# ESTIMATION OF CALORIFIC VALUE OF BIOMASS FROM ITS ELEMENTARY COMPONENTS BY REGRESSION ANALYSIS

By

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# CERTIFICATE

This is to certify that the work in this thesis report entitled **Estimation of calorific value of biomass from its elementary components by regression analysis** submitted by **Vijay Krishna Moka** in partial fulfillment of the requirements for the degree of Bachelor of Technology for the session 2011-2012 in the department of Mechanical Engineering, National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

Date:

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# ABSTRACT

*The calorific value is one of the most important properties of biomass fuels for design calculations or numerical simulations in thermochemical conversion systems for biomass. There are a number of formulae proposed in the literature to estimate the calorific value of biomass fuels from its elementary components by i.e. proximate, ultimate and chemical analysis composition. In this thesis, these correlations were evaluated statistically by Regression Analysis based on a larger database of biomass samples collected from the open literature. It was found that the correlations based on linear multiple regression analysis is the most accurate. The correlations based on the non-linear regression analysis have very low accuracy. The low accuracy of previous correlations is mainly due to the limitation of samples used for deriving them. To achieve a higher accuracy, new correlations were proposed to estimate the Calorific value by Regression analysis based on present database. The new correlation between the Calorific value and elemental components of biomass could be conveniently used to estimate the Calorific Value from Regression analysis. The new formula, based on the composition of main elements (in wt. %) C, H, O, N and S based on nonlinear regression analysis is*

$$C^2 + C \times O^2 + 0.03\ C \times H + 0.60\ C - O + 0.11\ O \times N + 0.53\ S - 0.33\ S \times O = \text{Calorific Value (Mj/Kg)}$$

*whose R-squared value is 0.956*

## ACKNOWLEDGEMENTS

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# Abbreviations and Acronyms

## Technical

HHV High heating value

LHV Low heating value

MC Moisture content

## Subscripts

Wt. Weight

t Total

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# 1. Introduction

Biomass is one of the most promising renewable energy resources on earth which is used in the form of solid, liquid and gaseous fuels. The demand for bioenergy systems in small scale industry is increasing at faster rate due to its lower investment cost. Currently bioenergy is the second largest commercial renewable energy source. Current total biomass energy usage ranges around 12% of world total primary energy consumption, mainly in traditional applications like cooking in developing nations like India. Also the usage of wood for heating purposes is increasing day-today. Normal domestic wood-burning appliances include fireplaces, pellet stoves and burners, central heating furnaces and boilers for wood logs and wood pellets [1]

Biomass can be converted into either heat energy or electrical or energy carriers like charcoal, oil, or gas using both thermochemical and biochemical conversion methods. Combustion is the most developed and frequently applied process used for solid biomass fuels because of its cheap cost and high reliability. During combustion, the biomass first loses its moisture at temperatures up to 100°C, using heat from other particles that release their heat value. As the dried particle heats up, volatile gases containing hydrocarbons, CO, $CH_4$ and other gaseous components are released. In a combustion process, these gases contribute about 70% of the heating value of the biomass. Finally, char oxidizes and ash remains [2]

Among the usage of biomass the wood pellet is also included. Many new techniques are available to turn wood and crop wastes into standardized pellets that are eco-friendly and easy to handle [3]

## 1.1 Wood Pellets

The wood is cut into small particles by grinding process and is dried. It may then be processed with readily available equipment to make wood pellets. These processed wood pellets have comparatively high calorific value, easy transportation and storage and can be utilized for heat and power. Pellet plants can be built at a wide range of sizes. Smaller plants require less feed. Larger plants will generally offer good economy of scale, but may also face greater costs for feed brought in from a larger growing area [4]

In the production of fuel pellets and briquettes, the feedstock has to be milled, pulped and undergoes steam before being transformed into a denser product. It is in either refined powder form or crop residue that has been put under high pressure so as to be formed into small cylinders like structures of different sizes. At a given pressure, in its phase of production and reduced humidity, the energy density of the wood pellet obtained is about almost double that of the wood. Hence reduction of size is an important treatment of biomass for energy conversion. Reduction of size of the particle increases the total surface area, pore size of the material and the number of contact points for inter-particle bonding in the compaction process [5] A number of properties are commonly known to affect the success of pelleting, including calorific value, moisture content of the material, bulk density, particle size, fiber strength of the material, lubricating characteristics of the material, and natural binders.

Utilization of wood and crop residues as an energy source will serve to reduce consumption of fossil fuels, thereby reducing the emission of greenhouse gases to the environment. Ideal in providing fuel for heating devices, the wood pellet it is pure, non-pollutant, and neutral in carbon dioxide ($CO_2$) emissions. In other words, it doesn't contribute to the destabilization of the ambient, as whatever carbon dioxide emissions occur from its combustion they are counterbalanced by equivalent amounts of ($CO_2$) that have been absorbed from the plant during its life, process of photosynthesis, it burns completely, without producing smoke, leaving minimum residue of ash, always less than 1%, which can be used as a precious fertilizer for the garden too [6]

## 1.2 Biomass Conversion Processes

The biomass conversion process (Bio conversion process) has several routes depending upon temperature, pressure, micro-organisms utilized, process and the culture conditions. These routes are classified in following three broad categories.

- Direct Combustion
- Thermochemical Conversion
- Biochemical Conversion

### 1.2.1 Thermochemical Conversion

Biomass is decomposed in thermo-chemical processes having various combinations of temperatures and pressures. Gasification is a process in which combustible materials are partially oxidized. The product of gasification is a combustible synthesis gas. Since gasification involves the partial oxidization of the feed rather than complete, gasification processes operate in an oxygen-lean environment.

Gasification of Biomass is carried out by one of the following two processes.

- Heating the biomass with limited air or oxygen.
- Heating at high temperature and high pressure in presence of steam and oxygen.

Biomass can be converted into gases, liquids, and solids through *pyrolysis* at temperatures of 500 -900°C by heating in a closed vessel in the absence of oxygen

## 1.2.2 Thermal Properties of Biomass

Each type of biomass has its specific properties which determine its performance as a fuel in combustion. Most important properties regarding thermal conversion of fuels is as follows.

- Moisture content
- Ash content
- Volatile matter content
- Elemental composition

- Calorific value
- Bulk density

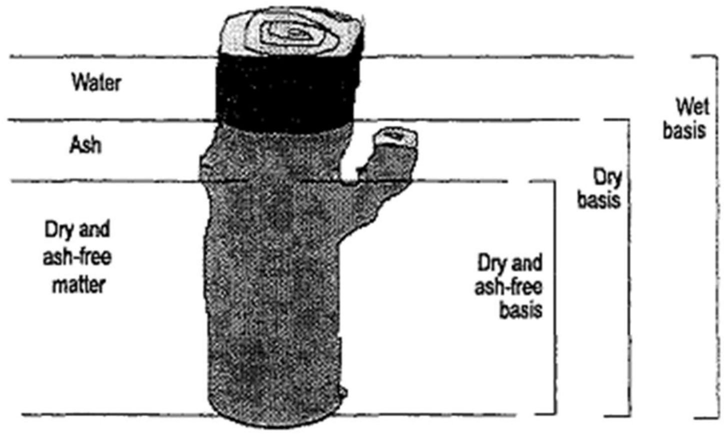


**Figure 1.1: Biomass composition [7]**

### 1.2.2.1 Moisture Content

The moisture content of biomass is the quantity of water in the material, expressed as a percentage of the material's weight. This weight can be referred to on wet basis and on dry ash free basis. If the moisture content is determined on a 'wet' basis, the water's weight is expressed as a percentage of the sum of the weight of the water, ash, and dry-and-ash-free matter. Similarly, when calculating the moisture content on a 'dry' basis (however contradictory that may seem), the water's weight is expressed as a percentage of the weight of the ash and dry-and-ash-free matter. Finally, the moisture content can be expressed as a percentage of the "dry and-ash-free" matter content. In that last case, the water's weight is related to the weight of the dry biomass. Because the moisture content affects the value of biomass as a fuel, the basis on which the moisture content is measured must always be mentioned. This is particularly important because biomass materials exhibit a wide range of moisture content (on a wet basis), ranging from less than 10 percent for cereal grain straw up to 50 to 70 percent for forest residues [7]

