CHAPTER SIX

BIOMASS CONVERSION WITH A THERMAL DECOMPOSITION ROUTE

CHAPTER - VI

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6.1 INTRODUCTION :

After recognition of biomass as a source of energy, many efforts have been made for its utilization as an energy resource. Recently improved methods of biomass utilization with different techniques have gathered a momentum (Vimal et.al. 1984, 1989). In general, these methods are classified into two groups i.e. physical conversion methods and chemical conversion methods. Physical conversion methods includes drying, densification, size reduction process and chemical conversion method includes thermochemical or photochemical, bioelectrical and biological conversion process. Among these processes thermochemical conversion process gained an importance for its conversion efficiency (Hofileter 1985, Kulkarni and Saluja 1988, Enrich 1985, Vahrman 1982, Knight 1975, 1982, Figueiredo et al. 1983, 1984).

The first step in thermochemical conversion process is pyrolysis. It involves thermal decomposition of wood in the absence of air or in limited air, the process was first performed in 1792 (Dayal 1989). Since then wood has been used to produce a variety of fuel and chemicals. Pyrolysis could be either exothermic (at higher temperature) or endothermic (at lower temperature) or endothermic (at lower temperature) (Mayers 1983). Higher temperature and long residence period lead to gas production, lower temperature and shorter residence period leads to liquid and char production (Wans et al. 1978, Paul 1982). By varying system temperature, heating rate, residence period and feed composition in the reactor, it is possible to obtain solid (charcoal), liquid (pyrolytic oil) or gasses (low energy gas) fuels by pyrolysis (Naguhiro et al. 1985, Peters, 1985, Prabhakar et al 1986). Thermal decomposition begins at about 100^{o}C and then it increases with rising temperature.

At about 270^{o}C exothermic reactions set in which a rise in temperature (usually held at 400 to 500^{o}C) bringing complete carbonization ((Hawley 1985, Milne 1979,[81,] Shafizadeh 1982, Neepchand et al.,1987).

In the earlier chapters, we have seen the physical aspects of the Leucaena leucocephala i.e. productivity, where, it gives the idea about fast growth and high rate of biomass productivity by photosynthesis. To utilize this stored chemical energy we have to convert it into useful form. The first step towards this is the charcolization of the Leucaena leucocephala by pyrolysis. The present chapter deals with the mechanism and kinetics of the chemical reactions involved in the chemical conversion process. Especially this chapter is devoted to study the pyrolysis mechanism in Leucaena leucocephala for charcolization and gassification. The technique employed for charcolization study was thermogravimetric (Reger, 1985) in which change in weight percent is correlated with the rise in temperature of the cellulosic charcoal. The energy content during various thermal stages of the cellulosic char has been studied from which it is tried to explain the best thermal stage of the cellulosic charcoal. Thermal degradation of cellulosic charcoal has also been discussed with time. With the help of oxygen bomb calorimeter the energy content of Leucaena leucocephala is discussed for its separate body parts (Venkataraman, Raman and Kohlis 1987).

6.2 MATERIALS AND METHODS :

6.2.1 Experimental :

Chemical degradation or pyrolysis involves series of physical transformation and chemical changes. To study these changes during process, six wooden blocks of Leucaena leucocephala of the size 40 m in length and 1.5 cm in diameter were used. A laboratory charcoal furnace has been fabricated for controlled pyrolysis study. Required temperature of the furnace was maintained constant by temperature controller, in contact to the system by (Chromel-Alumel) thermocouple. The system was made air tight by special silica glass stoppers. For accurate measurement of the weight of wooden blocks, one pan micro balance (upto the sensitivity 0.001 gm) was used.

The first part study was made by placing five Leucaena leucocephala wooden blocks at five different temperature (from 100 to 500^{o}C) in furnace for the duration of five minutes for each block. The pyrolysed wooden blocks at various temperature are then used to find out the energy values by oxygen bomb calorimeter (Fig. 6.1 a,b).

In second part of experiment, in order to study the kinetics of the pyrolytic process, the weight loss change in Leucaena leucocephala with time at the fixed pyrolytic temperature below and above 300^{o}C have been studied. The energy values of the whole Leucaena leucocephala plant, consisting individual part (leaves, stem, bark root, fruit etc.) have also been determined.

In third part of the study pyrolytic gassification were studied. For the study 20 k.w. Ankur gasifier engine system for electrical power genera tion were installed and used (Fig.6.2,6.3). To evoluate the performance of the gassifier, the system has been operated for about 55 hrs with Subabool (Leucaena leucocephala) and the thermochemical characteristics of Subabul were studied. The gas composition was studied by Junker calarimetry (fig. 6.4).

