric bonds are broken, and other specifics of the thermal processing. Fluidized bed systems with fast heat transfer followed by rapid quenching produce bio-oil yields ranging from 50% to 75% of feedstock weight, with pyro-gas and pyro-char representing most of the remainder material. Extensive R&D efforts are now underway to upgrade pyro-oils into more energy dense, water-free, and oxygen-reduced liquid fuels.^[61]

Since the 1973 oil embargo, vegetable oils such as corn, soybean, canola, rapeseed, sunflower, palm, and coconut have been given serious consideration for liquid fuels.^[62] In effect, this would be a return to what Rudolf Diesel used with his first compression ignition engine (CIE). Used vegetable oil from fast-food restaurants has become a favorite inexpensive source of such feedstock. The high viscosity of most vegetable oils presents CIE problems, but these problems can be overcome by suitable preheaters. Since the supply of used vegetable oil is limited, there has been rising interest in high-yield, non-food vegetable oils, such as *Jatropha*, *Camelina*, flax, and algae that can be grown on marginal lands.

The trend in bio-oil production is now towards converting vegetable oil to low-viscosity biodiesel by mixing it with an alcohol and a catalyst. In this esterification process, the oil’s glycerin is replaced by the alcohol, making a mono-alkyl ester, which greatly reduces the viscosity and slightly increases the HHV. Biodiesel can be used in unmodified diesel engines as a sole fuel or in mixtures with diesel. Emissions of sulfur oxides and other regulated pollutants, apart from NO_x, are generally lower from biodiesel than from conventional diesel. Since biodiesel is derived from plants that were made with solar energy, it is considered approximately carbon neutral.

Several states are initiating non-food vegetable oil programs to meet transportation needs beginning with the fuel

Table 7 Some key properties of biomass-derived liquid fuels and diesel.

Fuel	C (wt%)	H (wt%)	O (wt%)	HV (MJ/kg)	Density (kg/m ³)	E/vol (GJ/m ³)	Visc. cs
Ethanol	52.2	13.0	34.8	22.6	790	17.9	1.1
Pyro-oil	~38	~8	~49	~35	1050	~36.7	var.
Vegetable oil	74.5	10.6	10.8	40.4	906	36.6	46.7
Biodiesel	79.0	12.9	8.0	41.2	920	37.9	4.7
Diesel	87	13	0	45.3	852	38.6	3.2

needs of agriculture and particularly the needs of the individual farmer. In the Pacific Northwest, canola (rapeseed) has^[63] and is being studied but not yet adopted on a large scale because revenues from growing canola are generally somewhat lower than that from wheat. The differential is currently being subsidized in the form of a Federal blender's credit of \$1.00 per gallon to jump-start this new industry.

In Texas, flax, an annual plant and prolific biomass producer, is now under consideration as a source of vegetable oil for transportation applications. Flaxseed has long been used as the source of linseed oil, which is used as a component of many wood-finishing and other industrial products and as a nutritional supplement. In a description of recent developments by a Texas A&M researcher,^[64] "It's kind of like [Texas] is coming full circle. Flax was grown on about 400,000 acres in the 1950s and Texas AgriLife Research at A&M had an active flax breeding program." "Those varieties were known nationwide for having good cold tolerance. That's what we needed, a flax variety that was something you could plant in the fall, survive the winter, avoid late freezes, and produce seed in the spring. Now we're evaluating this as a possible biodiesel product or (one which) could be used in the vegetable oil industry."^[64]

Florida is developing a bio-oil production program utilizing *Camelina sativa* planted on non-food-producing land.^[65] When *Camelina* seed is cold pressed, 30% (by weight) oil is obtainable. The resulting pressed cake called meal has oil content between 10% and 12% (by weight) that can also be extracted with organic solvents, but this process is expensive. For biodiesel production to be economically competitive, it is essential to minimize production costs and maximize all potential revenue streams. The use of the meal as animal feed is one such stream. However, if non-food vegetable oil ever reaches its full transportation potential, the seed meal and plant residue would far exceed what could be consumed by existing cattle herds. With current budget deficits, the prospects for adequate subsidies in the future are not favorable. Thus, additional services or commodities must be developed to generate additional revenues.

