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# ANALYSIS AND FORMULATION OF COMBUSTIBLE COMPONENTS IN RUBBER SOLID WASTES

By:

Mu-Hao Sung Wang (Former Adjunct Professor of Stevens Institute of Technology) LENOX INSTITUTE OF WATER TECHNOLOGY Massachusetts, USA

> William C. McGinnis and Lawrence K. Wang STEVENS INSTITUTE OF TECHNOLOGY Hoboken, NJ 07030 USA

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# ABSTRACT:

This publication is the result of a study of the inherent properties of solid wastes with special emphasis on rubber solid waste. Ultimate analysis values can be used to find representative empirical chemical formulae for typical municipal solid wastes (MSW) or any non-hazardous industrial solid wastes. These formulae can be used by environmental planners and managers in evaluating the feasibility of alternative uses for a target solid waste such as its heat generation and material recycling possibilities. Unfortunately some technical data concerning rubber and plastic solid wastes are missing.

An attempt was made to improve the ultimate analysis model values by completing the table entries for rubber. A survey was undertaken to determine empirical chemical values for rubber products. Characteristics of the rubber industry's waste is discussed as well as some alternatives that have been tested or implemented. The ultimate analysis values of solid rubber wastes are concluded to be: Carbon 82.570%, Hydrogen 3.689%, Oxygen 0.496%, Nitrogen 0.166%, Sulfur 1.587%, and Ash 11.492%. The authors recommend that further similar research be conducted for the plastic solid waste as well as other solid wastes. This publication also introduces a general mathematical model for : (a) prediction of effect of the combustible solid waste on air pollution if the waste is to be used as a supplemental fuel; (b) solid waste characterization by burning the solid waste, effluent gases sampling and analysis, and reverse calculation using the model. This publication is one of the authors' memoirs. It is the authors' hope that this publication can be considered as a stepping stone by the readers for future solid waste research.

# **KEYWORDS**

Industrial Non-hazardous Solid Waste, Municipal Solid Waste (MSW), Rubber Solid Waste, Energy Value Analysis, Formulation, Mathematical Model, Air Pollution Control, Solid Waste Management, Planning, Call for Further Research, Plastic Solid Waste, Lenox Institute of Water Technology, Stevens Institute of Technology, Memoir.

# ACRONYM AND NOMENCLATURE

APWA American Public Works Association Carbon, percent С Hydrogen, percent Η MSW Municipal solid waste Nitrogen, percent N 0 Oxygen, percent RDF Refuse derived fuel S Sulfur, percent SBR Styrene butadiene rubber US Environmental Protection Agency USEPA

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#### ANALYSIS AND FORMULATION OF COMBUSTIBLE COMPONENTS

# IN RUBBER SOLID WASTES

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# 1. INTRODUCTION

This publication is the result of a study of the inherent properties of solid wastes with special emphasis on rubber solid waste. Ultimate analysis values can be used to find representative empirical chemical formulae for typical municipal solid wastes (MSW) or any non-hazardous industrial solid wastes. These formulae can be used by environmental planners and managers in evaluating the feasibility of alternative uses for a target solid waste such as its heat generation and material recycling possibilities. Unfortunately some technical data concerning rubber and plastic solid wastes are missing in the literature. [1]

A glance at Table 1 shows voids in the plastic and rubber categories. [1] This is due to a lack of research in these areas. The following sections of this publication examine rubber, the rubber industry, types of rubber, and rubber as a solid waste. Also solid wastes that are generated by the rubber industry are discussed. Finally, results of an empirical composition study to supplement the data in Table 1 are presented.

| COMPONENT   | CARBON | HYDROGEN | OXYGEN | NITROGEN | SULFUR | ASH  |
|-------------|--------|----------|--------|----------|--------|------|
|             |        |          |        |          |        |      |
| Food Wastes | 48.0   | 6.4      | 37.6   | 2.6      | 0.4    | 5.0  |
| Paper       | 43.5   | 6.0      | 44.0   | 0.3      | 0.2    | 6.0  |
| Cardboard   | 44.0   | 5.9      | 44.6   | 0.3      | 0.2    | 5.0  |
| Plastic     | 60.0   | 7.2      | 22.8   |          |        | 10.0 |
| Textiles    | 55.0   | 6.6      | 31.2   | 4.6      | 0.15   | 2.5  |
| Rubber      | 78.0   | 10.0     |        | 2.0      |        | 10.0 |
| Leather     | 60.0   | 8.0      | 11.6   | 10.0     | 0.4    | 10.0 |
| Garden      | 47.8   | 6.0      | 38.0   | 3.4      | 0.3    | 4.5  |
| Wood        | 49.5   | 6.0      | 42.7   | 0.2      | 0.1    | 1.5  |
| Dirt, Ashes | 26.3   | 3.0      | 2.0    | 0.5      | 0.2    | 68.0 |
|             |        |          |        |          |        |      |

TABLE 1: Ultimate Analysis (% Dry Weight) of the Combustible Components In Municipal Solid Wastes.

# 1.1 Rubber

Rubber is an elastic, waterproof substance obtained in nature from several tropical trees. It is produced synthetically from chemicals. Highly resistant to electricity and moisture, rubber is the most elastic substance known to man. At present there are more than 44,000 different rubber products manufactured in the United States alone.

Consumption of rubber both natural and synthetic, has been growing constantly. Rubber used in the United States increased more than 39 percent in twenty years, reaching a high of over 2.1 million long tons.

Because of an intensive research effort on the part of the rubber industry, many new synthetic materials that have rubber characteristics have been discovered. These synthetics are generally called polymers, because the molecular structure is composed of a chain of identical molecules strung together in repeating units.

Natural rubber and many synthetic rubbers belong to the hydrocarbon chemical family. In natural rubber, the chemical structure is five carbon atoms and eight hydrogen atoms.