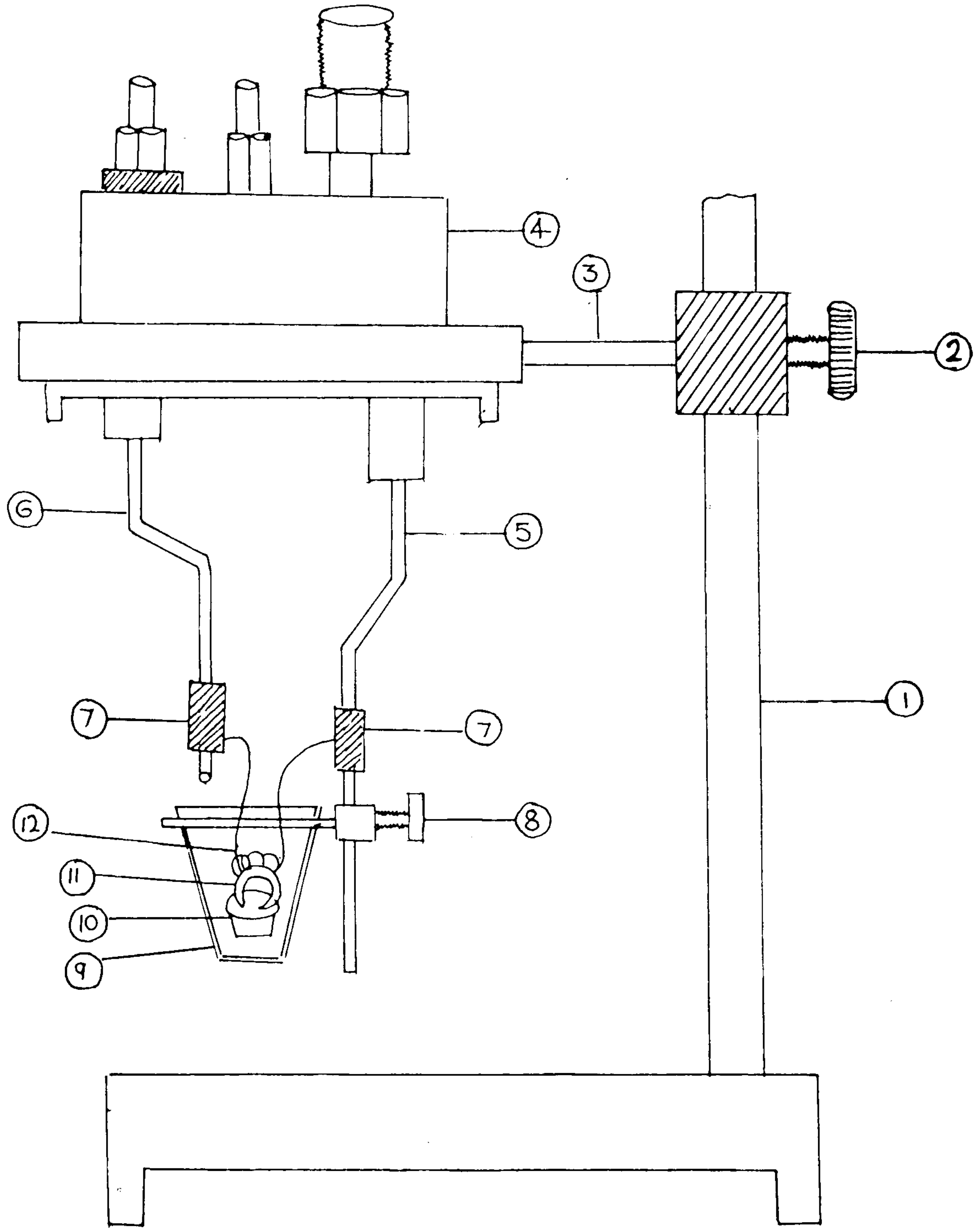

Fig. 6.1a : Infrared Block diagram of oxygen bomb calorimeter

1) Bomb lid stand 2) Stand bracket adjustment screw
3) Stand bracket 4) Bomby lid
5) Crucible holding electrode 6) Smaller electrode
7) Ignitian wire testing holders 8) Crucible holder adjusting screw
9) Crucible 10) Sample
11) Cotten thread 12) Ignitian wire

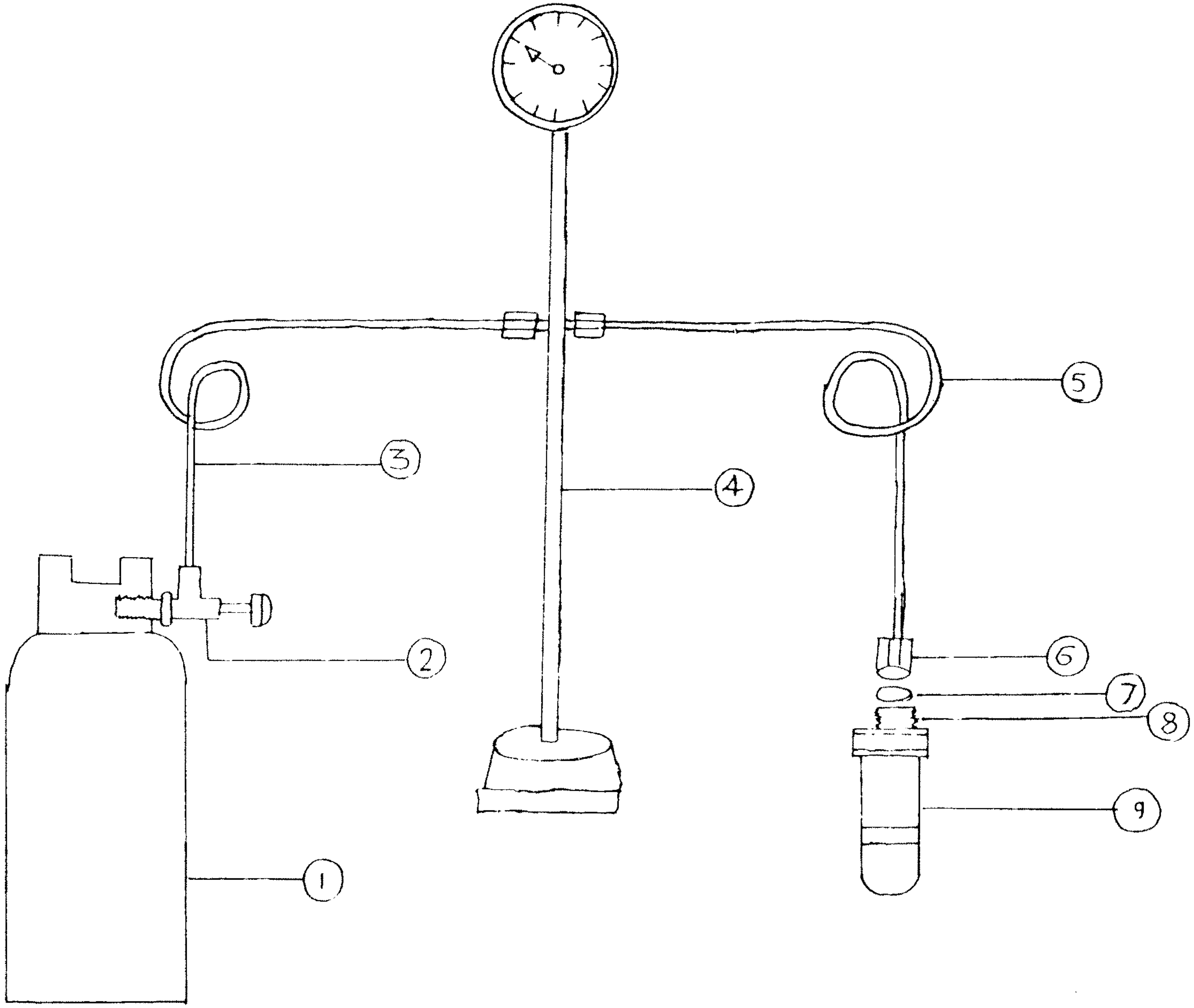

Fig. 6.1b : Block diagram for oxygen filling in the bomb

1) Oxygen cylinder 2) Fine regulating valve (for oxygen)
3) Copper tube to connect oxygen cylinder and pressure gauge
4) Pressure gauge 5) Copper tube to connect pressure gauge and bomb
6) Coupling nut with bomb 7) 'O' ring
8) Bomb value 9) Bomb body