### 1.2.2.2 Ash Content

The inorganic component can be expressed as same as the moisture content on a wet, dry and ash free basis. In general it is expressed on dry basis. It is the inorganic matter left out after complete combustion of the biomass. Generally contains mainly Calcium, Potassium, Magnesium and Phosphorus elements that affect the ash fusion.

The ash value is an integral part of the plant structure that consists of a wide range of elements that represents less than 0.5 % in wood and 10 % in diverse agricultural crop material and up to 30-40 % in rice husks and milfoil.

The total ash content in the biomass and the chemical composition of the ash are important. The composition of the ash affects its behavior under the high temperatures of combustion and gasification. For example, melted ash may cause problems in both combustion and gasification reactors. These problems may vary from clogged ash-removal caused by slagging ash to severe operating problems in fluidized-bed systems [7]

#### 1.2.2.3 Volatile Matter Content

Volatile matter refers to the part of the biomass that is released when the biomass is heated (up to 400 to 500°C). During this heating process the biomass decomposes into volatile gases and solid char. Biomass typically has a high volatile matter content (up to 80 percent), whereas coal has a low volatile matter content (less than 20 percent) or, in the case of anthracite coal, a negligible one [7]

#### 1.2.2.4 Elemental Composition

The composition of the ash-free organic component of biomass is relatively uniform. The major components are carbon, oxygen, and hydrogen. Most biomass also contains a small proportion of nitrogen and sulphur. Table 1.1 presents the average range of percentages.

The carbon (C), hydrogen (H), oxygen (O), sulphur(S) and nitrogen (N) determination in biomass represents the so called elementary analysis. These elements are detected by an elemental analyzer. About 200 mg of sample are burned at 900 ° C in an oxygen atmosphere, so the C is converted into $CO_2$, H in H20, S into $SO_2$ and the N in $N_2$. The first three compounds are detected quantitatively by an IR detector, while $N_2$ is determined by a thermal conductivity detector [8]

#### 1.2.2.5 Calorific Value

The calorific value is one of the most important characteristics of a fuel, and it is useful for planning and control of the combustion plants. It indicates the amount of heat that develops from the mass (weight) in its complete combustion with oxygen in a calorimeter standardize. It is defined as the amount heat energy released during the complete combustion of unit mass of biomass.

There are two types of calorific value (usually expressed in kcal/kg or MJ/kg) might be considered:

1. Higher heating value (HHV): it is the amount of heat released by a complete combustion of a mass unit of a sample at constant volume in an oxygen atmosphere and at

the standard conditions (101.3 kPa, 25°C). The HHV takes into account the latent heat of vaporization of water, and it assumes that the water component is in liquid state at the end of combustion.

2. Lower heating value (LHV), doesn't include the water condensation heat. The high heating value can be determined experimentally in the laboratory with adiabatic calorimeter.

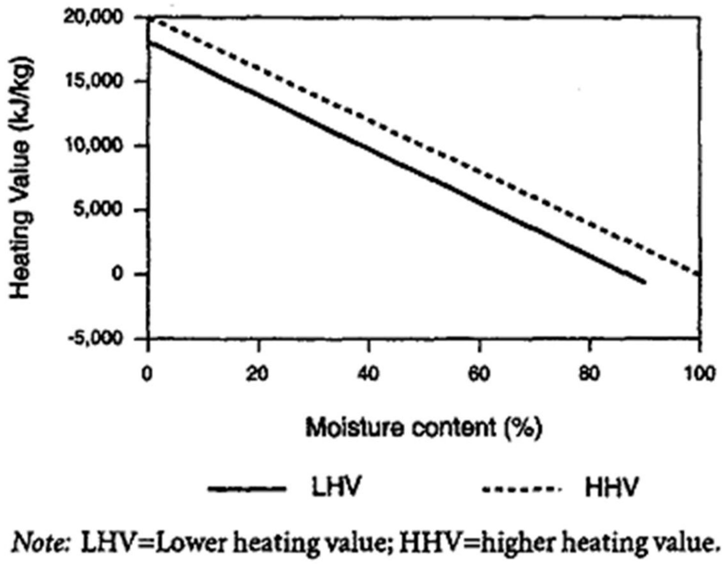


**Figure 1.2 : calorific value of biomass as a function of moisture content [7]**

The lower heating value is calculated net of fuel moisture and water that forms in the combustion reaction. In practice, the value is obtained by subtracting to the HHV the heat water condensation produced during combustion, using the following formula:

$$LHV = HHV - 51.14 \times H_t$$

Where HHV is the high heating value, $H_t$ is the total hydrogen percentage. To evaluate the performance of biomass combustion in plant we usually refer to the lower heating value, because the most common boilers do not allow to recover the heat of water condensation[8]

### 1.2.2.6 Bulk Density

Bulk density refers to the weight of material per unit of volume. For biomass it is generally expressed on an oven-dry-weight basis (zero moisture content) with a corresponding indication of moisture content. Similar to biomass moisture contents, biomass bulk densities show extreme variation, from lows of 150 to 200 kg/m$^3$ for cereal grain straws and shavings to highs of 600 to 900 kg/m$^3$ for solid wood.

Together, heating value and bulk density determine the energy density-that is, the potential energy available per unit volume of the biomass. In general, biomass energy densities are approximately one-tenth that of fossil fuels such as petroleum or high quality coal [7]

Table 1.1- Calorimeter parameters C2000 IKA [8]

| | |
|---|---|
| Analysis Mode: | hyperbolic |
| Sample weight: | 1 g |
| Range | 13.9 – 34.9 MJ/kg for 1 g sample |
| Precision | < 0.05 % RSD |
| Resolution | 1 kJ/kg |
| Temperature resolution | 0.0001 °C |
| Analysis temperature range | 13°C – 33°C |

### 1.2.2 Biochemical Conversion

There are two principal Biochemical conversion processes.

Anaerobic digestion involves microbiological digestion of biomass. The process and end products depend up to the microorganisms cultivated and cultured conditions.

Fermentation is a process of decomposition of organic matter by microorganisms especially bacteria and yeasts. About 15% of ethanol produced in the world is through fermentation of grains and molasses. Ethanol (Ethyl Alcohol) can be blended with gasoline (petrol) to produce gasohol (90% petrol and 10% ethanol). Processes have been developed to produce various fuels from various types of fermentations [9]

## Literature Review

1. Tillman (1978) [12] observed that the calorific value has a very strong influence of its carbon content and accordingly he derived the correlation for calorific value of biomass and its elementary components. The predictions of the correlations were found to be within 5%

2. Niessen (1995) [17] has derived the correlation for waste water sludge on dry basis. The predictions of the correlations were found to be within 6%

3. Khan and Abu Garah (1991) [18] found a new approach for finding calorific value of municipal solid waste based on the primary combustible components such as waste paper, plastic waste, leather, rubber and food.