More than 500 different synthetic rubbers have been created by juggling hydrogen and carbon atoms during the synthesis and linking them in different chain patterns. Manufacturers in the United States use more synthetic than natural rubber in their wide variety of products.

# 1.3. Many Rubber Companies

There are more than 1,450 rubber companies in the United States. The four largest are Good-Year Tire and Rubber Co., Firestone Tire and Rubber Co., Uniroyal, Inc. and B.F. Goodrich Co. Most of the companies in this country are expanding into many related, yet diversified, fields of manufacturing such as chemicals, plastics, textiles, and synthetics of all types.

Rubber was a billion dollar a year industry in America when production of synthetic rubber began in the 1940's. Today it has grown to a seven-billion dollar a year business.

The world use of natural rubber is over 2.2 million long tons a year, of which United States manufacturers use about 28 percent. Free world production of synthetic rubber is estimated to be about 4.5 million long tons a year. The United States, world's largest manufacturer of synthetic rubber, produces over 2.1 long tons each year.

# 1.4. The Rubber Molecule

Rubber is a hydrocarbon, which means it belongs to the family of substances composed of hydrogen and carbon. Other members of the hydrocarbon family include natural gas, gasoline and oil of turpentine. The reason most synthetic rubbers are made from petroleum products is because both are members of the hydrocarbon family.

In 1860, it was discovered that four carbon atoms, with hydrogen atoms surrounding them, form a chain which is the basic unit of a rubber molecule: isoprene. A fifth carbon atom, surrounded by three hydrogen atoms, branches off from one of the carbon atoms to form what is called a methyl group. Each of these rubber molecules has a total of five carbon atoms and eight hydrogen atoms ( $C_5$  H<sub>8</sub>). When thousands of these tiny isoprene molecules are linked together in a giant, chainlike molecule, the rubber molecule occurs. These chainlike molecules are called polymers; which means "many parts." The single molecule, isoprene, is called a monomer.

Rubber is elastic because of the specific structure of the rubber polymer. In un-stretched rubber, the polymer molecules fold back over themselves, spaghetti-like, in the same manner that irregular coils do. Stretching the rubber causes the molecules to unfold like the coils of a spring, and when released, return to their original position.

# 1.5 Summary

This publication is the result of a study of the inherent properties of solid wastes with special emphasis on rubber solid waste. Ultimate analysis values can be used to find representative empirical chemical formulae for typical municipal solid wastes (MSW) or any non-hazardous industrial solid wastes. These formulae can be used by environmental planners and managers in evaluating the feasibility of alternative uses for a target solid waste such as its heat generation and material recycling possibilities. Unfortunately some technical data concerning rubber and plastic solid wastes are missing.

An attempt was made to improve the ultimate analysis model values by completing the table entries for rubber. A survey was undertaken to determine empirical chemical values for rubber products. Characteristics of the rubber industry's waste is discussed as well as some alternatives that have been tested or implemented. The ultimate analysis values of solid rubber wastes are concluded to be: Carbon 82.570%, Hydrogen 3.689%, Oxygen 0.496%, Nitrogen 0.166%, Sulfur 1.587%, and Ash 11.492%. The authors recommend that further similar research be conducted for the plastic solid waste as well as other solid wastes. This publication also introduces a general mathematical model for : (a) prediction of effect of the

combustible solid waste on air pollution if the waste is to be used as a supplemental fuel; (b) solid waste characterization by burning the solid waste, effluent gases sampling and analysis, and reverse calculation using the model. This publication is one of the authors' memoirs. It is the authors' hope that this publication can be considered as a stepping stone by the readers for future solid waste research..

# 2. SYNTHETIC RUBBER

Material with characteristics similar to rubber are called synthetic rubbers because they are used as rubber substitutes.

There are two basic groups of synthetic rubbers: (a) general purpose rubbers and (b) special purpose rubbers. General purpose rubbers take the place of natural rubber while special purpose rubbers improve on the characteristics of natural rubber. For instance, some special purpose rubbers are made so that they will have a greater resistance to gasoline or oils, while others are made to withstand the effects of exposure to air or high temperatures.

Large scale advances in the development of synthetic rubber occurred, at the beginning of WW II when the Japanese cut the United States off from the natural rubbers of the East. The federal government set up synthetic rubber plants to make an all purpose rubber called Buna-S or GR-S. Buna-S gets its name from the two monomers and the chemical reagent used as a catalyst. The two monomers are butadiene and styrene and the catalyst was natrium (sodium).

# 2.1 Processing

Neither styrene nor butadiene can be found in nature. They are both petroleum by-products. Styrene is made from ethyl benzene by removing a hydrogen atom from the compound by a process called "cracking". Ethylene in the ethyl benzene compound is a petroleum refinery product and benzene is derived from coal and petroleum. To make GR-S, known today as SER or styrene-butadiene rubber, three parts of butadiene gas, compressed into liquid form, and one part liquid styrene are metered into a large tank called a polymerizer and mixed with a solution of soap and water. in the polymerizer, the butadiene and styrene form an emulsion in water. By raising the temperature and adding a catalyst, the polymerization process is started causing the butadiene and styrene molecules to hook up end to end. When the droplets become a milky latex, sulfuric acid and salt are added to coagulate the rubber. The synthetic rubber is then washed and the water is removed. Next, the newly created material is baled and shipped to a fabricator who compounds it with sulfur and pigments.

Since the development of general purpose synthetic rubber, the rubber industry has been creating many other special purpose synthetic rubbers.

# 2.2. Styrene-Butadiene Rubber (SBR)

SBR is the most important general purpose synthetic rubber in large scale production. It accounts for about 70 percent of all synthetic rubber produced in the United States. Some of the synthetic rubbers which have been commercially developed include Neoprene, Butyl, Polysulfide, Silicone, Polyurethane, Polyisoprene and Polybutadiene.