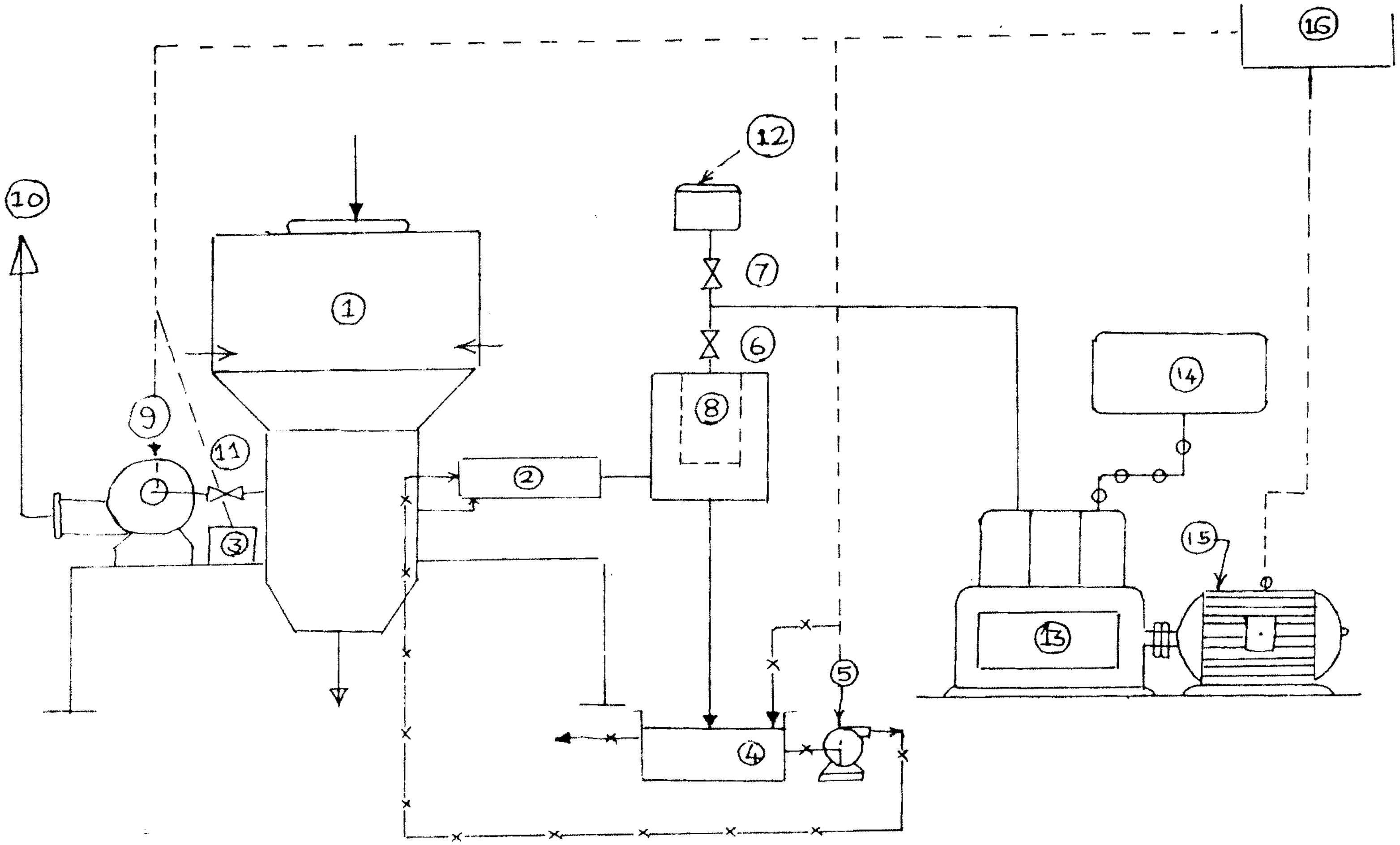

Fig. 6.2 Block diagram of Biomass Gassifier

1) Gassifier 2) Gas cooler-cleaner 3) Vibrator 4) Hot dirty water sump
5) Cooling tower sump 6) Gas valve 7) Air valve 8) Separator box with filter
9) Blower 10) Flare burner 11) Start-up valve 12) Air filter
13) C.I. Engine 14) Diesel supply tank 15) Electrical generator
16) Distribution panel.