In the spirit of this overall study of SWEATT, the use of on-site SWEATT systems to extract additional liquid fuel, energy, biochar, and specialty chemicals from the waste generated in a farmer's overall bio-oil production cycle warrants careful consideration. The meal produced by pressing the canola, flax, or *Camelina* seed and the plant stover could be dried and continuously fed into an on-site pyrolyzer yielding thermal energy, pyro-oil, biochar, and possibly activated carbon or other valuable products. The biochar then could be used together with local biosolids such as wastewater in sewage sludge to restore or improve the farmer's soil. The pyro-oil could be collected and distilled off-site into additional transportation fuel and chemicals.^[61] The thermal energy can be used on-site for heating, drying, hot water, and steam and other farm ap-

plications. Along with biochar and a productive outlet for sewage sludge (sometimes called biosolids) and its otherwise unusable water, such a comprehensive strategic program could provide cost-competitive renewable liquid fuel alternatives to diesel from imported petroleum.

The production of biodiesel in the United States increased from 75 million gallons in 2005 to 250 million gallons in 2006 and 450 million gallons in 2007, with an expected capacity of well over 1000 million gallons in the next few years.^[66] This is still a small rate compared to over 60,000 million gallons of petroleum-based diesel consumed in the United States in 2009.

Sewage sludge represents a potentially large source of the fatty acids and biodiesel. After completion of the treatment cycle inside a sewage plant, these biosolids can be chemically processed to extract a biodiesel.^[66,67] The waste residual solid and liquid can still serve for soil fertility enhancement thanks to its nitrogen, phosphate, and other mineral components.

The displacement of petroleum diesel can be further hastened and increased substantially with rendered animal fats, using thermal animal fat rendering technology, advanced greatly in 1811 by the French chemist Chevallot. This technology has been further advanced by recent research and development.^[68,69]

RECYCLING AND SWEATT

Waste to energy is viewed by some groups as a threat to recycling, but the opposite is more likely the case. Municipal or institutional recycling programs in which the household sorts the SW for collective pickup can actually help maximize the return on waste components and minimize environmental problems. For example, if, at a given time, waste newspaper has no recycling value but, instead represents a disposal cost, preprocessing it for use as dry high-energy feedstock for SWEATT systems could be the optimum response. In effect, the marketplace could decide whether to recycle via the material recovery route or via an energy or fuel recovery route. Separation at the source generally requires simpler, less expensive preprocessing technologies than if all the waste sorting was carried out at the SWEATT plant. Sorting at the source also lends itself to a front-end pollution prevention program in which problem materials are separated and directed to hazardous waste facilities.^[70]

Recycling with sorting at the source also facilitates application of beneficial feedstock-blending strategies. The analytical semi-empirical model (ASEM) study shows that polyethylene can serve as a rich source of energetic hydrogenic compounds. Thus, blending this plastic with biomass in a SWEATT pyrolysis system is expected to yield more energetic pyro-gas or pyro-liquid fuels and higher heat outputs than simple biomass. This has been demonstrated in high-temperature (1000°C) intermediate (between slow

and fast) pyrolysis processing of Meals Ready to Eat (MRE) waste in which the heating value of the pyro-gas measured about 900 Btu/ft³, quite close to the 980 Btu/ft³ of natural gas. Food waste pyrolysis generally is expected to yield a low HHV pyro-gas (<150 Btu/ft³). The high HHV of MRE pyrolysis is due to the large percentage of the ethylene monomer (C₂H₄) contributed by polyethylene plastic packaging. Plastics are used extensively in modern agriculture^[71] and, after a growing season, present either a disposal problem or a good SWEATT feedstock blending opportunity. Alternatively, since plastics melt at relatively low temperatures, a sorting–recycling program together with very low temperature pyrolysis can relatively easily restore hydrocarbon plastics to liquid fuel forms.^[72]