# 2.3. Neoprene

Neoprene is made by making a polymer of the monomer chloroprene ( $C_4H_5Cl$ ). Chloroprene is much like the basic molecule of rubber, isoprene, because it has a long chain of four carbons and five hydrogens. The basic materials which go into making chloroprene are salt, limestone, and coal. First acetylene gas is created from calcium carbide which is made by cracking natural gas. Hydrogen chloride, which is used to make muriatic acid, is then added to change the acetylene to chloroprene. Because the neoprene rubbers resist gasoline, oil, sunlight, oxygen and many chemicals better than natural rubber, they are widely used in such products as gasoline hose, wire and cable insulation on machines which are exposed to oil.

# 2.4. Butyl

Butyl\_is made by the copolymerization of isobutylene ( $C_4H_8$ ), a gas which is a product of petroleum refining, with a very small amount of another unsaturated hydrocarbon such as isoprene. Butyl rubber was first used in inner tubes for tires because it holds air much better than natural rubber. It has often been used in vibration mounts because of its ability to absorb shock. In addition to its air holding characteristic, it resists aging, heat, acids and is a good insulator for electricity.

# 2.5 Polysulfide

Polysulfide is made by the copolymerization of ethylene dichloride ( $C_2H_4Cl_2$ ) and sodium polysulfide ( $Na_2S_4$ ). These rubbers have very good resistance to softening and swelling in gasoline and greases. Therefore, it is widely used in products such as lining for gasoline hoses and for printing plates and rollers. Polysulfide rubbers also have good resistance to aging, air and sunlight.

# 2.6. Nitrile Rubber

Nitrile Rubber is another synthetic rubber which is oil and gasoline resistant. Besides its resistance to fuels, nitrile rubber exhibits good flexibility at low temperatures. Nitrile rubber is made by polymerizing a mixture of two monomers, butadiene and acronitrile which are obtained indirectly from petroleum and air.

# 2.7 Silicone Rubbers

Silicone Rubbers are made of oxygen and silicon, with hydrocarbons added. They keep their rubber properties at lower and higher temperatures than natural rubber or most other synthetic rubbers. They can be used in a temperature range of 130°F to 600°F. These rubbers are ideal for use in products which are exposed to extremely high or low temperatures such as seals, gaskets and other parts for jet airplanes. Silicone rubbers are different than other rubbers because the basic polymer chain contains no carbon atoms.

# 2.8. Polyurethane Rubbers

Polyurethane rubbers are made from ethylene or propylene glycols and adipic acid which form polyesters or polyethers which are further reacted with isocyanates. They resist age and heat and are able to withstand tremendous stresses and pressures. Polyurethane rubbers can be made extremely tough. They are used chiefly in manufacturing upholstery, foam rubber mattresses and insulating materials. Foams made from polyurethane can be made in a wide variety of densities and can be manufactured in either a flexible or rigid state.

# 2.9. Polyisoprene

Polyisoprene duplicates the natural rubber polymer chain in natural rubber. It therefore duplicates almost all the physical characteristics of natural rubber.

# 2.10. Polybutadiene

Polybutadiene is made from butadiene and is more elastic and generates less heat than other types of synthetic- rubber except polyisoprene. It is finding increasing usage in the rubber industry.

# 3. COMPOUNDING AND MIXING FOR RUBBER MANUFACTURING

The final step in making the rubber ready to be manufactured into a final product is compounding and mixing. During this process, different ingredients are compounded and mixed with the rubber to improve its characteristics. The main additives used in the compounding of rubber are fillers, antioxidants, pigments, accelerators and sulfur.

# 3.1. Fillers

Fillers are added to dry rubber to create a larger volume and to make it stronger and easier to handle. Clay is a neutral filler which makes the compound easier to handle but does not increase its strength.

# 3.2. Antioxidants

Antioxidants are added to rubber to help protect it from exposure to the air and sunlight. Some chemicals are used as antioxidants to prevent the cracking of rubber, which is a problem caused by oxidation.

# 3.3. Pigment

The most widely used of which is carbon black, are added to the rubber to give it greater wear resistance and to make the compound stronger.

# 3.4. Accelerators

Accelerators speed up the process of vulcanization and help make the final product more uniform. Many different chemicals are used by manufacturers as accelerators.

# 3.5 Sulfur

Sulfur is the usual material used in vulcanization. It helps rubber retain its characteristics in extreme hot and cold temperatures.

# 3.6. Fibers, Metals and Others

Although waste rubber products are not unique when compared to other types of solid waste they do possess inherent characteristics that make their disposal or their reuse difficult. Rubber is usually combined with other materials such as fibers and metals such as steel or nylon cord belted tires.

Rubber products are made in a variety of sizes and shapes. They resist compaction when disposed of in sanitary landfill operations and when incinerated, they give off sooty, noxious, high sulfur bearing fumes.

# 4. CHARACTERISTICS OF THE RUBBER INDUSTRY'S SOLID WASTES

# 4.1. Rubber Solid Wastes

In this description of the fabricated rubber products industry, the percentages cited are for the year 1968. However, they are treated as though they are indicative of today's operations.

About 1,500 different corporations in over 2000 plant sites produce approximately 20 billion pounds of finished product yearly. The manufacturing facilities are located predominantly in the central and northeast states. Ohio leads with about 20 percent of the nation's production capacity, and California is second with about 7 percent.

About 70 percent of the 10 billion pounds of industry products are tires and tire products.. About 200 million tires were produced in 1968. The rubber foot-wear segment of the industry makes up about 4 percent of total production; belting about 2 percent; rubber hose about 3 percent; foam and sponge rubber about 5 percent. The remaining 16 percent is classified as mechanical goods, heels and soles, washers, hot water bottles. All of the 10 billion pounds of useful products from these five industry segments eventually become solid waste. Tires wear out faster than most rubber products; they deposit an estimated 400 million pounds per year in thread loss on the nation's highways.