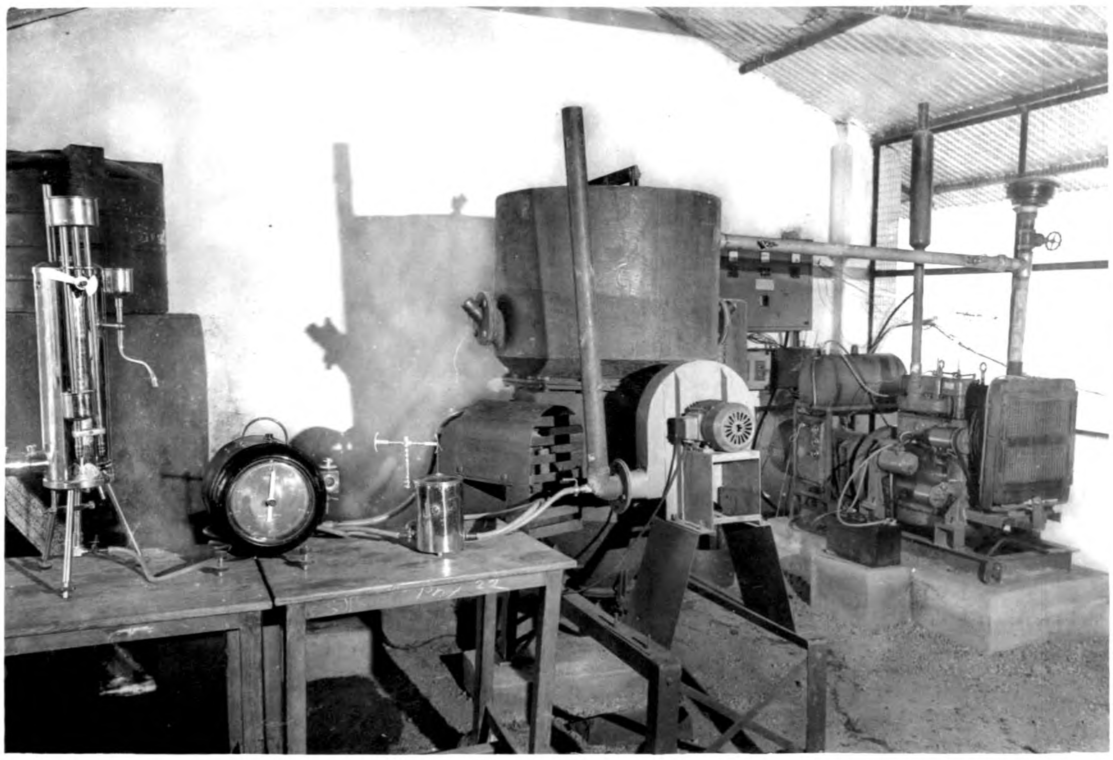

Fig. 6.3 : Experimental setup of Biomass Gassifier

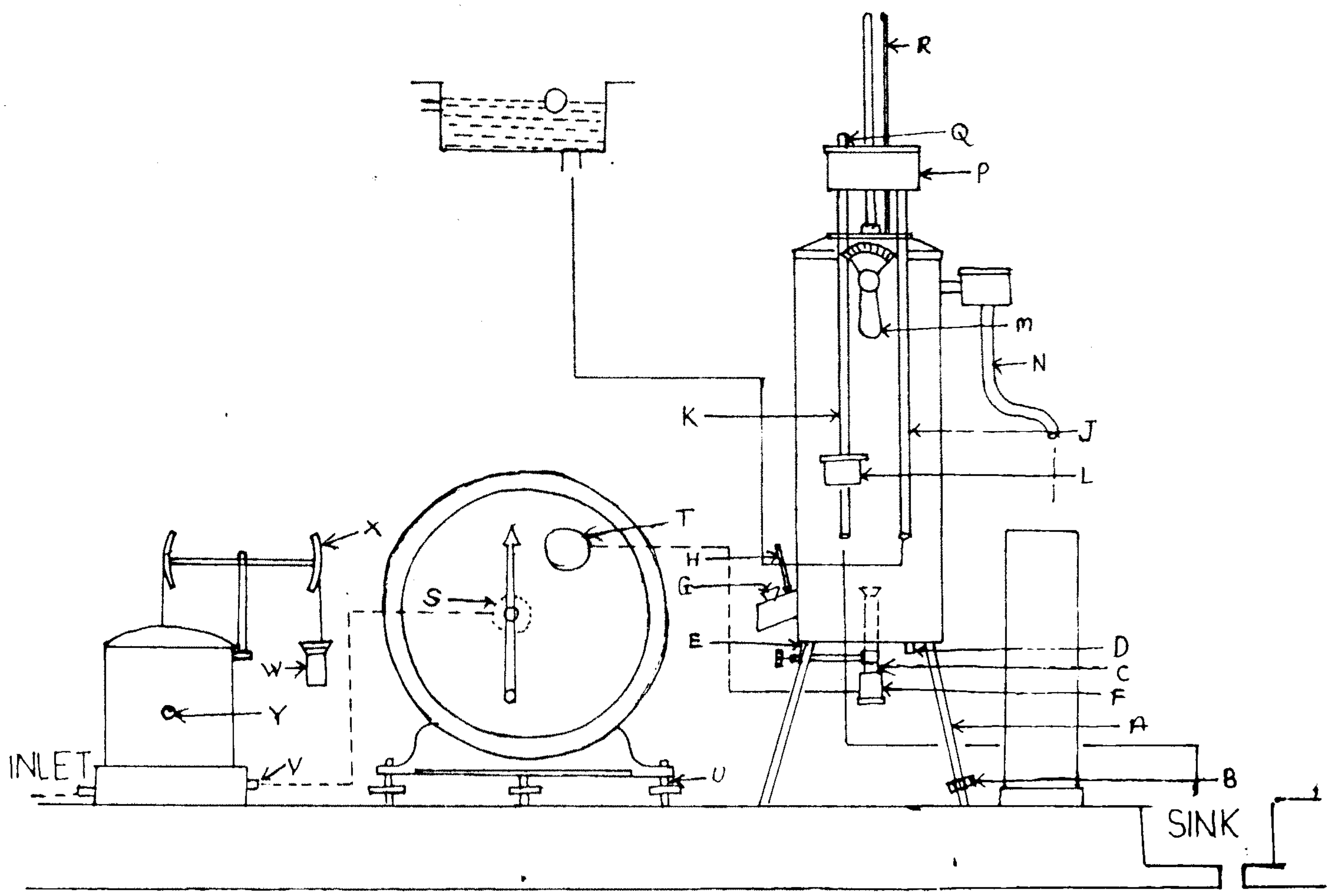

Fig. 6.4 : Junkers Calorimetry

A) Tripod leg
B) Leveling screw
C) Water drain cock
D) Outlet for condensare
E) Support rod for Burner
F) Burner
G) Damper for flue gases
H) Thermometers for flue gases
J) Water inlet
K) Water overflow tube
L) Sink
M) Water flow regulator
N) Water outlet for collection
P) Constant head funnel
Q) Air outlet tube
R) Water inlet and outlet thermometers

6.2.2 Experimental Procedure :

A) Pyrolysis of Leucaena leucocephala

1. Switch on the furnace and attain the temperature at about $100^{o}C$.
2. Take initial weight of the wooden block.
3. Place the wooden block in the furnace and wait for five minutes.
4. Remove the block from the furnace and find out weight after treatment.
5. Find out change in weight of the biomass.
6j. Increase the temperature of the furnace and repeat the same procedure for the second block and so on.
7. After completion of the thermochemical treatment make the 1 gram fine powder of each block and form the pellet for determination of calorific values.

B. Kinetics of Pyrolysis

1. In second part take the weight of Leucaena leucocephala wooden block (W.O.)
2. Keep it in furnace for five minutes at fixed temperature $300^{o}C$.
3. After five minutes take the weight of wooden block (Wt.)
4. Keep same block for another five minutes at same temperature.
5. Take the weight after five minutes, repeat the same procedure for further time upto an hour and find out final weight i.e. constant weight.
6. Find out the $\frac{W_t - W_\infty}{W_o - W_\infty}$ for the fixed temperature $300^{o}C$ which is turned as residual weight.
7. Repeat the same procedure for the change in biomass with time at the fixed pyrolytic temperature $275^{o}C$ and $310^{o}C$.

8. Plot the graph $\frac{Wt - W_\infty}{Wo - W_\infty}$ versus time for 275°C, 300°C and 310°C.

C) Energy Value Determination

A stirred liquid oxygen bomb calorimeter was used for determination of calorific value (Summer and Mansson 1979, Mathews 1985). Approximately 1 gram sample of each body part of Leucaena leucocephala was powdered and was made moisture free by drying. It was then pelletised in a container filled with oxygen to a pressure of about 20 atmosphere. The oxygen bomb was electrically connected and fired by control unit. The heat released by combustion was determined by measuring the rise in temperature of water around the sample container with Becknann Thermometer.

Before going to direct Leucaena leucocephala sample, the benzoic acid pellet was used to determine the water equivalent of the oxygen bomb calorimeter. It can be calculated from the expression :

$$W = \frac{HaMa + E'}{tc'} \quad \ldots \quad (1)$$

where,

W = Water equivalent of the system

Ha = Heat of combustion of benzoic acid (6319 cal/gram)

Ma = Mass of benzoic acid sample.

tc' = Corrected temperature rise on Beckmann Thermometer.

E' = Energy equivalent of the Nicrome wire and cotton fuse used to ignite the sample.

$$\therefore \quad E' = HwMw' + Hc\,Mc' \quad \ldots \quad (2)$$

$$= (\ .335 \text{ cal/mg.})\ (18.4 \text{ mg}) + (4.180 \text{ cal/mg})\ (5 \text{ mg})$$

$$= 6.2 + 20.9$$

$$= 27.1 \text{ Cal.}$$

where Mw' and Mc' are the respective masses of nichrome wire and cotton thread consumed in the firing.

After calculation of water equivalent the Energy Value of sample can be determined by the formula :

$$E.V. = \frac{W(Tc) - E}{Ms} \quad \ldots \quad (3)$$

where

W = Water equivalent of the system (Cal./deg.C)

tc = Corrected temperature rise (deg. C)

Ms = Mass of sample (gram)

E = Energy equivalent of the nichrome wire and cotton fuse used to ignite the sample and is given as per equation (2).

D) Pyrolytic Gassification of Leucaena Leucocephala :

1) Commissioning / Re-commissioning :

a) The space above the grate should be filled with good quality charcoal pieces (between 25 mm and 50 mm in size) all the way upto the air intake nozzles.

b) Dry *Leucaena leucocephala* wood biomass of appropriate size moisture (90 mm size and 5 to 10 % moisture) is then to be filled in the hopper above this charcoal bed.

c) Empty out the ash collection area and lock the ash door.

d) Lock the feed door.

e) Check lubricating oil level, diesel level etc. for the engine.