4. Beckman et al. (1990) [19] derived a correlation for biomass derived oils. The predictions of the correlations were found to be within 5%

5. Grabosky and Bain (1981) [20] has derived the correlation of biomass based on pertinent reactions of C, H, S and N to $CO_2$, $H_2O$, $SO_2$ and $NO_2$. The predictions of this correlations were found to be within 1.5%

6. Chang (1979) [21] has derived correlation for waste material and its predictions for 150 pure organic compounds was found to be within 1.48%

7. Jenkins (1980) [22] has derived correlation for 19 data points of the biomass material using multiple regression analysis. The predictions of this correlation were found to be within 7%. Later he derived the more general correlation by taking 57 data points of biomass materials

8. Librebti, Ceotto and Candilo (2010) [16] has done the proximate analysis for the biomass material and found out that increase nitrogen content in the biomass decreases the calorific value of the biomass i.e. a high C/N ratio of a biomass burns easily and suitable

for thermochemical conversion, similarly a low C/N ratio implies the sample is more suitable for biochemical conversion process.

9. Gravalos (2010) [6] has tested the biomass lignocellulose crop samples in the laboratory and found out that Root and main stem of the plant have the same calorific value and lowest calorific value can be obtained at the leaves. Also seeds and flowers of a plant can have the highest calorific value

10. Channiwala and Parikh (2002) [14] have derived a correlation for calorific value of solid, liquid and gaseous fuels. The predictions of the correlations were found to be within 1.45%

11. Sheng and Azevedo (2005) [23] has derived a correlation for high heating values of biomass using basic analysis data. The predictions of the correlations were found to be within 5%

# 3. METHODOLOGY

## 3.1. Derivation of correlation

Steps involved in development and derivation of correlation are as follows:

### 3.1.1. Collection of data

The data containing a large number of biomass materials like pits, shells, seeds, energy crops, cobs, fuel wood, bark, hull-husk, straws, stalks, fibrous materials etc., from the published literature have been used to cover different values of carbon, hydrogen, sulphur, oxygen and nitrogen contents. Major sources of data are given in Table 3.1, Ref. [9-16]

### 3.1.2. Selection of suitable data

Through the process of collection of data information about 170 samples has been collected. Out of these about 96 data points have been used for the purpose of derivation of correlation. While 90 used for correlation of C,H and N., 79 for C,H and O., 74 for C,H and S and C,H,N,O,S combination.

The samples were so selected such that they approximately represent the relative proportion of their occurrence in nature and thus permit a derivation of useful correlation.

The data points considered for correlation by regression analysis ranges in carbon content from (27.80% to 92.70)%, hydrogen content (0.10 to 8.80)%, oxygen content (0.20 to 49.50)%, nitrogen content (0.00 to 5.95)% and sulphur (0.00 to 1.05)(wt. % on dry basis).

### 3.1.3. Selection of Suitable forms of correlation

There are many correlations; both linear and nonlinear were proposed which were discussed in literature review. They mostly are rated on the basis of R-squared value. R-squared is Pearson's regression coefficient which ranges from 0 to 1. R-squared value above 0.5 is valid and above 0.7 is the best R-squared value for a given correlation. The R-squared value can be determined using Regression analysis for multivariable from 'Microsoft Excel 2010' (using Data analysis addin) or 'IBM SPSS Statistics 20' software.

### 3.1.4. Validation of correlation

To confirm the validity of these equations, a variety of various samples were examined. Table 5.1 shows the results obtained. Residual in the table gives the error obtained by statistical analysis. It is obtained by the difference in the actual calorific value to that of the predicted value. The actual and computed values have been represented graphically.

Table 3.1- Data collected from the published literature

| Serial no. | Raw materials (biomass) | Carbon (%) | Hydrogen (%) | Oxygen (%) | Nitrogen (%) | Sulphur (%) | Calorific value (Mj/kg) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | Peat | 56.00 | 5.00 | 35.00 | 1.00 | 0.00 | 20.66 | 9 |
| 2 | Coconut shell | 50.22 | 5.70 | 43.37 | 0.00 | 0.00 | 20.49 | 10 |
| 3 | Oak bark | 49.70 | 5.40 | 39.30 | 0.20 | 0.10 | 19.42 | 11 |
| 4 | Hemlock wood | 50.40 | 39.30 | 0.20 | 0.10 | 0.10 | 20.05 | 12 |
| 5 | Douglas fir wood | 50.64 | 6.18 | 43.00 | 0.06 | 0.02 | 20.37 | 13 |
| 6 | Chaparral wood | 46.90 | 5.08 | 40.17 | 0.54 | 0.03 | 18.61 | 22 |
| 7 | Eucalyptus globules wood | 48.18 | 5.92 | 44.18 | 0.39 | 0.01 | 19.23 | 22 |
| 8 | Cotton stalks | 39.47 | 5.07 | 38.09 | 1.25 | 0.02 | 15.83 | 24 |
| 9 | Bagasse | 44.80 | 5.35 | 39.55 | 0.38 | 0.01 | 17.33 | 22 |
| 10 | Rice husks patni- 23 | 38.92 | 5.10 | 37.89 | 2.17 | 0.12 | 15.67 | 25 |
| 11 | Dry subhabul wood | 48.13 | 5.86 | 40.35 | 0.65 | 0.16 | 19.97 | 14 |
| 12 | Ply wood | 48.15 | 5.87 | 44.75 | 0.03 | 0.00 | 18.95 | 14 |
| 13 | Saw dust | 47.13 | 5.86 | 40.35 | 0.65 | 0.16 | 19.97 | 26 |
| 14 | Soquel point grant brow-nkep | 27.80 | 3.73 | 23.69 | 1.63 | 1.05 | 10.74 | 27 |
| 15 | Olive pit | 48.81 | 6.23 | 43.48 | | | 19.87 | 13 |
| 16 | Peach pit | 49.14 | 6.34 | 43.52 | 0.48 | 0.02 | 19.42 | 13 |
| 17 | Macadamia shell | 54.41 | 4.99 | 39.69 | 0.36 | 0.01 | 21.01 | 24 |
| 18 | Pistachios shell | 48.79 | 5.91 | 43.41 | 0.56 | 0.01 | 19.26 | 24 |
| 19 | Hazel nut shell | 52.90 | 5.6 | 42.7 | 1.4 | | 19.30 | 24 |
| 20 | Spize mint | 37.23 | 5.34 | 33.38 | 5.95 | | 15.53 | 20 |
| 21 | Corn cob 1 | 46.58 | 5.87 | 45.46 | 0.47 | 0.01 | 18.77 | 25 |
| 22 | Corn cob 2 | 49.00 | 5.40 | 44.60 | 0.40 | | 17.00 | 25 |
| 23 | Akhrot pit | 49.81 | 5.64 | 42.96 | | | 18.85 | 24 |
| 24 | Groundnut shell | 45.72 | 5.96 | 43.41 | | | 19.20 | 13 |