A Biomass Alliance with Natural Gas is a promising fuel blending strategy. Partial combustion gasifiers using biomass feedstock produce a low heating gas (~150 Btu/ft³) that will result in de-rating a natural gas-designed turbine-generator system. Coupling the biomass pyro-gas with natural gas can insure that the input energy requirement matches the output needs at least until the maximum rating of the generator is required. In a SW/biomass alliance with natural gas, an additional option becomes available when the SW comes from a recycling community. Then, the utility as a means of getting a richer gas to follow peak loads without calling upon the full use of natural gas might prepare and store high-energy plastics for increased use during times of high electricity demand. Another type of course strategy might be profitable if natural gas prices remain low (~\$4/MMBtu) as they were at the end of 2010 but biodiesel is high (~\$35/MMBtu). Then, the SWEATT system should be configured and operated and use the pyro gas yield supplemented by cheap natural gas to maximize the most valued pyro-liquid and pyro-chemical yields.^[73] Many other opportunities for efficient use of domestic resources are described in the Proceedings of an International Conference on Co-utilization of Domestic Fuels.

SWEATT: SUMMARY AND CONCLUSIONS

The acronym SWEATT was inspired by the senior author (A.G.) recollection of Winston Churchill's historic call to arms in the darkest hours of World War II while admitting "I have nothing to offer but blood, toil, tears, and sweat." Today, the energy, environmental, economic, and security (EEES) problems of many nations are such as to bring to mind the problems of the World War II era and the need for bold imaginative solutions. The sustainable supplies of now wasted solids particularly in the United States that have an annual energy potential comparable to the total primary energy supply (TPES) contributed by coal as well as the TPES contributed by natural gas is a resource that should be a component of these solutions. Converting this SWEATT could multiply its current contribution to the U.S. TPES by a factor of about 10.

With low-energy density feedstock, minimizing transportation costs is very important. Thus, in addition to robust thermal technologies that can handle municipal solid waste (MSW), small on-site SWEATT systems have a particularly important role to play. Such systems should soon be available to harvest the energy and valuable chemicals in many of the SW categories listed in Table 1, most of which are greenhouse gas neutral and could gainfully be processed on-site, Table 1 does not list oil shale or tar sands in the United States that could substantially increase the available "solid waste" tonnage to address the U.S. need for liquid transportation fuels. A 2005 Rand study^[74] shows that with in situ thermal treatment, that is, essentially low-temperature pyrolysis, domestic oil shale could be used to extract oils to substantially lower the United States's oil import problem; unfortunately, as a fossil fuel, it does not mitigate the global CO₂ problem.

Marginal agricultural lands not in food production that could grow hardy, high-yield, fast-growing vegetable oil crops or can be improved to do so represent another form of waste that is gaining attention to solve energy security and climate change problems and particularly the need for biodiesel. Demonstration programs to date look favorable but the biodiesel price comes out higher than conventional diesel (see Table 2). Thus, it is important in such operations to generate additional revenue streams or to lower the costs of production. On-site SWEATT systems that convert the pressed seeds (meal) and plant residual (stover) into valuable pyro-oil, biochar, and thermal energy and reduce waste disposal costs could potentially make biodiesels more price competitive with diesel distilled from petroleum. It must be recognized, however, that imported petroleum is priced by cartels rather than a free market. Hence, countries poorly endowed with petroleum resources should not abandon biodiesel RD&D efforts or subsidies whenever this cartel to regain market share drastically lowers its price as in 1986.

Japan, a country with an outstanding sustainability record, has established the technical and environmental feasibility of large-scale conversion of SW to energy with thermal pyrolysis and gasification systems.^[75] This should allay the concerns of environmentalists and risk-averse utility decision makers in other countries. A recent comprehensive report on the environmental performance of thermal conversion technologies throughout the world^[76] identified more than 100 facilities that are using conversion technologies to convert MSW (mainly biomass) for energy production. The study used independently validated emissions data from operating facilities in five nations and found that pyrolysis and gasification facilities currently operating throughout the world with waste feedstocks meet each of their air quality emission limits. With few exceptions, most meet all of the current emission limits mandated in California, the United States, the European Union, and Japan. In the case of toxic air contaminants (dioxins/furans and mercury), every process evaluated met

the most stringent emission standards worldwide. Facilities with advanced environmental controls are very likely to meet regulatory requirements in California. Thus, the report concludes that thermochemical conversion technologies possess unique characteristics that as a part of an integrated waste management system can generate useful energy and substantially reduce the amount of material that must be landfilled.

Finally, the following are our main conclusions:

The United States and most industrial nations are excessively reliant on imported oil for their liquid fuels and imported natural gas for their gaseous fuels.

The United States is well endowed with solid coal and oil shale, which can be converted into useful liquid and gaseous fuels by ATTs to mitigate its energy security problem, albeit not its problem of excessive CO₂ emissions.

The United States is also well endowed (~2 billion dry tons) with many forms of carbon-neutral forms of SW that can be converted to natural gas supplements, bio-liquid fuels, thermal energy, and pyro-char by on-site SWEATT systems.

ATTs are the fastest and most efficient SW to energy conversion methods. The high volatile content of biomass makes high-temperature pyrolysis of the biomass component of SW a direct form of gasification.

- If environmental and security externalities are included, renewable energy often compete with fossil fuel energy.

Approximate analytic representations of cost of electricity vs. the important controlling variables can be helpful in making SWEATT policy decisions in the face of highly volatile natural gas prices and uncertainties as to values assigned to externalities.

- Cause of volatiles from the pyrolysis of SW with natural gas can be useful in overcoming a number of EEE problems.

SWEATT generally results in lower harmful emissions than traditional high-temperature waste to energy systems (incinerators).

- Given a free biomass source such as SW, SWEATT becomes cost competitive with NGCC energy production systems when NG fuel prices are above about \$4/MMBtu.
- Blending feedstock and including inexpensive catalysts can enhance production of energy and high-valued products.

Many areas of engineering research will be needed to optimize SWEATT systems.

The solid residuals of SWEATT, biochar, have potential value as soil amendments to boost fertility and as industrial and environmental adsorbents.

- The biochar dimension offers promise of achieving systems with carbon negativity. Thus, the economic profitability of pyrolysis SWEATT systems could be hastened if and when “C credits” or “C trading” becomes available.^[40,41]
- Optimizing the production of pyro-char products and its characteristics for specific needs could enhance the economic and environmental benefits of SWEATT systems without greatly reducing its energy benefits.
- SWEATT can be used in parallel with other fuel-generating enterprises such as biodiesel production and presorted waste recycling operations to increase cost-competitiveness and maximize environmental benefit.
- At present, biochar might only deliver climate change mitigation benefits and be environmentally and financially viable as a distributed system using waste biomass, i.e., small-scale on-site SWEATT.^[47]

Finally, the authors conclude that applications of SWEATT can play a significant role in the variety of solutions that will be needed to address today’s EEES problems.

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NOMENCLATURE AND ACRONYMS USED IN MANUSCRIPT

ABPC	Air Blown Partial Combustion
ACE	Analytical Cost Estimation
AGIR	Antares Group Inc. Report
Ar	Aromatics
ASEM	Analytical Semi-Empirical Model
ATT	Advanced Thermal Technologies
BTU	British Thermal Units
CCTL	Clean Combustion Technology Lab
CHP	Combined Heat and Power
CIE	Compressed Ignition Engines
DANSF	Dry Ash, Nitrogen and Sulfur Free
EU	European Union
FC	Fixed Carbon
GACE	Generalized Analytic Cost Estimation
HHV	Higher Heating Values
HRSG	Heat Recovery Steam Generator
ICE	Internal Combustion Engines
IGCC	Integrated Gasifier Combined Cycle

MSW	Municipal Solid Waste
NGCC	Natural Gas-Fired Combined Cycle
NPHR	Net Plant Heat Rate
OBPC	Oxygen Blown Partial Combustion
OFC	Omnivorous Feedstock Converter
PES	Primary Energy Supplies
PNA	Polynuclear Aromatics
PYRO	Pyrolysis Systems
QES	Quaternary Energy Supply quads Quadrillion BTUs
RDF	Refuse Derived Fuels
SES	Secondary Energy Supplies
SW	Solid Waste
SWANG	Solid Waste Alliance with Natural Gas
SWEATT	Solid Waste to Energies by Advanced Thermal Technologies
TES	Tertiary Energy Supply
TPES	Total Primary Energy Supply
V _T	Volatiles
WEC	Waste to Energy Conversion

REFERENCES

- Green, A., Ed. *An Alternative to Oil, Burning Coal with Gas*, University of Presses of Florida: Gainesville, FL, 1981.
- Green, A., et al. *Coal-Water-Gas, An All American Fuel for Oil Boilers*, Proceedings of the Eleventh International Conference on Slurry Technology, Hilton Head, SC, 1986.
- Green, A., Ed. *Solid Fuel Conversion for the Transportation Sector*, FACT-Vol 12 ASME New York, NY. Proceedings of Special Session at International Joint Power Generation Conference San Diego, 1991.
- Green, A. *A Green Alliance of Biomass and Coal (GABC)*, Appendix F, National Coal Council Report May 2002: Proceedings of 27th Clearwater Conference, Clearwater, FL, March 2003, 2002.
- Green, A.; Feng, J. *A Green Alliance of Biomass and Natural Gas for a Utility Services Total Emission Reduction (GANGBUSTER)*, Final Report to School of Natural Resources and the Environment, 2003.
- Green, A.; Hughes, E.; (EPRI), Kandiyoti, R.; (Imperial College London) conference organizers. Proceedings of the first international conference on co-utilization of domestic fuels. *Int. J. Power Energy Syst.* **2004**, *24*, 3.
- Green, A.; Smith, W.; Hermansen-Baez, A.; Hodges, A.; Feng, J.; Rockwood, D.; Langholtz, M.; Najafi, F.; Toros, U.; Multidisciplinary Academic Demonstration of a Biomass Alliance with Natural Gas (MADBANG). Proceedings of the International Conference on Engineering Education, University of Florida, Conference Center, Gainesville, FL, Oct 2004.
- Green, A.; Swanson, G.; Najafi, F. Co-utilization of Domestic Fuels Biomass Gas/Natural Gas, GT2004-54194, IGTI meeting in Vienna June 14–17, **2004**.
- Green, A.; Feng, J. Assessment of Technologies for Biomass Conversion to Electricity at the Wildland Urban Interface Proceedings of ASME Turbo Expo 2005: Reno-Tahoe, 2005.
- Green, A.; Bell, S. Pyrolysis in Waste to Energy Conversion (WEC), Proceedings of NAWTEC 14 Conference Tampa, FL, May, 2006.
- Jenner, M. Biomass Rules. LLC Cited in Natural Gas Futures NYMEX Jan 10th, 2010.
- Channiwala, S.; Parikh, P. A unified correlation for estimating HHV of solid liquid and gaseous fuels. *Fuel* **2002**, *81*, 1051–1064.
- Perlack, R.; Stokes, B.; Erbach, D. Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply, Oak Ridge National Laboratory, ORNL/TM-2005/66, U.S. Department of Energy, 2005.
- Green, A.; Peres, S.; Mullin, J.; Xue, H. *Co-gasification of Domestic Fuels*, Proceedings of IJPGC. Minneapolis, MN, ASME-NY, NY, 1996.
- Green, A.; Zanardi, M.; Mullin, J. Phenomenological models of cellulose pyrolysis. *Biomass Bioenergy* **1997**, *13*, 15–24.
- Green, A.; Zanardi, M. Cellulose pyrolysis and quantum chemistry. *Int. J. Quantum Chem.* **1998**, *66*, 219–227.
- Green, A.; Mullin, J. Feedstock blending studies with laboratory indirectly heated gasifiers. *J. Eng. Gas Turbines Power*; **1999**, *121*, 1–7.
- Green, A.; Mullin, J.; Schaefer, G.; Chancy, N.A.; Zhang, W. *Life Support Applications of TCM-FC Technology*, 31st ICES Conference, Orlando, FL, Jul 2001.
- Green, A.; Venkatachalam, P.; Sankar, M.S. Feedstock Blending of Domestic Fuels in Gasifier/Liquifiers, TURBO EXPO 2001, Amsterdam, GT, 2001.
- Green, A.; Chaube, R.; Pyrolysis Systematics for Co-utilization Applications. TURBO EXPO 2003, Jun 2003, Atlanta, GA, 2003.
- Green, A.; Chaube, R.A. A unified biomass-coal pyrolysis reaction model. *Int. J. Power Energy Syst.* **2004**, *24*(3), 215–223.
- Green, A.; Sadrameli, S. M. Analytical representations of experimental polyethylene pyrolysis yields. *J. Anal. Appl. Pyrolysis* **2004**, *72*, 329–335.
- Sadrameli, S.; Green, A. Systematics and modeling representations of naphtha thermal cracking for olefin production. *J. Anal. Appl. Pyrolysis*, **2005**, *73*, 305–313.
- Green, A.; Feng, J. Systematics of corn stover pyrolysis yields and comparisons of analytical and kinetic representations. *J. Anal. Appl. Pyrolysis* **2006**, *76*, 60–69.
- Feng, J.; Green, A. Peat pyrolysis and the analytical semiempirical model. *Energy Sources, Part A.* **2007**, *29*, 1049–1059.
- Feng, J.; YuHong, Q.; Green, A., Analytical model of corn cob pyroprobe-FTIR data. *J. Biomass Bioenergy* **2006**, *30*, 486–492.
- Gaur, S.; Reed, T. *Thermal Data for Natural and Synthetic Fuels*; Marcel Dekker: New York, NY, 1998.
- Xu, W.C.; Tomita, A. Effects of coal type on the flash pyrolysis of various coals. *Fuel* **1987b**, *66*, 627–636.
- Mastral, F.J.; Esperanza, E.; Garcia, P.; Juste, M. Pyrolysis of high-density polyethylene in a fluidised bed reactor. Influence of the temperature and residence time. *J. Anal. Appl. Pyrolysis* **2002**, *63*, 1–15.
- Mastral, F.J.; Esperanza, E.; Berruco, C.; Juste, M. Fluidized bed thermal degradation products of HDPE in an inert

- atmosphere and in air-nitrogen mixtures. *J. Analy. Appl. Pyrolysis* **2003**, *70*, 1–17.
31. Stultz, S.; Kitto, J., Ed., *Steam* 40th Ed.; Babcock & Wilcox: Barberton, OH, 1992.
 32. Liscinsky, D.; Robson, R.; Foyt, A.; Sangiovanni, J.; Tuthill, R.; Swanson, M. *Advanced Technology Biomass-Fueled Combined Cycle*, Proceedings of ASME Turbo Expo 2003, Power for Land, Sea and Air, Atlanta, GA, GT2003-38295, 2003.
 33. Phillips, B.; Hassett, S., *Technical and Economic Evaluation of a 79 MWe (Emery) Biomass IGCC*, Gasification Technologies Conference, San Francisco, 2003.
 34. Antares Group, Inc. Assessment of Power Production at Rural Utilities Using Forest Thinnings and Commercially Available Biomass Power Technologies. Landover, MD, Sept 2003.
 35. ICF Consulting. *Options for Meeting the Electrical Supply Needs of Gainseville* Report March 6, 2006.
 36. Roth, I.; Ambs, L. Incorporation externalities into a full cost approach to electric power generation life-cycle costing. *Energy* **2004**, *129*(12–15), P2125–P2144.
 37. Green, A.; Palacio, J.; Bell, S.; Avery, M. Sustainable Energy for Communities and Institutions, Proceedings of Sustainability Conference, University of Florida 2006.
 38. Green, A. Operations Analysis and the 20th Air Force Slide Rules of WW II, *J. Oughtred Soc.* **2000**, *9*, 212.
 39. Mirasgedis, S.; Diakoulaki, D. Multicriteria analysis vs. externalities assessment for the comparative evaluation of electricity generation systems. *Eur. J. Oper. Res.* **1997**, *102*(2), 364–379.
 40. Lehmann, J.; Joseph, S. Eds., *Biochar for Environmental Management: Science and Technology*. Proceedings of Newcastle UK Conference, Earthscan Publishers Ltd., 2009.
 41. Woods, W.; Teixeira, W.; Lehmann, J.; Steiner, C.; Winkler Prins, A.; Rebellato, L. Eds. *Amazonian Dark Earths*; Springer Publishers: Berlin, 2009.
 42. Antal, M.J.; Gronli, M. The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res.* **2003**, *42*, 1619–1640.
 43. Falcão, N.; Comerford, N.; Lehmann, J. Determining nutrient bioavailability of amazonian dark earth soils—methodological challenges. In *Amazonian Dark Earths: Origin, Properties, and Management*; Lehmann, J., Kern, D., Glaser, B., Woods, W., Eds.; Kluwer Academic Publishers: MA, 2003, 255–270.
 44. Downie, A.; Crosky, A.; Munroe, P. Physical properties of biochar. In *Biochar for Environmental Management: Science and Technology*; Lehmann, J.; Joseph, S., Eds.; Earthscan: London, 2009; pp. 183–205.
 45. Glaser, B. Prehistorically modified soils of central Amazonia: A model for sustainable agriculture in the twenty-first century. *Phil. Trans. R. Soc. B Biol. Sci.* **2007**, *362*, 187–196.
 46. Lehmann, J. Bio-energy in the black. *Front. Ecol. Environ.* **2007**, *5*, 381–387.
 47. Roberts, K.; Gloy, B.A.; Joseph, S.; Scott, N.R.; Lehmann J. Life cycle assessment of biochar systems: Estimating the energetic, economic, and climate change potential. *Environ. Sci. Technol.* **2010**, *44*, 827–833.
 48. Zimmerman, A. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environ. Sci. Technol.* **2010**, *44*(4), 1295–1301, DOI: 10.1021/es903140c.
 49. Kasozi, G.N.; Zimmerman, A.R.; Nkedi-Kizza, P.; Gao, B. Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars). *Environ. Sci. Technol.* **2010**, *44*, 6189–6195.
 50. Mukherjee, A.; Zimmerman, A.R.; Harris, W. Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma*, *in press*.
 51. Bansal, R.; Goyal, M. *Activated Carbon Adsorption*; Taylor and Francis, 2005; 497 pp.
 52. Inyang, M.; Gao, B.; Pullammanappallil, P.; Ding, W.; Zimmerman, A.R.; Cao, X. Enhanced lead removal by biologically activated biochar from sugarcane bagasses. *Water Res.*, submitted.
 53. Khodadad, C.L.M.; Zimmerman, A.R.; Uthandi, S.; Foster, J.S. Changes in microbial community composition in soils amended with pyrogenic carbon. *Soil Biol. Biochem.*, *in press*.
 54. Woolf, D.; Amonette, J.E.; Street-Perott, A.; Lehmann, J.; Joseph, S. Sustainable biochar to mitigate global climate change. *Nat. Commun.* **2010**, *1*, 1–9.
 55. Inyang, M.; Gao, B.; Pullammanappallil, P.; Ding, W.; Zimmerman, A.R. Biochar from anaerobically digested sugarcane bagasse. *Bioresour. Technol.* **2010**, *101*, 8868–8872.
 56. Green, A. Transportation. In *Encyclopedia of Climate and Weather*; Schneider, S.H., Ed.; Oxford University Press: Oxford, N.Y., 1996 (2011 update, *in press*); 771–773.
 57. Green, A.; Schaefer, G. What to Do with CO₂. Proceedings Turbo Expo 2001, New Orleans paper IGTI 2001-GT-1.
 58. Hansen, J., et al. Target atmospheric CO₂: Where should humanity aim? *Open Atmos. Sci. J.* **2008**, *2*, 217–231.
 59. Princiotta, F. Global climate change and the mitigation challenge. *J. Air Waste Manage. Assoc.* **2009**, *59*(10), 1194–1211.
 60. Ingram, L., et al. Simultaneous saccharification and fermentation and partial saccharification and co-fermentation of lignocellulosic biomass for ethanol production. *Biofuels Methods Mol. Biol.* **2009**, *581*, 263–280.
 61. Holmgren, J.; Marinangeli, R.; Elliott, D.; Bain, R. Consider upgrading pyrolysis oils into renewable fuels. *Hydrocarbon Process.* **2008**, *Sept*, 95–103.
 62. Peterson, C.; Ault, D. Technical overview of vegetable oil as a transportation fuel. *ASME FACT* **1991**, *12*, 45–54 in Ref. 3.
 63. Brown, S.; Henry, C. Natural Selection Farms (Nov. 29, 2010), available at <http://www.kingcounty.gov/environment/wastewater/Biosolids/BiosolidsRecyclingProjects/NaturalSelectionFarms.aspx> (accessed Nov. 30, 2010).
 64. Morgan, G. *Flax Finding New Life as Biodiesel Stock—Domestic Fuel*.
 65. Vasden, B. *Commercial Biomass and Biofuel Feedstock Farming in Florida*; 2010; available at www.uscjo.com (accessed Dec. 1, 2010).
 66. Kargbo, D.M. Biodiesel production from municipal sewage sludges. *Energy Fuels* **2010**, *24* (5), 2791–2794.
 67. Dufreche, S.; Hernandez, R.; French, T.; Sparks, D.; Zappi, M.; Alley, E. Extraction of lipids from municipal wastewater plant. *Microorganisms for production of biodiesel*. *J. Am. Oil Chem. Soc.* **2007**, *84*, 181–187.

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- Q12 68. Dias J., et al. Production of biodiesel from acid waste lard. *Bioresour. Technol.* **2009**, *100*, 6355–6361.
69. Green, A., Ed. *Pollution Prevention and Medical Waste Incineration*; Van Nostrand Reinhold: New York, 1992
70. Wisconsin Department of Natural Resources Agricultural Plastics (Sept. 1, 2010) available at <http://dnr.wi.gov/org/aw/wm/recycle/newpages/agplastics.htm> (accessed Nov. 30, 2010).
71. Smith, C. Plastic to Oil Fantastic (Apr. 4, 2009), available at <http://www.rexresearch.com/ito/ito.htm> (accessed Nov. 30, 2010).
72. Akinori Ito Invents a Machine Converting Waste Plastic into Oil (Aug. 23, 2010), available at <http://www.neverthelessnation.com/2010/08/akinori-ito-invents-machine-converting.html> (accessed Nov. 30, 2010).
73. Vispute, T.P.; Zhang, H.; Sanna, A.; Xiao, R.; Huber, G.W. Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. *Science* **2010**, *330*(6008), 1222–1227.
74. Bartis, J.; LaTourrette, T., et al. *Oil shale development in the United States: Prospects and policy issues*; RAND Corp. ISE Division, NETL, US DoE: Pittsburgh, PA, 2005.
75. California Integrated Waste Management Board. Conversion Technologies Report to the Legislature; 2005, available at <http://www.ciwmb.ca.gov/Organics/Conversion/Events>.
76. Bioenergy Producers Association. UC-R Issues Report on Thermal Conversion Technologies (Jan. 19, 2010), available at <http://www.bioenergyproducers.org/index.php/ucr-report> (accessed Nov. 31, 2010).

Q1: Please expand DASNF.

Q2: “including of lead” here is vague. Please clarify.

Q3: Is EPA correctly defined here?

Q4: Tables 2 and 7 were changed to Tables 1 and 2, respectively.

Q5: Please provide publisher location.

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