2) Start-up

a) Fill the hopper with biomass, if necessary, and lock the feed door.

b) Empty the ash collection area and lock the ash door.

c) Open the start-up gas outlet valve on the gassifier.

d) Close the gate valve located above the separator box.

e) Check diesel level lubricating oil level etc.for the engine.

f) Open the air intake valve fully.

g) Start the diesel engine genset normally as per genset manual (on 100% diesel), start the motor pumpset and ensure that the pump starts delivering water through the cooler-cleaner sub system.

h) Start the vibrator as well as the blower.

i) Fire the gasifier using a flame through one of the air nozzles after removing the caps from both the nozzler.

j) After about three minutes of engine operation on 100% diesel the gas can be fed to the engine by fully opening the gas valve and partially closing the air intake valve after switching off the blower.

k) At this point the start-up gas outlet valve should be fully closed.

l) The air intake valve should now be adjusted for maximum diesel replacement. This can be achieved by progressively closing this valve until engine emits black smoke/makes irregular sound.

6.3 RESULTS AND DISCUSSION :

The wood biomass has different components with different properties The main components i.e. carbohydrates and liqnin give volatile and chared carbonaceous residues. This phenomenon is well observed in thermogravimetry of wood. The detailed analysis of thermal degradation of Leucaena leucocephala is given below :

6.3.1 Effect of Temperature on Change in Weight of Leucaena leucocephala Charcoal

Fig. 6.5 shows the effect of temperature on change in weight of Leucaena leucocephala charcoal. The relation between temperature and change in weight is somewhat linear in the initial stage and finally it becomes sleeper. The lower rate of change in weight in initial is only due to the different types of dead and living plants, cells, cellulose, hemicellulose, liqnin, extractives, mineral compounds and water present in Leucaena leucocephala biomass. These components have different heat of combustion and combustion characteristics which reduce rate of weight change in initial temperature upto 300^{o}C. At this stage extractives becomes volatile gaseous and only cellulose, hemicellulose and mineral compounds remain in the pre-charred biomass. The removal of volatile and gasseous matter upto 500^{o}C directly reflects on rate of weight change in pyrolysed char. After 300^{o}C direct combustion of products starts and forms the tarry products at higher temperature above 400^{o}C ash formation takes place where, weight of pyrolysed char reduces fastly. Its better clarification is given by thermogravimetric plot.

6.3.2 Effect of Temperature on Changes in Weight Percentage Pyrolysed Leucaena leucocephala

The thermogravimmetric plot of Leucaena leucocephala wood is given in Fig. 6.6 upto the 270 to 300^{o}C. The change in weight percent of pyrolysed Leucaena leucocephala is minimum as shown in graph and then suddenly it goes on increasing. In initial stage the percentage weight of product is maximum (this is due to biomass products and water upto 100^{o}C,water part of the biomass is removed and upto 270^{o}C all volatile and

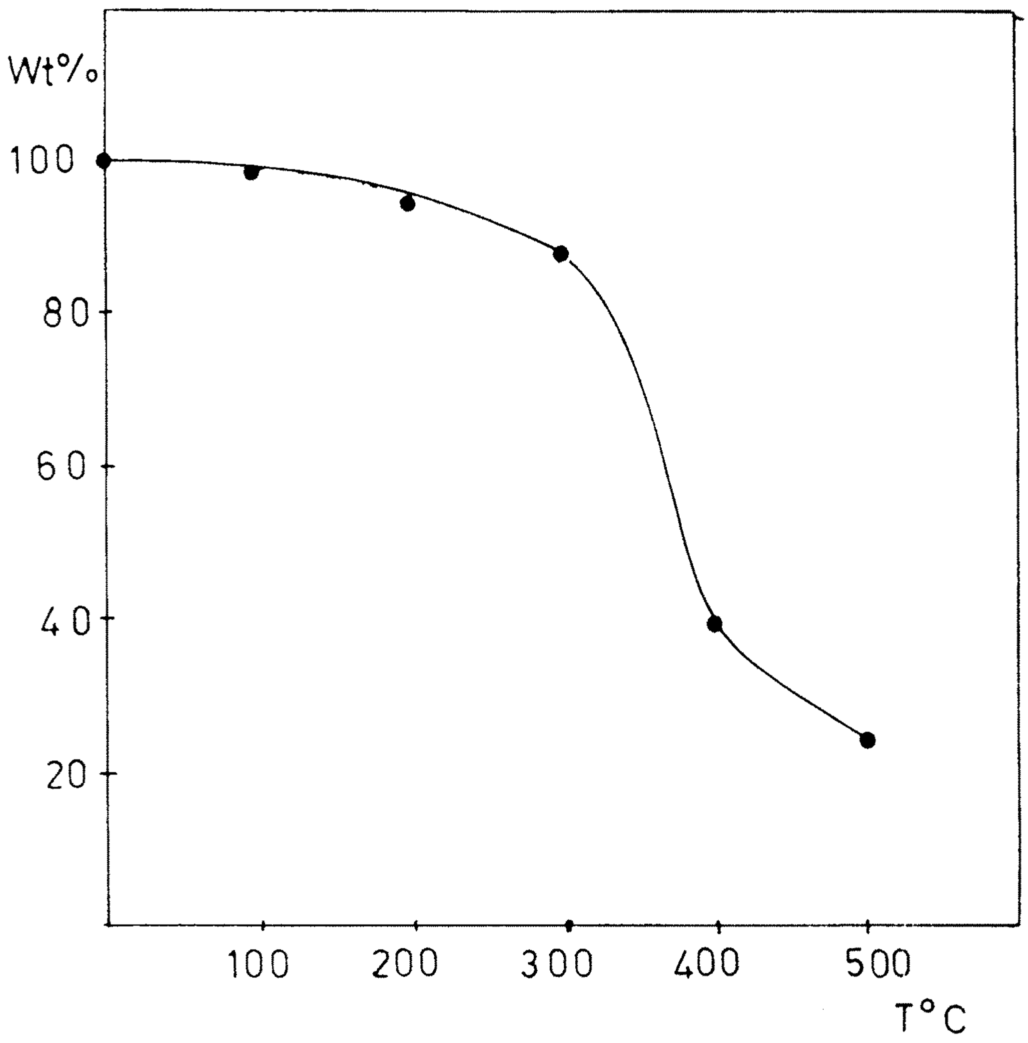

Fig. 6.6 : Thermogravimetric plot of Leucaena leucocephala.