It is estimated that the entire industry generates just over 1 billion pounds of solid waste annually, or about 10 percent as much as the products it produces. The tire production segment contributes about 40 percent of the 1 billion pounds. The mechanical goods segment is the next biggest solid waste producer at about 37 percent. In terms of minimizing the generation of solid waste, tire production is the most efficient and mechanical goods the least efficient. For example, only 5 percent of a tire's weight results in solid waste but 25 percent of a washer's weight is wasted.

Solid waste from the fabricated rubber products industry is made up of: shipping materials (paper and cardboard), rubber material, textile materials (high strength cording), metals (tire beads), and office wastes.

Adding the waste in these five categories from the five basic segments of the industry shows the composite industry solid waste to be about 20 percent paper, 34 percent rubber, 12 percent textiles, 10 percent metals, and 24 percent miscellaneous materials. Little or no attempt is made to segregate waste into its component parts to aid in its reuse or its disposal, except for rubber waste sold directly to waste reprocessors such as reclaimers.

In most cases, contractors haul the solid waste from the plant site for disposal elsewhere, generally to a landfill, but few are sanitary landfills. In plant collection costs range from \$4 to \$27 per ton of solid waste, and contractors fee's for disposal range from \$4 to \$20 per ton. For the entire industry, the weighted average cost for both in plant collection and offsite disposal approximates \$18 per ton of solid wastes.

Specially designed incinerators for burning the rubber industry's waste is a favored

alternative for solid waste management in the future. One such rubber incinerator operates in Hannover, Germany, at the Continental Tire Factory, but it is reported to be a Fairly expensive operation. To improve the economics of such a disposal method, groups of neighboring rubber industry plants may find it advantageous to group support a centrally located disposal-treatment facility.

A technique in which useful value is being extracted from waste rubber has been tried in England. A British firm operates a plant that incinerates 7 tons of waste tires per hour and uses the heat to generate 3,500 pounds per hour of low pressure steam needed in adjoining operations. The firm, the Watts Tire and Rubber Company, claims a savings of about \$100 per day over the use of coal to generate the steam.

Another rubber recycling technique under investigation is the pyrolysis, or thermal decomposition, of waste tires. In this method waste rubber is subjected to elevated temperatures, in the near absence of oxygen to break the .complex rubber molecule into its many components. Over 50 distinguishable compounds were found during bench scale testing of the process. At the lower pyrolysis temperatures (900 °F), the highest yields of the heavy and light oil liquid streams were found. At higher temperatures (1,700 °F), more gaseous products and more carbonaceous solid residue were found. Most of the sulfur in the tires appeared in this char product.

The key to energy or material recovery processes is the initial composition of the rubber when it was produced. If such recovery processes are proven to be economical then planners and managers will need some information about the empirical formula of discarded rubber products.

# 4.2. The Survey

In consulting with American Public Works Association (APWA), and the US Environmental Protection Agency (USEPA), a survey of approximately a dozen rubber manufacturing companies was undertaken. Information requested concerned amount of dry weight percent of the elements: Carbon, Hydrogen, Oxygen, Nitrogen, Sulfur and Ash present in the company's rubber products. The names of responding companies were to be kept confidential. A copy of the letter and the survey form and the 13 companies surveyed are filed at the library of the Stevens Institute of Technology, Hoboken, NJ, USA In addition to the data acquired through the survey, information was obtained from a report published by the US Department of The Interior, Bureau of Mines on the Destructive Distillation of Scrap Tires. All surveyed data are compiled in Table 2.

|        |       |       | %     | dry weight |      |       |
|--------|-------|-------|-------|------------|------|-------|
| SAMPLE | С     | Н     | 0     | N          | S    | ASE   |
| А      | 83.2  | 7.1   | 2.5   | 0.3        | 1.2  | 5.7   |
| в      | 83.2  | 7.4   | 2.6   | 0.3        | 1.1  | 5.4   |
| С      | 86.5  | 1.3   | 0     | 0.2        | 2.0  | 9.6   |
| D      | 90.2  | 0.5   | 0     | 0.2        | 1.7  | 8.3   |
| E      | 87.5  | 1.1   | 0     | 0.2        | 1.9  | 9.2   |
| F      | 83.4  | 1.3   | 0.5   | 0.1        | 2.0  | 12.7  |
| G      | 84.1  | 0.5   | 0     | 0.2        | 2.5  | 13.6  |
| н      | 84.7  | 2.1   | 0.5   | 0.2        | 2.3  | 10.2  |
| Ι      | 90.8  | 0.5   | 0     | 0.1        | 1.7  | 8.0   |
| J      | 84.3  | 0.7   | 0     | 0.4        | 2.5  | 12.7  |
| К      | 79.1  | 1.0   | 0     | 0.4        | 3.2  | 16.5  |
| L      | 89.5  | 0.6   | 0     | 0.2        | 2.2  | 8.0   |
| Μ      | 90.9  | 0.5   | 0     | 0.2        | 1.9  | 7.0   |
| Ν      | 79.4  | 3.5   | 1.1   | 0          | 0.7  | 15.3  |
| 0      | 89.95 | 9.84  | 0.01  | 0          | 0    | 0.2   |
| Р      | 54.26 | 5.69  | 0     | 0          | 0    | 40.05 |
| Q      | 63.02 | 8.56  | 1.74  | 0          | 1.74 | 24.94 |
| R      | 85.62 | 14.38 | 14.38 | 0          | 0    | 0     |