| Serial no. | Raw materials (biomass) | Carbon (%) | Hydrogen (%) | Oxygen (%) | Nitrogen (%) | Sulphur (%) | Calorific value (Mj/kg) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 25 | Brazil nut shell | 49.15 | 5.70 | 41.02 | | | 18.30 | 15 |
| 26 | Castor seed shell | 44.25 | 5.64 | 42.80 | | | 17.60 | 15 |
| 27 | Wall nut shell | 53.50 | 6.60 | 41.5 | 1.10 | 0.06 | 18.86 | 15 |
| 28 | Almond shell | 47.80 | 6.00 | 41.50 | 1.10 | 0.06 | 18.86 | 15 |
| 29 | Sunflower shell | 47.40 | 5.80 | 41.30 | 1.40 | 0.05 | 18.23 | 15 |
| 30 | Wood chips | 48.10 | 5.99 | 45.74 | 0.08 | 0.00 | 19.91 | 13 |
| 31 | Canyon live Oak | 47.84 | 5.80 | 45.76 | 0.07 | 0.01 | 18.98 | 17 |
| 32 | Red wood | 50.64 | 5.98 | 42.88 | 0.05 | 0.03 | 20.72 | 19 |
| 33 | Soft wood | 52.10 | 6.10 | 41.00 | 0.20 | | 20.72 | 22 |
| 34 | Spruce wood | 51.90 | 6.10 | 41.90 | 0.30 | | 20.00 | 22 |
| 35 | Es | 47.30 | 6.00 | 46.50 | 0.10 | | 20.08 | 22 |
| 36 | Subabul wood | 48.15 | 5.87 | 44.75 | 0.03 | 0.00 | 19.77 | 22 |
| 37 | Eucalyptus | 46.04 | 5.82 | 44.75 | 0.03 | 0.00 | 18.64 | 23 |
| 38 | Eucalyptus grandis | 48.33 | 5.89 | 44.49 | 0.30 | 0.00 | 19.35 | 25 |
| 39 | Sudan grass | 44.58 | 5.35 | 39.18 | 1.21 | 0.01 | 17.39 | 15 |
| 40 | Douglas fir | 56.20 | 5.90 | 36.70 | 0.00 | 0.00 | 22.09 | 15 |
| 41 | Loblolly pine | 56.30 | 5.60 | 37.70 | 0.00 | 0.00 | 21.77 | 20 |
| 42 | Almond | 51.3 | 5.29 | 40.90 | 0.66 | 0.01 | 20.01 | 14 |
| 43 | Carbernet saurignon | 46.59 | 5.85 | 43.9 | 0.83 | 0.04 | 19.03 | 16 |
| 44 | Walnut | 48.2 | 6.25 | 43.24 | 1.61 | | 19.96 | 24 |
| 45 | Wheat straw (1) | 45.50 | 5.10 | 34.10 | 1.80 | | 17.00 | 24 |
| 46 | Paddy straw (ground) | 35.97 | 5.28 | 43.08 | 0.17 | | 14.522 | 20 |
| 47 | Cotton stalk | 39.47 | 5.07 | 39.14 | 0.45 | 0.16 | 20.05 | 20 |
| 48 | Mulberry stick | 44.23 | 6.61 | 46.25 | 0.51 | | 18.35 | 23 |
| 49 | Coconut coir | 50.29 | 5.05 | 39.63 | 0.45 | 0.16 | 20.05 | 24 |
| 50 | Sean leaves | 36.20 | 4.72 | 37.49 | 4.29 | | 18.12 | 20 |
| 51 | Olive mare | 39.75 | 5.55 | 46.82 | 0.17 | | 17.41 | 15 |
| 52 | Tea bush | 47.67 | 6.13 | 43.16 | 1.33 | | 19.84 | 17 |

| Serial no. | Raw materials (biomass) | Carbon (%) | Hydrogen (%) | Oxygen (%) | Nitrogen (%) | Sulphur (%) | Calorific value (Mj/kg) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 53 | Sal seed husk | 48.12 | 6.55 | 35.93 | 0.00 | 0.00 | 20.60 | 17 |
| 54 | Eucalyptus saw dust | 49..37 | 6.40 | 42.01 | 2.02 | | 18.50 | 19 |
| 55 | Tea waste | 48.60 | 5.50 | 39.50 | 0.50 | | 17.10 | 15 |
| 56 | Cotton gin waste | 42.66 | 6.05 | 49.50 | 0.18 | 0.00 | 17.48 | 18 |
| 57 | Cotton gin trash | 39.59 | 5.26 | 36.38 | 2.09 | 0.00 | 16.42 | 21 |
| 58 | Almond oak wood waste | 49.50 | 5.70 | 41.30 | 0.20 | 0.00 | 19.22 | 20 |
| 59 | White fir | 49.00 | 5.98 | 44.75 | 0.05 | 0.01 | 19.95 | 13 |
| 60 | Tan oak | 48.67 | 6.03 | 44.99 | 0.06 | 0.04 | 18.93 | 23 |
| 61 | Red wood char(790$^0$F) | 75.60 | 3.30 | 18.40 | 0.20 | 0.20 | 28.84 | 23 |
| 62 | Oak char(820$^0$ F) | 67.70 | 2.40 | 14.40 | 0.40 | 0.20 | 24.79 | 23 |
| 63 | Coconut shell char(750$^0$ C) | 88.95 | 0.76 | 6.04 | 1.38 | 0.00 | 31.12 | 22 |
| 64 | Qr 550 | 87.10 | 2.40 | 6.90 | 0.50 | | 32.72 | 14 |
| 65 | PhC300 | 57.80 | 5.00 | 36.50 | 0.20 | | 22.84 | 14 |
| 66 | EsC700 | 92.70 | 1.60 | 3.30 | 0.40 | | 32.20 | 14 |
| 67 | MSW | 47.60 | 6.00 | 32.90 | 1.20 | 0.30 | 19.87 | 14 |
| 68 | Sewage sludge | 14.20 | 2.10 | 10.50 | 1.10 | 0.70 | 4.74 | 14 |
| 69 | Missippi hyacinth digested slurry | 31.70 | 3.82 | 23.20 | 1.98 | 0.00 | 12.28 | 14 |
| 70 | RDF | 44.72 | 6.21 | 38.36 | 0.69 | 0.00 | 19.49 | 15 |
| 71 | Animal waste | 35.10 | 5.30 | 38.70 | 2.50 | 0.40 | 13.40 | 15 |
| 72 | Redwood char(800-1725)$^0$F | 78.80 | 3.50 | 13.20 | 0.20 | 0.20 | 30.47 | 14 |
| 73 | ERW char | 54.90 | 0.80 | 1.80 | 1.10 | 0.20 | 18.65 | 14 |
| 74 | Lignite char | 89.00 | 1.10 | 8.90 | 0.70 | 0.30 | 31.30 | 14 |
| 75 | Hemp | 46.90 | | | | | 18.20 | 14 |
| 76 | Sorghum | 46.10 | 5.90 | | 0.84 | | 18.30 | 14 |
| 77 | Miscanthus | 47.70 | 5.70 | | 0.79 | | 18.50 | 14 |