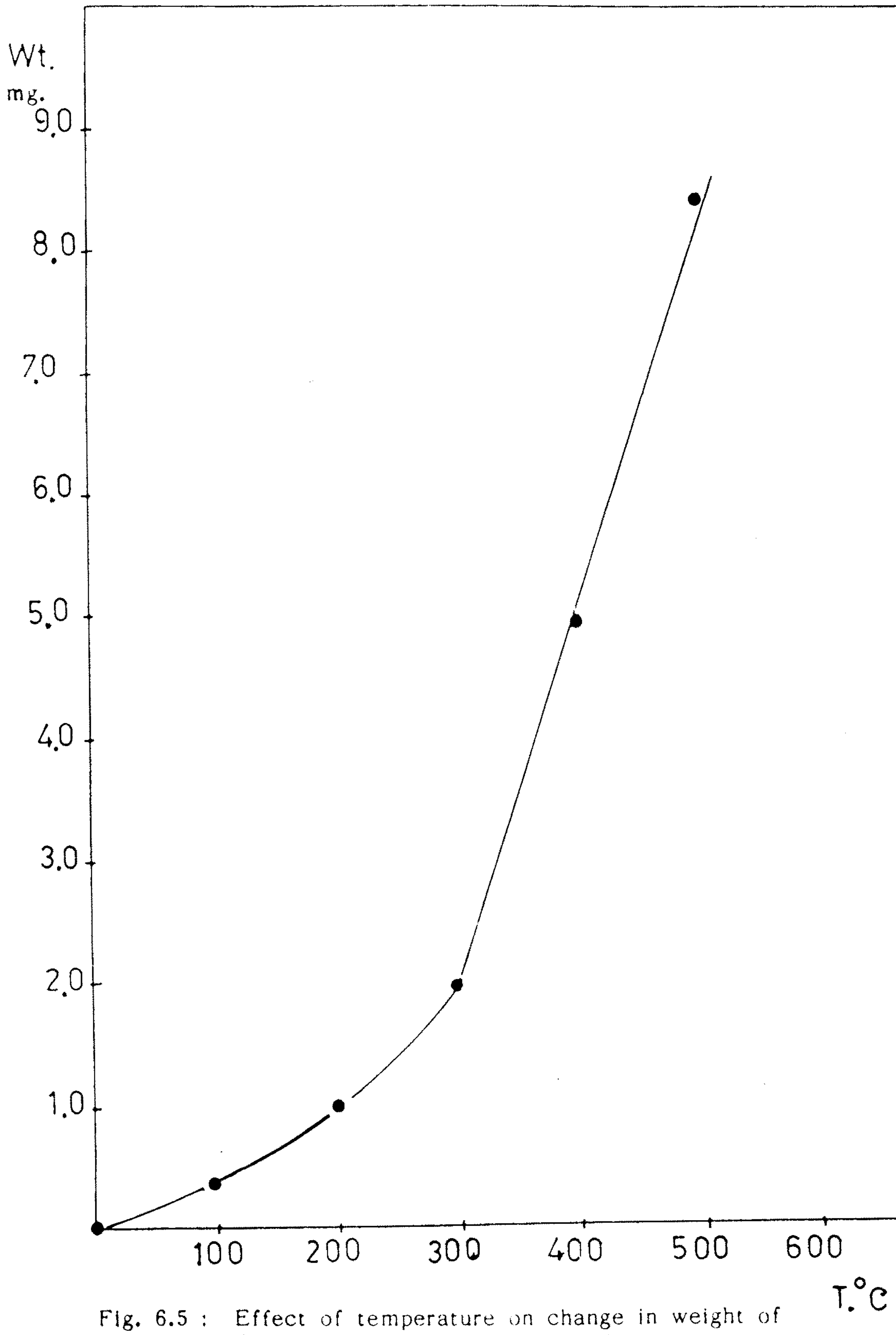

Fig. 6.5 : Effect of temperature on change in weight of Leucaena leucocephala charcoal.

gasseous matters are given out resulting fast change in weight percentage after 300^{o}C. It shows that for ideal charcoalization, it is necessary to optimise the charcoal temperature or in other words we can say that for good quality charcoal optimum temperature is required. Temperatures around 300^{o}C form two stages of the chemical transformations and reactions. The clearcut idea of these two stages can be clarified by Arrhenious plot.

6.3.3 Identification of Optimum Temperature for Charcolization of Leucaena leucocephala

Figure 6.7 shows the Arrhenious plot of the pyrolysed Leucaena leucocephala biomass. the plot shows direct transition at 300^{o}C by giving two different stages i.e.Allothermal stages (heat is supplied from an external agency) and Autothermal stage (heat is given out by product itself). In allothermal stage chemical reactions dominates with rising temperature. The increased pyrolysis temperature involves reduction in molecular weight, appearance of free radicals, elimination of water, formation of carbonyl, carboxyl and hydroperoxide groups, evolution of carbon monoxide and carbon dioxide. Above 300^{o}C the direct combustion of these products starts, which evolves heat in autothermal stage giving rise to char and some tary products. At higher temperature these tarry products and char is converted into ash with degradation of char quality. Hence the yield and properties of char are highly dependant on the pyrolysis temperature. The mechanism and kinetics of it at isothermal condition is necessary to study. The detailed analysis of it is clarified by rate of change of residual weight.