TABLE 2. Ultimate Analysis (Percent Dry Weight) of Rubber Ascertained Through

Survey and Research

# 5. DATA ANALYSIS, FORMULATION, MATHEMATICAL MODELING AND RECOMMENDATIONS

# 5.1. Data Analysis

A statistical analysis of the surveyed data is presented in Table 3. The original rubber solid waste ultimate analysis values in Table 1 are compared with that of the surveyed values in Table 3. Table 4 shows the differences, and the authors suggested Ultimate Analysis values. The suggested ultimate analysis values are calculated statistically by assigning the total percentage of C, H, O, N, S, and ASH to be equal to 100.000 percent.

|                    | С      | Н      | 0     | N     | S     | ASH    |  |
|--------------------|--------|--------|-------|-------|-------|--------|--|
| Average Value      | 82.775 | 3.698  | 0.497 | 0.166 | 1.591 | 11.521 |  |
| Standard Deviation | 9.537  | 4.146  | 0.884 | 0.132 | 0.922 | 9.199  |  |
| Variance           | 85.907 | 16.240 | 0.738 | 0.016 | 0.803 | 79.934 |  |
|                    |        |        |       |       |       |        |  |

|            | с      | Н     | o     | Ν     | s     | ASH    | TOTAL   |
|------------|--------|-------|-------|-------|-------|--------|---------|
| Table 1:   | 78.0   | 10.0  |       | 2.0   |       | 10.0   | 100.000 |
| Table 3:   | 82.775 | 3.698 | 0.497 | 0.166 | 1.591 | 11.521 | 100.248 |
| Suggested: | 82.570 | 3.689 | 0.496 | 0.166 | 1.587 | 11.492 | 100.000 |
|            |        |       |       |       |       |        |         |

TABLE 4. Comparison of Ultimate Analysis Data (% Dry Weight) in Table 1 and Table 3

# 5.2. Formulation and Mathematical Model

A survey was successfully undertaken by the authors to determine empirical chemical values for rubber products. The ultimate analysis values of solid rubber wastes are concluded to be: Carbon 82.570%, Hydrogen 3.689%, Oxygen 0.496%, Nitrogen 0.166%, Sulfur 1.587%, and Ash 11.492%, shown in Table 4. Based on the statistically analyzed data, an empirical chemical formula can then be written for the rubber solid waste as follows:

# $C_{82.570}\,H_{3.689}\,O_{0.486}\,\,N_{0.166}\,\,S_{1.587}\text{-}Ash_{11.492}$

The authors propose an over-simplified complete combustion mathematical model for the solid waste (Equation 2) assuming (a) the solid waste formula is  $C_aH_bO_cN_dS_e$ -Ash, (b) all nitrogen oxides (NOx) are in the form of nitrogen dioxide; (c) all C, H&O, N, and S are completely converted to carbon dioxide, water, nitrogen dioxide, and sulfur dioxide, respectively under ideal situation; and (d) the ash portion is not combustible.

 The coefficient numbers of a, b, c, d, and e will be 82.570, 3.689, 0.486, 1.666, and 1.587, respectively, for the rubber solid waste shown in Equation 1. By substituting a, b, c, d, and e from Equation 1 to Equation 2, one may obtain Equation 3 for the rubber solid waste:

C82.570 H3.689 O0.486 N0.166 S1.587-Ash11.492

$$+ (82.570 + 0.166 + 1.587 + 0.25x3.689 - 0.5x0.468) O_2$$
  
= 82.57(CO<sub>2</sub>) + 0.166(NO<sub>2</sub>) + 1.587(SO<sub>2</sub>) + 0.5x 3.689 (H<sub>2</sub>O) + Ash<sub>11.492</sub> .....(3)

Equation 2 is a general mathematical model for any solid waste to be completely incinerated. Equation 3a is a specific mathematical model for combustion of rubber solid waste only.

 $C_{82.570}\,H_{3.689}\,O_{0.486}\,\,N_{0.166}\,\,S_{1.587}\text{-}Ash_{11.492}\ +\ (85.011)\,O_2$ 

It has been known that the municipal solid waste (MSW) can be partially reused as a refuse derived fuel (RDF). The rubber solid waste can also be used as a RDF, under the condition that the nitrogen oxides and sulfur dioxide gases from the incinerator's stacks will meet the air pollutant discharge limitations. An environmental planner or plant manager may use Equation 3a to calculate the amount of rubber solid waste to be used as a supplemental RDF, and the air pollution control regulations can still be met.

# 5.3 Recommendations

Table 1 indicates the original ultimate analysis of the combustible components in municipal solid wastes (MSW) from the literature which are very useful for environmental planners and managers in evaluating the feasibility of alternative uses for solid waste such as heat generation and materials recycling. [1]. Table 1 shows that the data of ultimate analysis for both plastic solid wastes and rubber solid wastes were incomplete. Based on the authors' surveyed data from the rubber companies, and the statistical analysis, the technical ultimate analysis data for rubber solid waste are known to be :

# $C_{82.570} H_{3.689} O_{0.486} N_{0.166} S_{1.587} Ash_{11.492}$

Accordingly Table 1 has been revised. A replacement ultimate analysis of the combustible components in municipal solid wastes is now presented in Table 5.

| COMPONENT   | CARBON | HYDROGEN | OXYGEN | NITROGEN | SULFUR | ASH    |
|-------------|--------|----------|--------|----------|--------|--------|
|             |        |          |        |          |        |        |
| Food Wastes | 48.0   | 6.4      | 37.6   | 2.6      | 0.4    | 5.0    |
| Paper       | 43.5   | 6.0      | 44.0   | 0.3      | 0.2    | 6.0    |
| Cardboard   | 44.0   | 5.9      | 44.6   | 0.3      | 0.2    | 5.0    |
| Plastic     | 60.0   | 7.2      | 22.8   |          |        | 10.0   |
| Textiles    | 55.0   | 6.6      | 31.2   | 4.6      | 0.15   | 2.5    |
| Rubber      | 82.57  | 3.689    | 0.496  | 0.166    | 1.587  | 11.492 |
| Leather     | 60.0   | 8.0      | 11.6   | 10.0     | 0.4    | 10.0   |
| Garden      | 47.8   | 6.0      | 38.0   | 3.4      | 0.3    | 4.5    |
| Wood        | 49.5   | 6.0      | 42.7   | 0.2      | 0.1    | 1.5    |
| Dirt, Ashes | 26.3   | 3.0      | 2.0    | 0.5      | 0.2    | 68.0   |
|             |        |          |        |          |        |        |

TABLE 5: Ultimate Analysis (% Dry Weight) of the Combustible Components In Municipal Solid Wastes.

The authors recommend that (a) the missing information (marked in red color) for the plastic solid waste be investigated and completed; (b) perhaps all the rest MSW elements, such as the food wastes, paper wastes, cardboard wastes, plastic wastes, textiles wastes, leather wastes, garden trimmings, wood wastes, and dirt and ashes be individually investigated one-by-one by the researchers.

Current research rely on surveyed data and statistical analysis for characterization of municipal solid wastes (MSW) including the rubber solid waste. A proper solid waste

sampling method has been introduced in another authors' report [1]. If solid waste sampling method is adequate, the collected solid waste sample can be totally incinerated according to the general mathematical model of Equation 2. With accurate air sampling and analysis, the input solid waste, the output carbon dioxide, nitrogen oxides, sulfur dioxide, water steam, and residual ash can all be collected and measured. In turn, the target solid waste's formula can be mathematically calculated. This is so-called "reverse engineering" For instance, if a researcher has the information of [ $82.57(CO_2) + 0.166(NO_2) + 1.587(SO_2) + 1.845(H_2O) + Ash_{11.492}$ ] in Equation 3a, he/she may be able to approximately determine [ $C_{82.570}$  H<sub>3.689</sub> O<sub>0.486</sub> N<sub>0.166</sub> S<sub>1.587</sub>-Ash<sub>11.492</sub> + (85.011) O<sub>2</sub>] by reverse calculation.

The authors further recommend that future solid waste characterization research be done by complete solid waste combustion, effluent gas sampling, chemical analyses, and mathematical calculations using the general mathematical model (Equation 2).

# 6. SUMMARY AND CALL FOR FURTHER RESEARCH

# 6.1 Summary

This publication and its sister report [1] are the results of a study of the inherent properties of solid waste. Ultimate analysis values are used to find representative empirical chemical formulae for typical municipal solid waste (MSW). These formulae can be used by planners and managers in evaluating the feasibility of alternative uses for solid waste such as heat generation and materials recycling.

An attempt was made to improve the ultimate analysis model values with special emphasis on rubber solid waste. A survey was undertaken to determine empirical chemical values for rubber products. Characteristics of the rubber industry's waste is discussed as well as some alternatives that have been tested or implemented. The ultimate analysis values of rubber solid wastes are concluded to be: carbon 82.570%, hydrogen 3.689%, oxygen 0.496%, nitrogen 0.166%, sulfur 1.587%, and ash 11.492%. A general mathematical model has been developed for predicting the air pollution to be caused by carbon dioxide, sulfur dioxide and nitrogen dioxide, if the rubber solid waste is reused as a supplemental refuse derived fuse (RDF). The same model can also be applied to other solid wastes when the solid waste is to be considered as an heat energy source. Accelerators: Accelerators speed up the process of vulcanization and help make the final product more uniform. Many different chemicals are used by manufacturers as accelerators.

Antioxidants: Antioxidants are added to rubber to help protect it from exposure to the air and sunlight. Some chemicals are used as antioxidants to prevent the cracking of rubber, which is a problem caused by oxidation.

**Butyl rubber:** Butyl\_is made by the copolymerization of isobutylene ( $C_4H_8$ ), a gas which is a product of petroleum refining, with a very small amount of another unsaturated hydrocarbon such as isoprene. Butyl rubber was first used in inner tubes for tires because it holds air much better than natural rubber. It has often been used in vibration mounts because of its ability to absorb shock. In addition to its air holding characteristic, it resists aging, heat, acids and is a good insulator for electricity.

**Compounding and mixing for rubber manufacturing:** It is the final step in making the rubber ready to be manufactured into a final product. During this process, different ingredients are compounded and mixed with the rubber to improve its characteristics. The main additives used in the compounding of rubber are fillers, antioxidants, pigments,

accelerators and sulfur.

**Fibers and metals for rubber:** Rubber is usually combined with other materials such as fibers and metals such as steel or nylon cord belted tires.

**Fillers:** Fillers are added to dry rubber to create a larger volume and to make it stronger and easier to handle. Clay is a neutral filler which makes the compound easier to handle but does not increase its strength.

**Neoprene:** Neoprene is a synthesis rubber made by making a polymer of the monomer chloroprene ( $C_4H_5Cl$ ). Chloroprene is much like the basic molecule of rubber, isoprene, because it has a long chain of four carbons and five hydrogens. The basic materials which go into making chloroprene are salt, limestone, and coal.

**Nitrile rubber:** Nitrile rubber is another synthetic rubber which is oil and gasoline resistant. Besides its resistance to fuels, nitrile rubber exhibits good flexibility at low temperatures. Nitrile rubber is made by polymerizing a mixture of two monomers, butadiene and acronitrile which are obtained indirectly from petroleum and air.

**Pigment:** The most widely used of which is carbon black, are added to the rubber to give it greater wear resistance and to make the compound stronger.

**Polybutadiene rubber:** Polybutadiene is made from butadiene and is more elastic and generates less heat than other types of synthetic- rubber except polyisoprene. It is finding increasing usage in the rubber industry.

**Polyisoprene rubber:** Polyisoprene duplicates the natural rubber polymer chain in natural rubber. It therefore duplicates almost all the physical characteristics of natural rubber.

**Polysulfide rubber:** Polysulfide is made by the copolymerization of ethylene dichloride  $(C_2H_4Cl_2)$  and sodium polysulfide  $(Na_2S_4)$ . These rubbers have very good resistance to softening and swelling in gasoline and greases. Therefore, it is widely used in products such as lining for gasoline hoses and for printing plates and rollers. Polysulfide rubbers also have good resistance to aging, air and sunlight.

**Polyurethane Rubber:** Polyurethane rubbers are made from ethylene or propylene glycols and adipic acid which form polyesters or polyethers which are further reacted with isocyanates. They resist age and heat and are able to withstand tremendous stresses and pressures. Polyurethane rubbers can be made extremely tough. They are used chiefly in manufacturing upholstery, foam rubber mattresses and insulating materials. Foams made from polyurethane can be made in a wide variety of densities and can be manufactured in either a flexible or rigid state.

**Rubber solid waste empirical chemical formula:** It can then be written for the rubber solid waste as :  $C_{82.570} H_{3.689} O_{0.486} N_{0.166} S_{1.587}$ -Ash<sub>11.492</sub>

**Rubber:** Natural rubber is an elastic, waterproof substance obtained in nature from several tropical trees. Synthesis rubber is produced synthetically from chemicals. Highly resistant to electricity and moisture, rubber is the most elastic substance known to man. Rubber belongs to the family of substances composed of hydrogen and carbon. Other members of the hydrocarbon family include natural gas, gasoline and oil of turpentine. The reason most synthetic rubbers are made from petroleum products is because both are members of the hydrocarbon family.

**Silicone Rubber:** Silicone Rubbers are made of oxygen and silicon, with hydrocarbons added. They keep their rubber properties at lower and higher temperatures than natural rubber or most other synthetic rubbers. They can be used in a temperature range of 130°F to 600°F. These rubbers are ideal for use in products which are exposed to extremely high or low temperatures such as seals, gaskets and other parts for jet airplanes. Silicone rubbers are different than other rubbers because the basic polymer chain contains no carbon atoms.

**Solid Wastes:** The term solid wastes is all inclusive and encompasses all sources, types of classifications, composition, and properties. Wastes that are discharged may be of significant value in another setting, but they are of little or no value to the possessor who wants to dispose of them. In the USA, a solid waste is officially defined by the US Environmental Protection Agency (USEPA) as the following: any garbage, refuse, sludge from a waste

treatment plant, water supply treatment plant or air pollution control facility discarded materials including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations and from community activities Sect. 6903(27). The regulatory definition is found at 40CFR261.2(a)(1). Therefore, a solid waste is defined by the US regulation as any "discarded material" not expressly excluded by the US regulations. A material is considered "discarded" if it is "abandoned", "recycled", or "considered inherently waste-like". Accordingly, the discarded, abandoned, recycled, or waste-like materials generated from a laboratory facility, or an industrial plant are all considered to be solid wastes.

**Styrene-Butadiene Rubber (SBR):** SBR is the most important general purpose synthetic rubber in large scale production. It accounts for about 70 percent of all synthetic rubber produced in the United States. Some of the synthetic rubbers which have been commercially developed include Neoprene, Butyl, Polysulfide, Silicone, Polyurethane, Polyisoprene and Polybutadiene.

**Sulfur:** Sulfur is the usual material used in vulcanization. It helps rubber retain its characteristics in extreme hot and cold temperatures.

**Synthesis rubber**: It is produced synthetically from chemicals. There are two basic groups of synthetic rubbers: (a) general purpose rubbers and (b) special purpose rubbers. General purpose rubbers take the place of natural rubber while special purpose rubbers improve on the characteristics of natural rubber. For instance, some special purpose rubbers are made so that they will have a greater resistance to gasoline or oils, while others are made to withstand the effects of exposure to air or high temperatures.

Ultimate analysis values of rubber solid wastes: They are concluded to be: Carbon 82.570%, Hydrogen 3.689%, Oxygen 0.496%, Nitrogen 0.166%, Sulfur 1.587%, and Ash 11.492%.

# ACKNOWLEDGMENT

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Wang, LK, McGinnis, WC, and Wang, MHS (1986). Analysis and Formulation of combustible components in Wasted Rubber Tires. US National Technical Information Service (NTIS), Springfield, VA, USA. Technical Report No. PB86-169281/AS, 39 pages.

This publication is an updated and expanded version of the above LIWT-Stevens research report. At the time of the research, Dr. Lawrence K. Wang and Dr. Mu-Hao Sung Wang were Adjunct Professors of Stevens. 1. Wang, LK, McGinnis, WC and Wang, MHS (2022). Analysis and formulation of combustible components in non-hazardous solid wastes. In: *"Evolutionary Progress in Science, Technology, Engineering, Arts and Mathematics (STEAM)"*, Wang, LK and Tsao, HP (eds.), 4 (9A), STEAM-VOL4-NUM9A-SEPT2022, 37 pages, Lenox Institute Press, Massachusetts, USA. <u>https://doi.org/10.17613/0p7c-wp38</u>

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6. Wang, LK, Wang, MHS, Hung, YT, and Aziz, HA (2022). Solid Waste Engineering and Management, Volume 2, Springer Nature Switzerland, 728 pages.

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# **APPENDIX** A

# Editors of "EVOLUTIONARY PROGRESS IN SCIENCE, TECHNOLOGY, ENGINEERING, ARTS AND MATHEMATICS (STEAM)"

# 1. Dr. Lawrence K. Wang (王抗曝)

Editor Lawrence K. Wang has served the society as a professor, inventor, chief engineer, chief editor and public servant (UN, USEPA, NY, Albany) for 50+ years, with experience in entire field of environmental science, technology, engineering, arts and mathematics (STEAM). He is a licensed NY-MA-NJ-PA-OH Professional Engineer, a certified NY-MA-RI Laboratory Director, a MA-NY Water Operator, and an OSHA Train-the-Trainer Instructor.

He has special passion, and expertise in developing various innovative technologies, educational programs, licensing courses, international projects, academic publications, and humanitarian organizations, all for his dream goal of promoting world peace. He is a retired Acting President/Professor of the Lenox Institute of Water Technology (LIWT), USA, a United Nations Industrial Development Organization (UNIDO) Senior Advisor in Vienna, Austria, and a former professor/visiting professor of Rensselaer Polytechnic Institute, Stevens Institute of Technology, University of Illinois, National Cheng Kung University, Zhejiang University, and Tongji University.

Dr. Wang is the author of 750+ papers and 60+ books, and is credited with 29 invention patents. He holds a BSCE degree from National Cheng Kung University, Taiwan, ROC, a MSCE degree from the University of Missouri, a MS degree from the University of Rhode

Island and a PhD degree from Rutgers University, USA. Currently he is the book series editor of CRC Press, Springer Nature Switzerland, Lenox Institute Press, World Scientific Singapore, and John Wiley.

Dr. Wang has been a Delegate of the People to People International Foundation, an American Academy of Environmental Engineers (AAEE) Diplomate, a member of WEF, AWWA, ASCE, AIChE, ASPE, CIE and OCEESA, and a recipient of WEF Kenneth Research Award (NY), Five-Star Innovative Engineering Award (first DAF drinking water plant in Americas), and Korean Pollution Control Association Award (Transfer of flotation technology to South Korea).

# 2. Dr. Hung-ping Tsao (曹恆平)

Editor Hung-ping Tsao has been a mathematician, a university professor, and an assistant actuary, serving private firms and universities in the United States and Taiwan for 30+ years. Dr. Tsao has been an Associate Member of the Society of Actuaries and a Member of the American Mathematical Society.

His research have been in the areas of college mathematics, actuarial mathematics, management mathematics, classic number theory and Sudoku puzzle solving. In particular, bikini and open top problems are presented to share some intuitive insights and some type of optimization problems can be solved more efficiently and categorically by using the idea of the boundary being the marginal change of a well-rounded region with respect to its inradius; theory of interest, life contingency functions and pension funding are presented in more simplified and generalized fashions; the new way of the simplex method using cross-multiplication substantially simplified the process of finding the solutions of optimization problems; the generalization of triangular arrays of numbers from the natural sequence based to arithmetically progressive sequences based opens up the dimension of explorations; the introduction of an innovative way to solve Sudoku puzzles makes everybody's life so much easier and other STEAM project development.

Dr. Tsao is the author of 10+ books and over 40 academic publications. Among all of the above accomplishments, he is most proud of solving manually in the total of ten hours the hardest Sudoku posted online by Arto Inkala in early July of 2012 and introducing an easy way to play Sudoku in 2019.

He earned his high school diploma from the High School of National Taiwan Normal University, his BS and MS degrees from National Taiwan Normal University, Taipei, Taiwan, his second MS degree from the UWM in USA, and a PhD degree from the University of Illinois, USA.



Editors of the eBOOK Series of the "EVOLUTIONARY PROGRESS IN SCIENCE, TECHNOLOGY, ENGINEERING, ARTS AND MATHEMATICS (STEAM)"

Dr. Lawrence K. Wang (王抗曝) - - left

Dr. Hung-ping Tsao (曹恆平) -- right

# **APPENDIX B**

# THE E-BOOK SERIES OF

# "EVOLUTIONARY PROGRESS IN SCIENCE, TECHNOLOGY, ENGINEERING, ARTS AND MATHEMATICS (STEAM)"

The acronym STEM stands for "science, technology, engineering and mathematics". In accordance with the National Science Teachers Association (NSTA), "A common definition of STEM education is an interdisciplinary approach to learning where rigorous academic concepts are coupled with real-world lessons as students apply science, technology, engineering, and mathematics in contexts that make connections between school, community, work, and the global enterprise enabling the development of STEM literacy and with it the ability to compete in the new economy".

The problem of this country has been pointed out by the US Department of Education that "All young people should be prepared to think deeply and to think well so that they have the chance to become the innovators, educators, researchers, and leaders who can solve the most pressing challenges facing our nation and our world, both today and tomorrow. But, right now, not enough of our youth have access to quality STEM learning opportunities and too few students see these disciplines as springboards for their careers." STEM learning and applications are very popular topics at present, and STEM related careers are in great demand.

According to the US Department of Education reports that the number of STEM jobs in the United States will grow by 14% from 2010 to 2020, which is much faster than the national

average of 5-8 % across all job sectors. Computer programming and IT jobs top the list of the hardest to fill jobs.

Despite this, the most popular college majors are business, law, etc., not STEM related. For this reason, the US government has just extended a provision allowing foreign students that are earning degrees in STEM fields a seven month visa extension, now allowing them to stay for up to three years of "on the job training". So, at present STEM is a legal term.

The acronym STEAM stands for "science, technology, engineering, arts and mathematics". As one can see, STEAM (adds "arts") is simply a variation of STEM. The word of "arts" means application, creation, ingenuity, and integration, for enhancing STEM inside, or exploring of STEM outside.

It may also mean that the word of "arts" connects all of the humanities through an idea that a person is looking for a solution to a very specific problem which comes out of the original inquiry process. STEAM is an academic term in the field of education. The University of San Diego and Concordia University offer a college degree with a STEAM focus.

Basically STEAM is a framework for teaching or R&D, which is customizable and functional, thence the "fun" in functional. As a typical example, if STEM represents a normal cell phone communication tower looking like a steel truss or concrete column, STEAM will be an artificial green tree with all devices hided, but still with all cell phone communication functions. This e-book series presents the recent evolutionary progress in STEAM with many innovative chapters contributed by academic and professional experts.