| Serial no. | Raw materials (biomass) | Carbon (%) | Hydrogen (%) | Oxygen (%) | Nitrogen (%) | Sulphur (%) | Calorific value (Mj/kg) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 78 | Switch grass | 48.30 | 5.90 | | 1.00 | | 18.50 | 16 |
| 79 | Poplar | 47.50 | 5.90 | | 0.23 | | 19.20 | 16 |
| 80 | Willow | 48.80 | 5.90 | | 1.02 | | 19.00 | 16 |
| 81 | Black locust | 48.60 | 5.80 | | 0.46 | | 19.10 | 16 |
| 82 | Gaint reed | 48.70 | 6.00 | | 0.37 | | 18.90 | 16 |
| 83 | Bagasse | 47.00 | 6.50 | | 0.00 | | 17.50 | 16 |
| 84 | Coir pitch | 41.27 | 4.02 | | 0.51 | | 16.75 | 16 |
| 85 | Ground nut | 33.90 | 4.97 | | 1.10 | | 18.85 | 15 |
| 86 | Saw dust | 52.28 | 5.20 | | 0.47 | | 18.50 | 15 |
| 87 | Straw | 35.90 | 5.28 | | 0.17 | | 15.50 | 15 |
| 88 | Wood | 52.30 | 5.20 | | 0.50 | | 18.50 | 15 |
| 89 | Fruit bunches | 45.53 | 5.46 | | 0.45 | | 20.41 | 15 |
| 90 | Mesocarp fiber | 46.92 | 5.89 | | 1.12 | | 22.71 | 15 |
| 91 | Kernel shell | 46.68 | 5.86 | | 1.01 | | 21.68 | 15 |
| 92 | Black wood | 46.90 | 6.07 | 43.99 | 0.95 | 0.00 | 18.26 | 14 |
| 93 | Plywood | 48.15 | 5.87 | 44.75 | 0.03 | 0.00 | 19.72 | 14 |
| 94 | Wood tar | 63.30 | 5.31 | 12.06 | 1.76 | 0.00 | 25.79 | 14 |
| 95 | Oil form digested sludge | 71.40 | 8.80 | 14.20 | 5.60 | | 34.30 | 14 |

# 4. Data Analysis

The correlation of the calorific value of the biomass and its elementary components is usually determined by *ultimate analysis* which requires very expensive investment such as laboratory equipment and highly skilled and trained analysts. The *proximate analysis* on the other hand requires simple standard laboratory equipment and a normally skilled scientist or engineer can run the experiment. But it is limited to ash content and volatile material content in the biomass. Hence for the correlation of calorific value and elemental components it is better to use Statistical analysis. The best available statistical process for this project is *Regression analysis.*

## 4.1 Regression Analysis

Regression Analysis is a statistical tool for analyzing the variables when the focus is on the determination of the relationship between the dependent variable and the independent variables. More specifically, it depicts the typical value of the independent variable which has the more influence on the dependent variable with its change. The estimation target which is a function of independent variables called *Regression function,* which can be described by a probability distribution.

Regression analysis is widely used for prediction and forecasting. It is also used to determine the relationships between the dependent variable and independent variables. There are many techniques have been developed in Regression analysis of which Linear Regression analysis and Nonlinear regression analysis are vital for the current analysis.

### 4.1.1 Multiple Regression Analysis

Regression analysis dealing with the equations either linear or nonlinear with variables more than two is called as *multiple regression analysis.* It allows us to control the several other factors that simultaneously affect the dependent variable.

Multiple regression models can accommodate many explanatory variables that can be correlated which are often mislead in simple regression analysis. It is generally used to predict the better model equation for dependent variable. Since the biomass consists of multiple (elemental components) independent variables and calorific value as dependent variable, multiple regression analysis is used to find the better correlation. Hence a linear and nonlinear multiple regression analysis gives the better estimation of correlation between the calorific value of biomass and its elemental components.

### 4.1.2 Linear Regression Analysis

It is one of the statistical approaches for modeling the relationship between the dependent variable and one or more independent variables. More than one independent variable is a linear multiple regression.

Most commonly, linear regression refers to a model in which the conditional mean of dependent variable given the value of independent variable is function of it. Less commonly, linear regression could refer to a model in which the median or some other quantity of the conditional distribution is expressed as a linear function of dependent variable. Like all forms of regression analysis, *linear regression* focuses on the conditional probability distribution, rather than on the joint probability distribution of independent and independent, which is the domain of multivariate analysis.

$$Y = a_o + a_1 X_1 + a_2 X_2 + \ldots + a_p X_p + \alpha$$

Where Y is dependent variable, $X_i$ are independent variables and α is the error term.

### 4.1.3 Nonlinear Regression Analysis

Nonlinear regression is another type of regression analysis in which data is modeled by a function which is a nonlinear combination of the model parameters and depends on one or more independent variables. The data are fitted by a method of successive approximations. Nonlinear regression constitutes of many types like logistic, exponential, quadratic, power etc.

Since it's not always possible to solve the nonlinear equations there are some models proposed to obtain approximate absolute solutions by employing iterative procedures. Three main methods of this kind are:

1. Taylor Series Method
2. Steepest Descent Method
3. Levenberg-Marquardt's Method

The Taylor series method uses linear least square theory. However, neither Taylor Series method nor the Steepest Descent method is ideal. The most widely used method for computing nonlinear equations is Levenberg-Marquardt's method. This method represents a compromise between both above methods and combined successful features are obtained.

Hence for the case of estimation of calorific value of biomass from its elementary components in case of nonlinear equations we use Levenberg-Marquardt's method [28]

### 4.1.4 Regression Parameters

- R-squared
- Adjusted R-squared

#### *4.1.4.1 R-squared*

R-squared is Pearson's regression coefficient which ranges from 0 to 1. R-squared value above 0.5 is valid and above 0.7 is the best R-squared value for a given correlation.

$$\text{R-squared} = 1 - \sum_{i=1}^{n} |(C.Ve - C.Vm)^2)/(C.Vm^2)| \times 100\ \%$$

Where, C.Ve and C.Vm are calorific value estimated and actual value respectively.

#### *4.1.4.2 Adjusted R-squared*

It is calculated by correcting the number of independent variables in multiple regression analysis. It can be calculated by,

$$\text{Adj. R-squared} = (1 - (1 - Rsq) \times (n-1)/(n-k))$$

Where, k = number of independent variables, n = number of observations.

It is often used where the number of coefficients is more.

# 5. Results and Discussion

The Regression analysis gives the estimation of calorific value of the biomass from its elemental components. It is the easiest method for finding the correlation to characterize a biomass fuel. Hence the following graphical representations and tables give the relationship between the calorific values and the elemental components of biomass and their correlation.

The regression analysis is carried out by two soft wares, 'Microsoft Excel 2010' for linear regression analysis and 'IBM SPSS Statistics 20' for both linear and nonlinear regression analysis. The results were shown for both the cases.

## 5.1 Linear Regression analysis

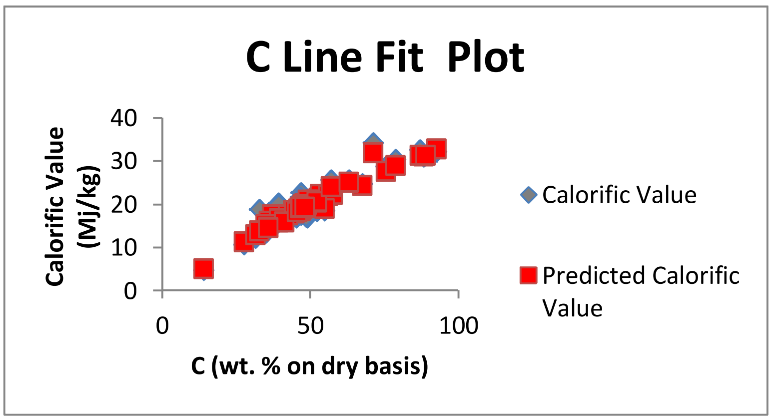


**Figure 5.1 C Line Fit Plot**

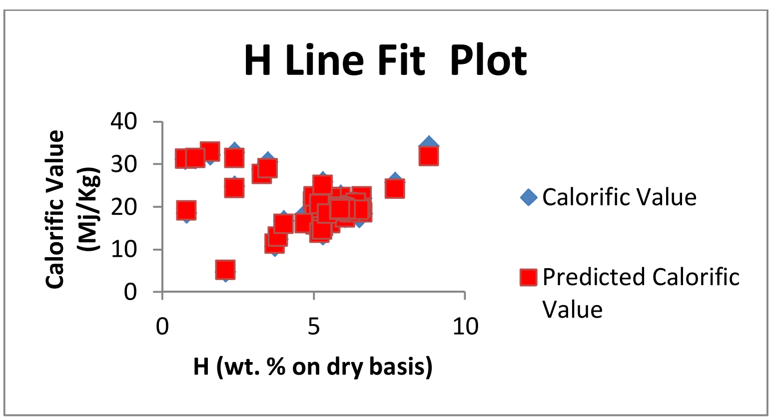


**Figure 5.2 H Line Fit Plot**

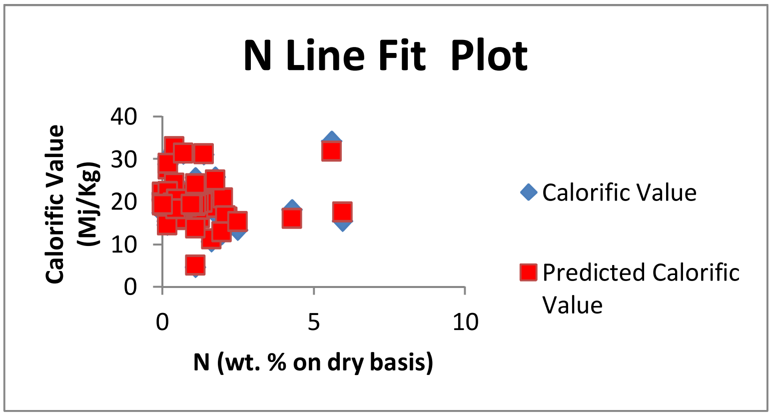


**Figure 5.3 N Line Fit Plot**

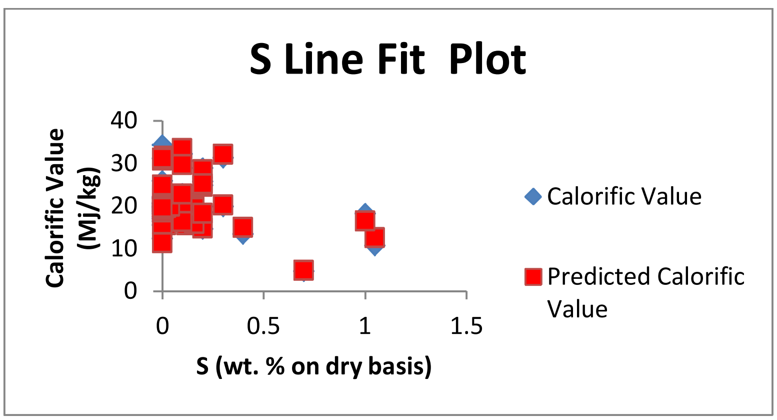


**Figure 5.4 S Line Fit Plot**

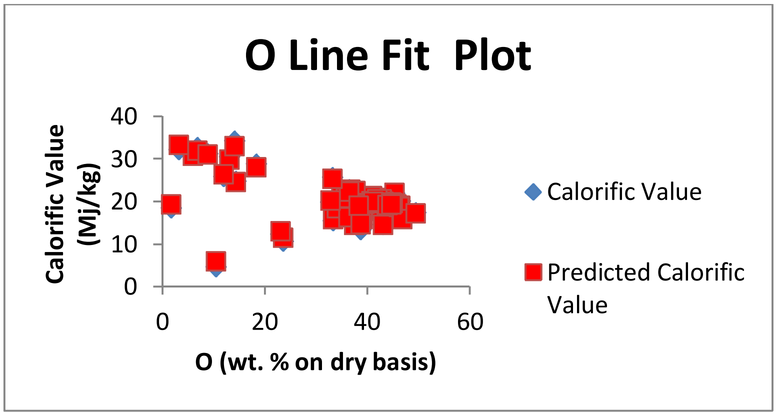


**Figure 5.5 O Line Fit Plot**

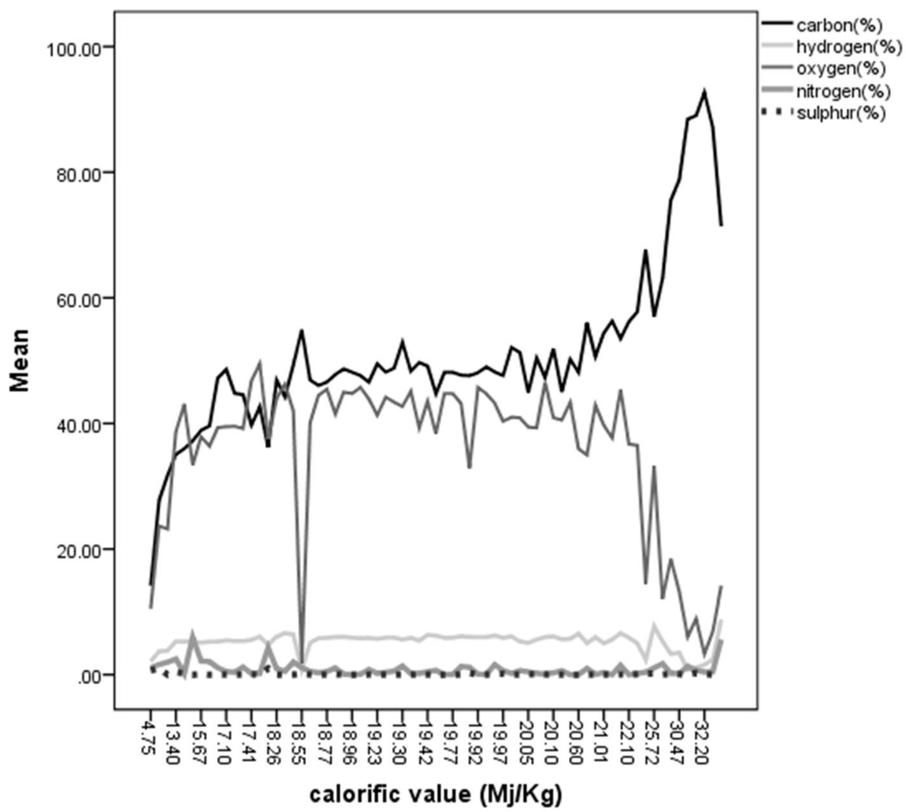


**Figure 5.6 Graphical representation of calorific value as a function of elementary components**

Table 5.1- Linear regression analysis for carbon, hydrogen, nitrogen, oxygen and sulphur using 'IBM SPSS Statistics 20'.

Table 5.1 - Model Summary by SPSS

| Model | R | R Square | Adjusted R Square | Std. Error of the Estimate |
|---|---|---|---|---|
| 1 | .973[a] | .946 | .942 | 1.14343 |

a. Predictors: (Constant), sulphur %, carbon %, nitrogen %, hydrogen %, oxygen %

Table 5.2 – Coefficients by SPSS

| Model | | Unstandardized Coefficients | | Standardized Coefficients | t | Sig. |
|---|---|---|---|---|---|---|
| | | B | Std. Error | Beta | | |
| 1 | (Constant) | -2.667 | 1.378 | | -1.936 | .057 |
| | carbon % | .369 | .015 | 1.023 | 24.137 | .000 |
| | hydrogen % | 1.074 | .166 | .325 | 6.462 | .000 |
| | oxygen % | -.050 | .024 | -.126 | -2.063 | .043 |
| | nitrogen % | .136 | .149 | .032 | .915 | .363 |
| | sulphur % | 1.606 | .887 | .065 | 1.811 | .075 |

Table 5.3 – Regression analysis by Microsoft Excel

| *Regression Statistics* | |
|---|---|
| Multiple R | 0.972696 |
| R Square | 0.946137 |
| Adjusted R Square | 0.942177 |
| Standard Error | 1.143431 |
| Observations | 74 |

Table 5.4 – Correlation by Microsoft Excel

| | *Calorific Value* | *C* | *H* | *O* | *N* | *S* |
|---|---|---|---|---|---|---|
| Calorific Valu | 1 | | | | | |
| C | 0.944777988 | 1 | | | | |
| H | -0.189712647 | -0.39037 | 1 | | | |
| O | -0.479883919 | -0.56293 | 0.764351 | 1 | | |
| N | -0.025337749 | -0.12375 | 0.055805 | -0.25635 | 1 | |
| S | -0.272239907 | -0.26977 | -0.32961 | -0.28961 | 0.286187 | 1 |

Figures 5.1 to 5.5 give the line fit plot for the predicted calorific value and the actual calorific value with respect to each elemental composition such that it give the brief information about the influence of particular component on the correlation function. From the above graphs it is evident that the calorific value has a very strong influence of its carbon content. Figure 5.6 gives the combined graph of elemental components varying with mean calorific value.

Tables 5.1 to 5.2 are generated from 'IBM SPSS Statistics 20' software by taking elemental components as independent variables and calorific value as dependent variable. Tables 5.3 and 5.4 are generated from 'Microsoft Excel 2010'. From the resulted coefficient values we get the equation as,

$$0.94\,C - 0.18\,H - 0.4\,O - 0.02\,N - 0.27\,S = \text{Calorific Value (Mj/kg)}$$

Where, C, H, O, N and S are the wt. % on dry basis. The R-squared value is 0.946. Hence predictions of the correlations were found to be within ±5% error

## 5.2 Nonlinear Regression Analysis

Table 5.5 - Correlations of Parameter Estimated by SPSS

| | a1 | a2 | a3 | a4 | a5 | a6 | a7 | a8 |
|---|---|---|---|---|---|---|---|---|
| a1 | 1.000 | .999 | .026 | .592 | -.993 | .118 | .531 | -.335 |
| a2 | .999 | 1.000 | .042 | .602 | -.989 | .104 | .525 | -.333 |
| a3 | .026 | .042 | 1.000 | -.274 | -.006 | -.304 | .075 | -.047 |
| a4 | .592 | .602 | -.274 | 1.000 | -.553 | -.054 | .019 | .040 |
| a5 | -.993 | -.989 | -.006 | -.553 | 1.000 | -.162 | -.539 | .331 |
| a6 | .118 | .104 | -.304 | -.054 | -.162 | 1.000 | .236 | -.333 |
| a7 | .531 | .525 | .075 | .019 | -.539 | .236 | 1.000 | -.906 |
| a8 | -.335 | -.333 | -.047 | .040 | .331 | -.333 | -.906 | 1.000 |

Table 5.6 – ANOVA by SPSS

| Source | Sum of Squares | df | Mean Squares |
|---|---|---|---|
| Regression | 31573.366 | 8 | 3946.671 |
| Residual | 72.137 | 66 | 1.093 |
| Uncorrected Total | 31645.504 | 74 | |
| Corrected Total | 1650.595 | 73 | |

Dependent variable: calorific value (Mj/Kg)

a. R squared = 1 - (Residual Sum of Squares) / (Corrected Sum of Squares) = .956.

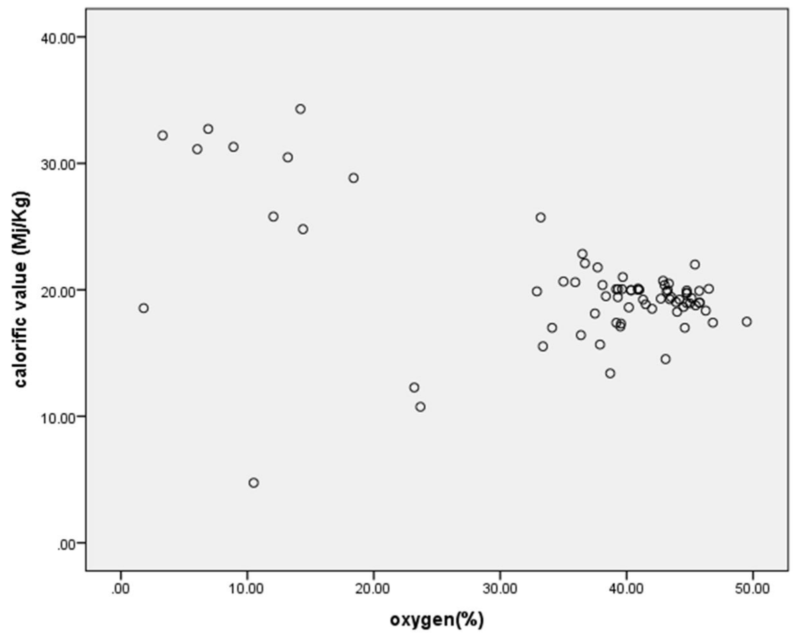


**Figure 5.7 Variation of Calorific value with Oxygen**

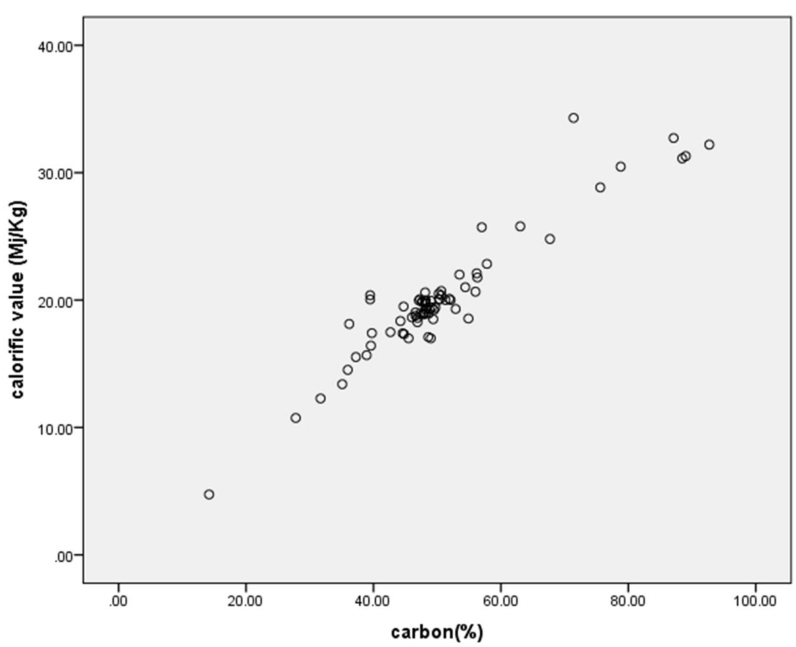


**Figure 5.8 Variation of Calorific value with carbon**

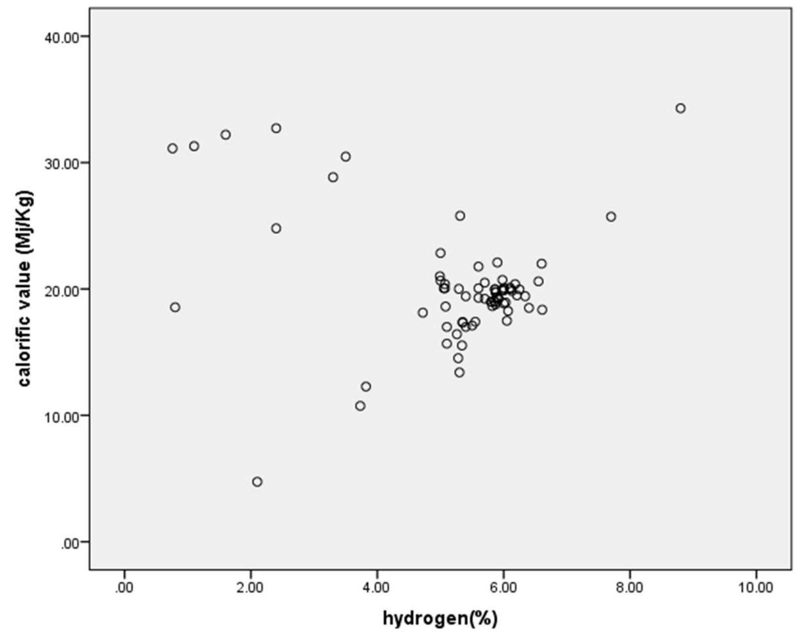


**Figure 5.9 Variation of Calorific value with Hydrogen**

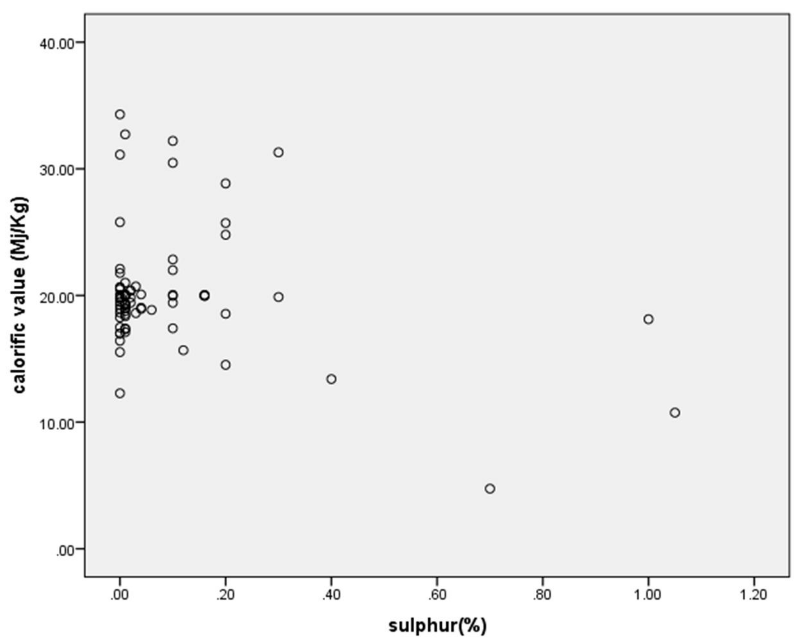

Figure 5.10 Variation of Calorific value with Sulphur

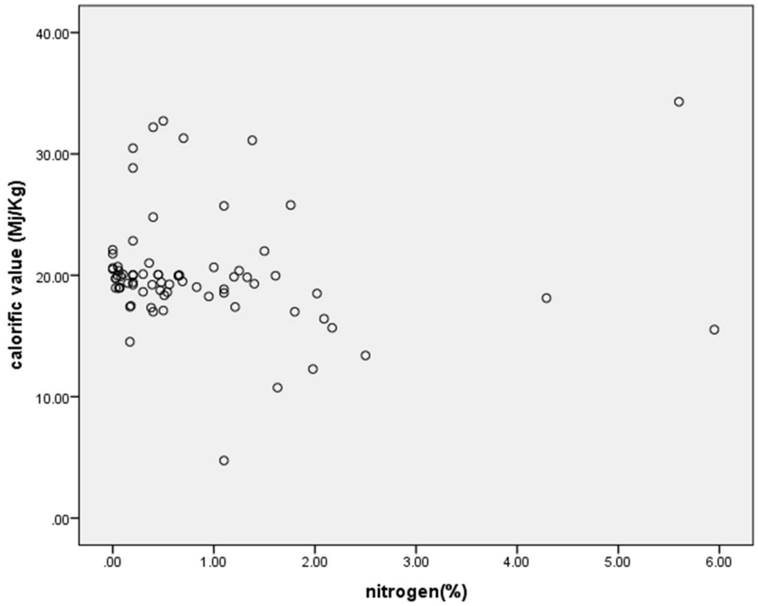


Figure 5.11 Variation of Calorific value with Nitrogen

Figures 5.7 to 5.11 give the variation of calorific value of biomass with respect to elemental components. We can see that carbon is increasing linearly with the increase in calorific value and at the same time there decrease of nitrogen content with the increase in calorific value.

Tables 5.5 to 5.6 are generated from 'IBM SPSS Statistics 20' software by taking elemental components as independent variables and calorific value as dependent variable. Here we used Levenberg-Marquardt's Technique for nonlinear regression analysis. Most of the correlations generally found and used were linear equations, since there is very less accuracy in nonlinear equations. The low accuracy of these correlations is mainly due to the limitation of samples used for deriving them and the lack of combination influencing variable in the equation. To achieve a higher accuracy, new correlations were proposed to estimate the Calorific value from the Regression analysis based on the current available database,

$$C^2 + C \times O^2 + 0.03\, C \times H + 0.60\, C - O + 0.11\, O \times N + 0.53\, S - 0.33\, S \times O = \text{Calorific Value (Mj/Kg)}$$

Where, C, H, O, N and S are the wt. % on dry basis. The R-squared value is 0.956. Hence predictions of the correlations were found to be within ±4% error

# CONCLUSION

The correlations have been derived based on the collection of large number of data from the published or open literature, which is having widely varying elemental composition. The data points considered for correlation by regression analysis ranges in carbon content from (27.80% to 92.70)%, hydrogen content (0.10 to 8.80)%, oxygen content (0.20 to 49.50)%, nitrogen content (0.00 to 5.95)% and sulphur (0.00 to 1.05) wt. % on dry basis, the derived correlations can be accepted as 'general correlations' for the estimation of calorific value of biomass from its elemental components within the above specified ranges.

It was found that the correlations based on linear multiple regression analysis is the most accurate. The correlations based on the non-linear regression analysis (except the quadratic equations) have low accuracy. The low accuracy of the nonlinear correlations is mainly due to the limitation of samples used for deriving them. To achieve a higher accuracy we have use the influence of a particular individual variable i.e. the influence of carbon(C) and oxygen (O) wt. %, in the correlations since their influence in the elemental composition is vital and their contribution in total amount of biomass is around 90%. Moreover the changes in nitrogen and sulphur and hydrogen are very minure that their influence on the correlation is negligible.

The main advantage of these correlations is that, using these we can analyze the economical estimation of elemental components of the given biomass. This depends on the interest of person where expensive laboratory equipment and more sophisticated methods are not available.

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