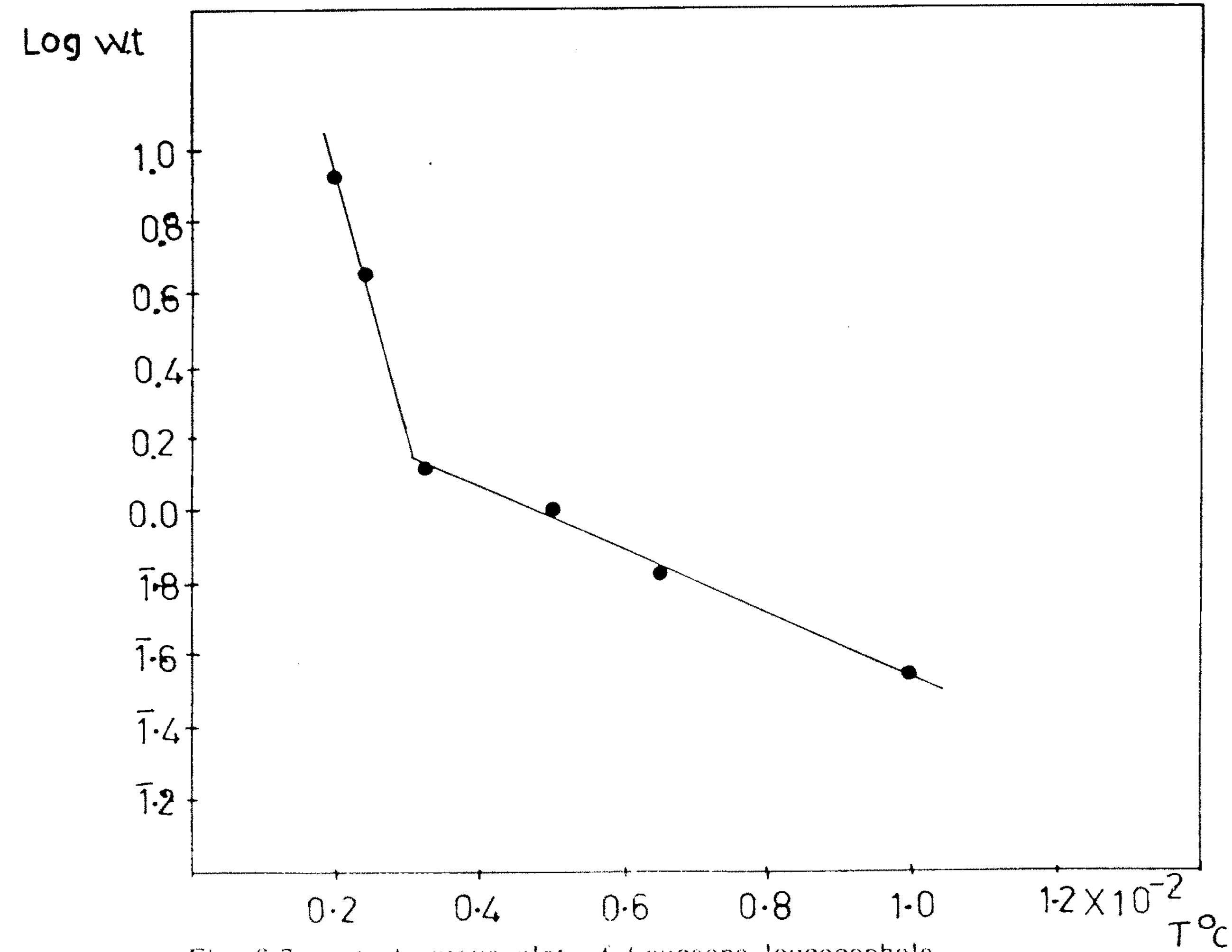

Fig. 6.7 . Arrhenious plot of Leucaena leucocephala

6.3.4 Effect of Isothermal Temperature on Residual Weight of Leucaena leucocephala Biomass

The rate of pyrolysis followed by weight loss under isothermal condition is shown in figure 6.8. The plot gives initial period of faster acceleration upto the 15 minutes for 300°C. For increasing period kinetic studies shows that tar-farming reactions accelerate rapidly and overshadow the production of char and gases which results in lowering the activities of residual wt. change. Above 300°C for 310°C, these reactions rapidly increases by reducing time period. Since the reaction is in autothermal stage; tary products immediately covered by ash and char quality goes on reducing. Below 300°C it 275°C this situation gives exactly opposite result where allothermal reactions increasing its time period by given chemical changes for cellulosic char formation. The linear plot shows that the change in residual wt. goes on increasing linearly with time. The overall result shows that for best quality charcoal the allothermal stage is best one i.e. pyrolysis temperature must be in the range 275 to 300°C. For better quality charcoal we have to study in detail the energy values of the product at various allothermal and autothermal stages. The detailed analysis of it is given in below paragraphs.

6.3.5 Energy Content of the Leucaena leucocephala Biomass

An initial step in the development and evolution of good quality charcoal is to determine the energy content of these potential fuel. The energy value of the Leucaena leucocephala charcoal at various stages during pyrolysis has been studied. The graphical representation of it with pyrolysis temperature is given in figure 6.9. It is found that the calorific

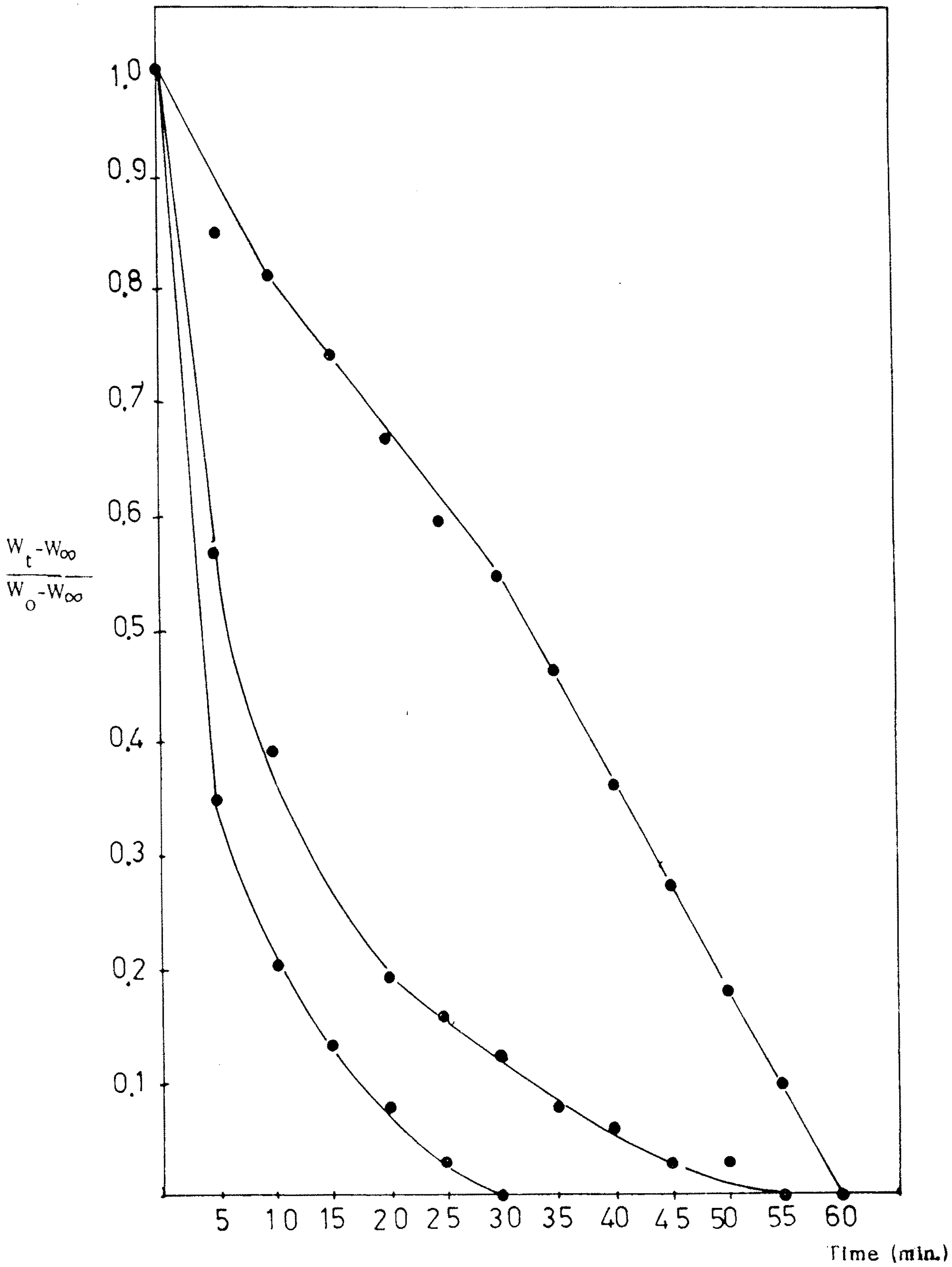

Fig. 6.8 : Weight loss under isothermal condition of Leucaena leucocephala

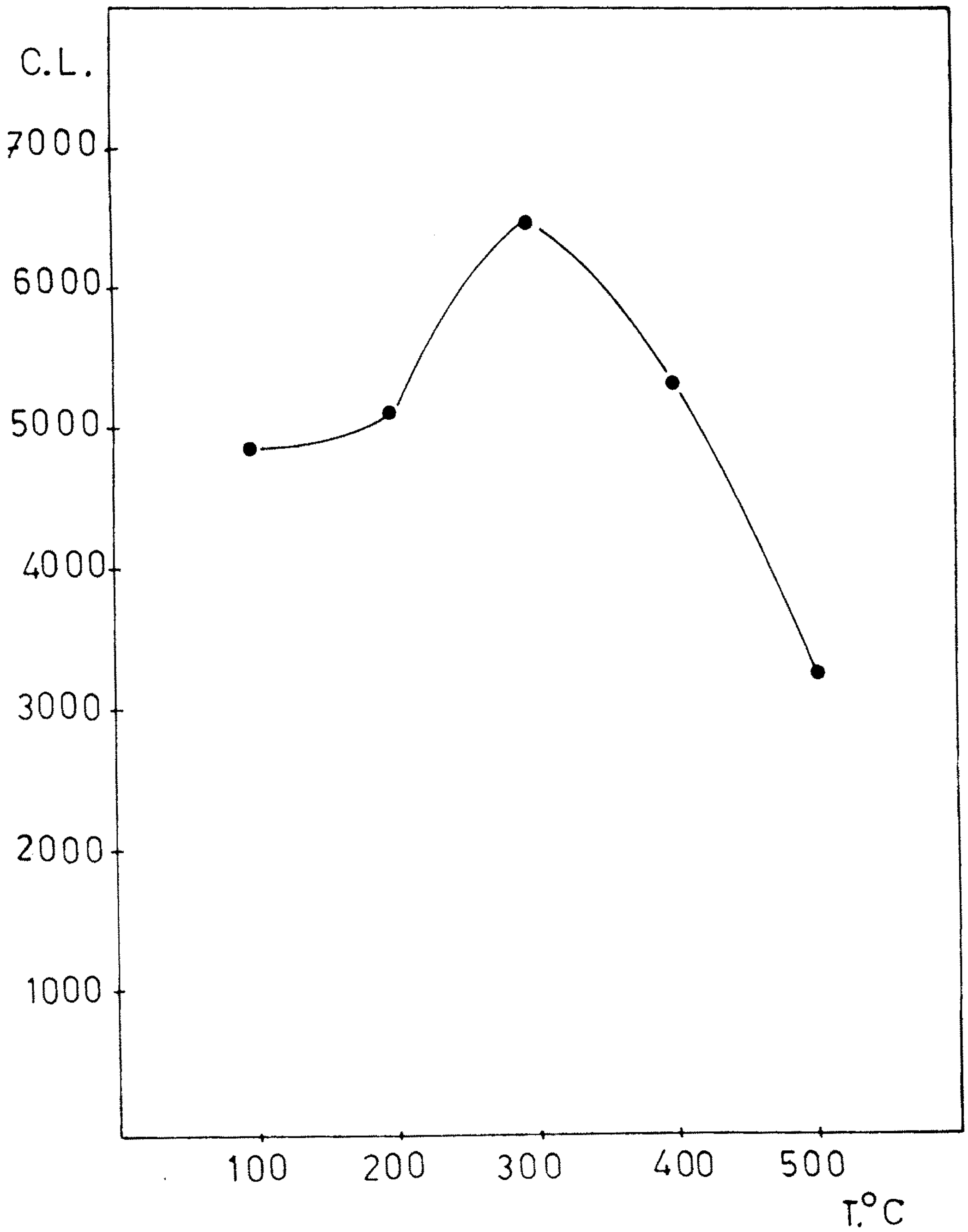

Fig. 6.9 : Energy content of the pyrolysed char of *Leucaena leucocephala*

value increases with rise in temperature upto 300^{o}C and after that it goes on decreasing. It concludes that upto 300^{o}C the good quality cellulosic charcoal formation takes place. After 300^{o}C the cellulose and hemicellulose converts into tarry products and gives out by reducing the cellolosic percentage and ultimately it reduces the energy values of the charcoal. After determination of calorific values of the pyrolysed Leucaena leucocephala it is necessary to determine the energy content of the all parts of the Leucaena leucocephala plant. Table I gives the calorific values of the Leucaena leucocephala plant parts from the table the net calorific value of the biomass are in the range 3500 to 4600 which are in agreement with the energy values of Leucaena leucocephala given by the other workers (NarinderGautam 1985). It is found that the energy value obtained by Leucaena leucocephala seed has the higher value than the other body part of the plant. his may be due to some oils present in the seeds.

TABLE - I

Calorific values of the Leucaena leucocephala plant parts

	Biomass Product	Calorific Value Cal/Kg
1.	Leaves	3290
2.	Bark	3500
3.	Stem	4200
4.	Root	4400
5.	Seeds	4599

6.3.6 Thermochemical Characteristics of Leucaena leucocephala

The complete asembly of Ankur biomass gassifier with Zunkers calorimetry have been developed. The ankur biomass gassifier system has been operated for about 55 hrs. with Leucaena leucocephala and its performance has been found to be satisfactorily. The thermochemical characteristics of Leucaema leucocephala wood are given inable-2.

TABLE - II

Thermochemical Characteristics of Leucaena leucocephala.

Sr.No.	Parameter	Characteristic value
1)	Moisture content (dry basis)	8-10 %
2)	Higher calorific value (dry basis)	19.45 kj/g
3)	Proximate analysis (dry basis)	
	a) Voltalie matter	78.80 %
	b) Fixed carbon	19.50 %
	c) Ash	1.35 %
4)	Ash deformation temperature	1140-1200^{O}C

During the operation of gassifier, Junker calorimetry assembly were attached to find out the gas composition. The percentage gas composition obtained are listed in Table No.3.

TABLE - III

Percentage gas composition of Leucaena leucocephala

Sr.No.	Typical gas composition	Average %
1.	Co	$19 \pm 4\%$
2.	H_2	$18 \pm 2\%$
3)	CO_2	$10 \pm 3\%$
4)	CH_4	Upto 3%
5)	N_2	50%
6)	Tar	0.005%
7)	Soot	0.005%

6.4 CONCLUSION :

From the overall study it is found that, Leucaena leucocephala could be used satisfactorily for charcoal production and pyrolytic gas production. The systematic studies on charcoal production by pyrolytic method gives the idea about mechanism of charcoal production. It was found that good quality charcoal of Leucaena leucocephala was obtained in the range of 270 to 310^{o}C. The obtained calorific value is also high. The pyrolytic gassification of Leucaena leucocephala gives 70 to 85% disel replacement.

REFERENCES

1. Enerich W. : Handbook on Charcoal Making. Solar Energy R & D in the European Community Series E, Vol. 7, Energy from Biomass D. Reidel Publishing Dardrecht, Netherlands, pp 110 (1985).

2. Fiqueiredo J.L. and S. Alves : Thermochemical Conversion of Wood Wastes. Proceedings of the European Congress on Economics and Management of Energy in Industry, held in Algarve Portugal (2 April, 1984). A Reis and Ismith (eds.). Pergman Press, Elmsfard, NY. USA. pp. 97-101 (1984).

3. Figueiredo J.L., Orfao J.M., Monteiro J.C. and Alvess : Pyrolysis of Wood Wastes. Proceedings of NATO Advanced Study Institute on Biomass Utilization held at Cabideche, Portugal W.A. Cote (eds) Plenum Press, New York, USA pp. 553-557 (1983).

4. Hawley C.F. : Combustion of wood in wood chemistry edited by L.E. Wise and C.E. John (Reinhold, New York) (1952).

5. Hofiletter E.N. : Thermal processing of biomass carbonization, pyrolysis state of the art and applications. Proceedings of the experts meeting on Energy from Biomass, