BIOMASS PYROLYSIS FOR DISTRIBUTED ENERGY GENERATION

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Introduction

Renewable sources of energy can include solar, wind, ocean tides or temperature gradients, and biomass. However, biomass is the only renewable energy source that is capable of displacing significant amounts of solid, liquid, and gaseous fossil fuels. The historical energy consumption patterns in the U.S. indicate that wood was the dominant energy source for most of the 1800's, followed by coal in the late 1800's and early 1900's and oil and gas in the latter part of the 1900's [1]. In the future, it is likely that the dominance of fossil fuels will gradually diminish in favor of renewable sources of energy, including biomass.

Examples of candidate biomass feedstocks include wood residues and byproducts (e.g., wood chips, sawdust, tree prunings), agricultural residues and byproducts (e.g., corn stover, bagasse, rice husks) or dedicated energy crops (e.g., fast-growing trees, shrubs and grasses) [2]. An important potential source of biomass feedstocks, that is often overlooked, are the livestock and poultry manures, which are generated in significant quantities in the U.S. [2-5].

Besides landfill disposal, many different processes have been considered for utilizing biomass wastes: combustion (incineration), aerobic and anaerobic biodigestion, wet oxidation, supercritical oxidation, steam reforming, etc. [3]. However, all of these approaches have disadvantages which have prevented their widespread use. For example, combustion produces undesirable byproducts such as oxides of sulfur and nitrogen. A staged pyrolysis process has several advantages when compared to other possible approaches: 1) it can be used for all types of solid products and can be more easily adapted to changes in feedstock composition than alternative approaches; 2) the technology is relatively simple and can be made compact and low cost; 3) it can produce several usable products from solid waste streams (e.g., H_2, CH_4, CO, liquid fuels, fertilizers, activated carbon, etc.); 4) the technology is environmentally friendly (low net emissions of CH_4, CO_2, SO_2, NO_x, HAP's, VOC's); 5) it can be integrated into microturbine, fuel cell or thermophotovoltaic (TPV) systems for power generation. The main disadvantage of pyrolysis processing is that the product stream is more complex than for many of the alternative treatments. While many pyrolysis studies have been done on biomass materials, most of these have focused on production of liquid fuels, chemicals, or hydrogen [6-8], and not fuel gas mixtures (H_2, CO, CH_4).

Pyrolysis Processing of Waste Materials

The word *pyrolysis* has its roots in Greek, πυρ meaning fire, and λυσισ meaning to loosen or untie. Pyrolysis is, therefore, a process of thermal decomposition to produce gases, liquids (tar) and char (solid residue). Pyrolysis is usually understood to be thermal decomposition which occurs in an oxygen-free atmosphere, but oxidative pyrolysis is nearly always an inherent part of combustion processes. Gaseous, liquid and solid pyrolysis products can all be used as fuels, with or without prior upgrading, or they can be utilized as feedstocks for chemical or material industries. The types of materials which are candidates for pyrolysis processes include plant biomass, human and animal wastes, food scraps, crop residues, prunings, paper, cardboard, plastics, rubber [9-11]. These products are primarily polymeric in nature and pyrolysis represents a method of processing all of these materials into useful products. In the case of plant biomass, human and animal wastes, food scraps, paper and cardboard, pyrolysis can be used to produce fuels or chemicals in gaseous and/or liquid form. In the case of plastics and rubber, pyrolysis can sometimes be used for "recycling" previously manufactured materials back to monomers. Of course, pyrolysis has been used for over 100 years in the processing of coal in coke ovens [9]. Before the large oil discoveries in the Middle East, the chemical industry was largely based on byproducts from the coking process. Advanced Fuel Research, Inc. (AFR) recently completed a study which indicated that pyrolysis of used tires could be an economical way to dispose of this troublesome solid waste stream and, at the same time, produce valuable products [11]. There are several excellent reviews of the biomass pyrolysis literature [1,12-19]. Commercial processes for pyrolysis of plastics and biomass have been developed [1,6-8,9-10]. Most of these have focused on the production of liquid fuels, chemicals, or hydrogen, and not fuel gas mixtures, which are usually considered less valuable.

A recently proposed AFR scheme [20-22] for the pyrolysis processing of spacecraft wastes is shown in Figure 1. In many respects, this scheme is analogous to a "solid waste refinery" and a similar approach could be used for most types of biomass waste in terrestrial applications. The waste stream is heated in the absence of oxygen to temperatures between 673 and 873 K. Thermal decomposition occurs, producing a mixture of liquids (0-50%), gases (30-80%), and a solid residue (20-35%). The initial pyrolysis products are primarily liquids, but these liquids are easily cracked to gases (and small amounts of carbon) as the temperature is raised an additional 100-200 K. The major gas products are H_2, CO, H_2O, CO_2, CH_4. Other gas products, present in much smaller amounts, will include N_2, NH_3 and H_2S, since nitrogen and/or sulfur compounds are present in most solid wastes. The liquids will initially include a large yield of a complex mixtures of chemicals, including levoglucosan and glycoaldehyde for cellulosic wastes. This characteristic of the pyrolysis of waste streams allows for the possibility of staging the pyrolysis process. The initial stage will convert the solids to liquids and will significantly reduce the volume of the waste. In the second stage, the liquids are cracked almost completely to gases. Subsequently, the char residue can be gasified or combusted and the minerals can be recovered for later disposal or use as fertilizer or blended with concrete. The char residue will typically be less than 20% of the initial mass of the solid waste, unless there is a high inorganic content, in which case it could be as high as 35%. The gas stream will need to be cleaned to remove NH_3 and/or H_2S and then the gas can be sent to an energy conversion device (e.g., microturbine, incinerator, TPV or a fuel cell).

A significant advantage of pyrolysis processing is that these stages can be separated in time by minutes, days, or weeks, depending on the demand for the products that are being recovered from the waste. For example, adjusting the pyrolysis conditions to produce primarily liquids will significantly reduce the waste storage volume without significantly increasing the volume of gases that must be used, stored, or discarded. The char residue can also be saved for disposal rather than gasified to simplify the system operation, which may be desirable in certain installations. Alternatively, two systems can be operated in tandem, one in pyrolysis mode and one in gasification mode and the resultant gas streams can be blended to give a more constant off-gas composition. Another possibility would be to use a continuous flow reactor system such as a moving bed, fluidized-bed, or transport reactor. Direct combustion does not allow such a fine degree of control of the outcome and will convert all of the nitrogen to NO_x, an undesirable
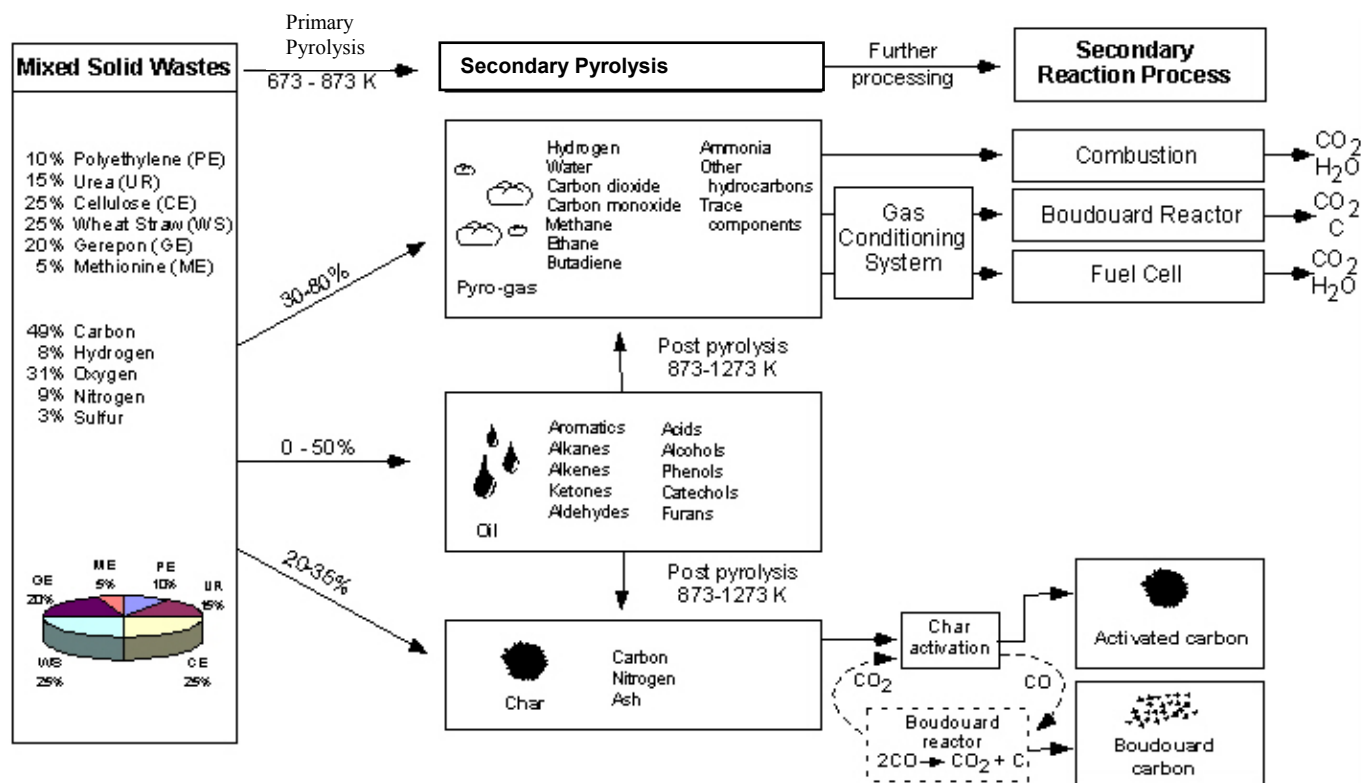
Figure 1. Pyrolysis processing scheme for Controlled Ecological Life Support System (CELSS).

product. In addition, most direct combustion systems will be adversely affected by the high mineral matter contents in many biomass materials. Direct gasification of the biomass wastes will produce a fuel gas with a lower heating value, since the hydrocarbons like CH_4 will be lost.

Experimental Methods

An extensive set of pyrolysis experimental studies at AFR has utilized a TG-FTIR instrument (thermogravimetric analysis combined with FT-IR analysis of evolved products). The application of TG-FTIR to coal analysis at AFR has been described in several publications [23-27]. By using a range of heating rates, kinetic rate constants for volatiles evolution have been obtained [26]. TG-FTIR analysis has also been used at AFR to characterize other hydrocarbon materials such as modified coal samples, [28] coal liquefaction resids [29], petroleum source rocks, [30] lubricants, [31] biomass, [32-35] waste tires, [36] and polymers [37]. This section will briefly review the use of the TG-FTIR technique at AFR for the study of biomass pyrolysis.

Details of the TG-FTIR method can be found in reference [23]. The apparatus consists of a sample suspended from a balance in a gas stream within a furnace. As the sample is heated, the evolving volatile products are carried out of the furnace directly into a 5 cm diameter gas cell (heated to 150 °C) for analysis by FT-IR. In a typical analysis procedure, a 35 mg sample is taken on a 30 °C/min temperature excursion in helium, first to 80 °C to dry, then to 900 °C for pyrolysis. After cooling, a small flow of O_2 is added to the furnace, and the temperature is ramped to 700 °C (or higher) for oxidation (or gasification). During this excursion, infrared spectra are obtained once every forty-one seconds. The spectra show absorption bands for several gases, including CO, CO_2, CH_4, H_2O, C_2H_4, HCl, NH_3, and HCN. The spectra above 300 °C also show aliphatic, aromatic, hydroxyl, carbonyl and ether bands from tar (heavy liquid products). The evolution of gases and tars derived from the IR absorbance spectra are obtained by a quantitative analysis program.

The TG-FTIR method provides a detailed characterization of the gas and liquid compositions and kinetic evolution rates from pyrolysis of materials under a standard condition (usually 30 °C/min). While the heating rates are slower than what will be experienced in most practical processes, it is a useful way of benchmarking materials. The ultimate analysis data for several biomass materials that have been studied using the TG-FTIR approach are given in Table 1. The typical TG-FTIR results from pyrolysis at 30 °C/min for these materials are given in Table 2. AFR has developed kinetic models based primarily on TG-FTIR data which can be extrapolated over a wide range of conditions. The TG-FTIR apparatus can also be used to study the reactivity of the pyrolysis residue (char) by introducing appropriate gases. Finally, a secondary reaction zone can be added to examine secondary pyrolysis of the volatile products. These secondary reactions are important in order to maximize the fuel gas production from biomass materials. Additional details can be found in Refs. 32-35.

In recent work, AFR has been involved in building and testing larger scale pyrolysis reactors with NASA support that could be used for solid waste resource recovery in space [20-22]. That project is studying the pyrolysis of mixed solid waste streams, including paper, soap, plastic, and inedible plant biomass, which are relevant to long term space travel.

A schematic of the NASA prototype reactor system is shown in Figure 2. During the initial processing step, the first stage is the primary pyrolysis zone, for thermal decomposition of the sample into gases, liquids and a char residue, while the second stage contains a catalyst bed for decomposition of the liquids. Each of these stages are heated independently (~673-873 K for the first stage, 873-1273 K for

the second stage). During the second-processing step, the purge gas is switched to CO_2 (or H_2O) and gasification of the char can occur in the first stage (if desirable) while gasification of the carbon deposits from the cracked oils will occur in the second stage. Alternatively, the conditions in the first stage can be adjusted to provide activation of the char or no reaction at all, in which case the char can be removed and used for some other purpose. A picture of the current prototype the reactor is shown in Figure 3. It is anticipated that a suitably modified system could be used in terrestrial applications to produce fuel gases for distributed power generation.
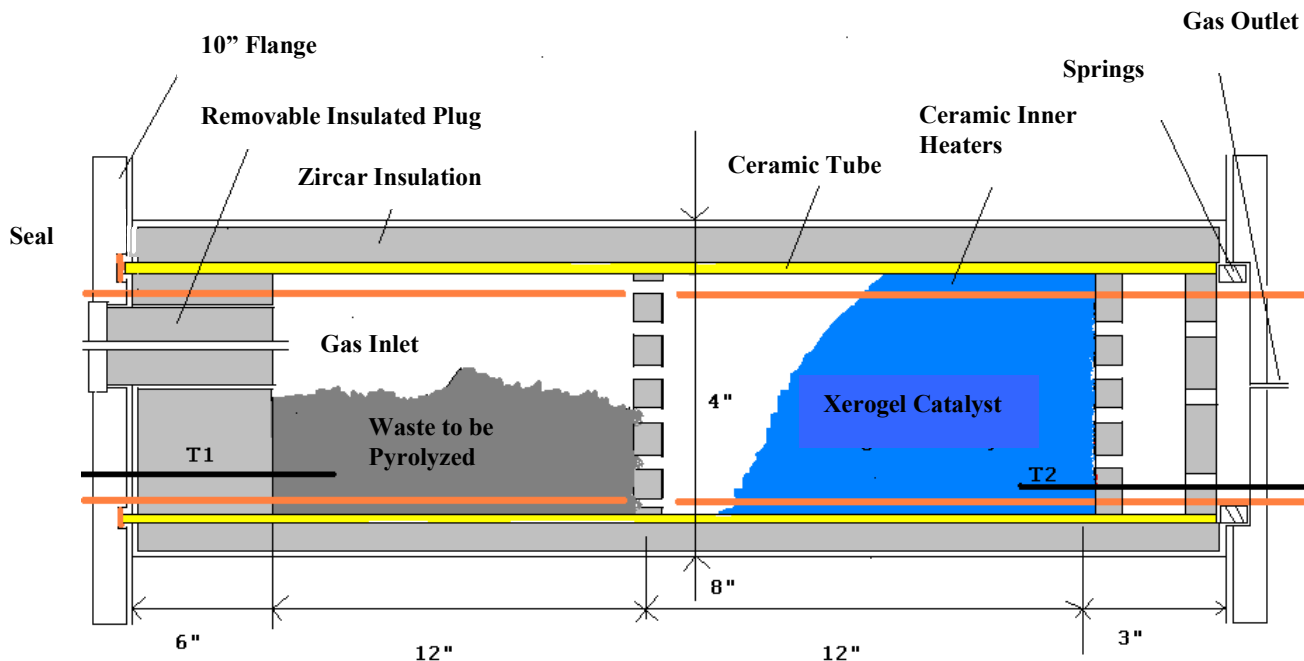
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Figure 2. Schematic of First Generation Unit (FGU) two-stage pyrolysis reactor system.
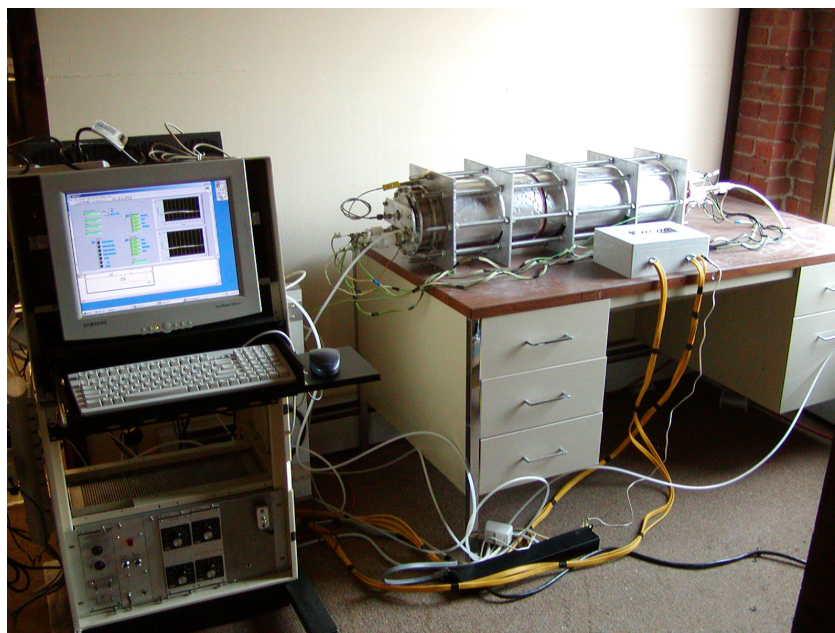

Figure 3. Picture of AFR Prototype Pyrolyzer and Control Console

Table 1. - Ultimate analysis of biomass samples

Sample	Chicken Manure[a]		Lignin[b]		Wheat Straw[c]		Miscanthus Giganteus[d]		Cellulose[e]		Xylan[f]		Wood Pellets[g]	
	AR	DAF	AR	DAF	AR	DAF	AR	DAF	AR	DAF	AR	DAF	AR	DAF
Moisture	11.4		1.9		7.9		8.7		5.0		11.0		8.2	
Ash	20.0		0.0		8.3		2.5		0.0		3.6		0.3	
C		47.4		67.4		48.0		49.4		44.0		45.0		52.1
H		6.5		6.2		6.2		5.5		6.2		6.0		5.2
O		39.5		26.2		44.9		44.0		49.8		48.9		42.2
S		1.0		0.0		0.2		0.2		0.0		0.0		0.1
N		5.6		0.2		0.7		0.6		0.0		0.0		0.3

Notes: AR = As-received; D=Dry; DAF=Dry, Ash Free
a-Plant Right (Purdy, MO); b- ALCELL Technologies, Inc., (Valley Forge, PA (ADI/L952)); c- NIST, (Gaithersburg, MD); d-Delft University of Technology; e- Avicel (pH-102/Lot 2822); f – Philip Morris USA; g – Labee Company, the Netherlands.

Table 2. Results from TG-FTIR experiments at 30 °C/min for various biomass samples

Sample	Chicken Manure	Lignin	Wheat Straw	Miscanthus Giganteus	Cellulose	Xylan	Wood Pellets
Moisture	11.2	1.9	7.5	2.5	12.4	9.5	6.3
Ash	18.3	0.0	7.9	3.8	0.0	2.0	0.0
Volatile Matter	59.1	69.5	68.0	74.4	85.3	67.6	80.8
Fixed Carbon	11.4	29.2	16.6	19.3	2.3	21.0	12.9
Tars	28.5	39.5	35.1	21.9	81.5	13.3	38.8
CH4	0.98	2.40	1.20	1.14	0.13	0.87	1.3
H2O (pyr)	18.7	7.6	21.8	18.4	5.1	24.2	16.0
CO2	14.3	1.9	14.5	9.4	2.0	15.9	5.1
CO	6.37	6.50	9.26	7.15	1.49	9.64	6.77
C2H4	0.25	0.22	0.26	0.27		0.42	0.23
SO2	0.08		0.36	0.00		0.12	0.12
COS	0.61		0.23	0.16			0.11
NH3	1.91		0.18	0.10			0.02
HCN	1.21	0.04	0.25	0.14	0.03	0.15	0.09
Formic Acid	0.72		1.61	1.66	0.34	1.75	1.73
Acetic Acid	1.63		5.52	3.59	0.57	2.65	2.37
CH3OH	0.10	2.20	1.21	1.12	0.75	1.72	0.74
Formaldehyde	0.00	0.22	0.92	1.12	1.23	0.45	2.93
Acetaldehyde	6.31	1.55	8.62	9.02			8.11
Acetone	1.04	3.91	2.38	1.86			2.15

Notes: Yields are given on wt.% dry, ash-free basis except for moisture, ash, volatile matter, and fixed carbon which are given on an as-received basis.

Application to Distributed Power Generation

In the past few years, the level of commercial interest in distributed power generation has increased dramatically. According to recent data, the amount of venture capital investment in "micropower" technology has increased from $100 million in 1996 to $200 million in 1998 and an estimated $800 million for 2000 [38]. Fuel cell systems that are currently commercial operate at relatively low temperatures and use pure hydrogen as a fuel [39]. Examples are the phosphoric acid system and the polymer electrolyte membrane (PEM) systems. In order to use these cells with a fuel gas which contains CH_4, CO, and H_2, a reformer and shift converter must be used. However, also under development are high temperature fuel cells (HTFC) which have molten carbonate (MCFC) or solid oxide electrolytes (SOFC). The latter fuel cells are especially interesting for combination with a biomass pyrolysis process, since these can tolerate a mixture of CO, CH_4, and H_2, and operate at temperatures ranging from 650 °C to 1000 °C. This high temperature heat could be used to help drive the pyrolysis and char gasification reactors and/or provide heat for building operations. Some of these HTFC systems have been successfully operated on landfill gas and digester gas,

which produce similar gas streams to the fuel gas that is produced from biomass pyrolysis.

Thermophotovoltaic (TPV) systems are also of interest because they can operate on fuel gases which contain mixtures of H_2, CH_4, and CO. These systems involve using the radiant energy from a flame to produce electricity from specially designed photovoltaic cells. TPV systems are also lower in cost and closer to commercialization than the HTFC's. A company in the Pacific Northwest (JXCrystals) is marketing TPV generation equipment for residential and mobile uses [40]. The military is also sponsoring the development of TPV systems for mobile power generation units.

A third possibility, which has near term potential, is to couple the pyrolysis process with a microturbine, such as those produced by Capstone Turbine Corp (Chatsworth, CA). These systems are much cheaper when compared to fuel cell and TPV systems and are already available in significant quantities at appropriate power generation rates. Approximately the size of a large refrigerator, Capstone's Model 330 Microturbine generates approximately 30 kilowatts of electrical power which is enough power to power a convenience store, and approximately 300,000 kilojoules per hour of heat, enough energy to heat 20 gallons of water per minute with a 20 degree heat rise. The Capstone Microturbine can operate connected to the electric utility grid or on a stand-alone basis. It remains to be seen how well microturbines can operate on hydrogen-rich fuel gas streams.

Summary

The conversion of fuel gases from biomass pyrolysis to power using either a fuel cell, TPV or microturbine system would provide numerous technical, economic, and social benefits:

- It would remove biomass from landfills where they take up valuable space and decompose to produce CH_4 and CO_2, both greenhouse gases.
- It would provide a means of generating power in remote agricultural areas, a benefit from an economic and quality-of-life standpoint to both farms in the U.S. and in underdeveloped nations.
- It would provide a means of generating off-grid power in business and residential applications where significant quantities of biomass wastes (e.g., paper, food residues) are readily available.
- The power generated would most likely replace power produced at central power stations and diesel generators from fossil fuels, thus providing a net reduction in CO_2, NO_x, and SO_2.

The technology would contribute to and benefit from the expected growth in the emerging distributed power generation industries over the next several years. Challenges remain in reducing the costs of the next generation power generation equipment and in economical production of clean fuel gases from biomass pyrolysis. It is likely that early demonstration projects will require tax incentives in order to compete with conventional power generation equipment utilizing fossil fuels.

Acknowledgements.

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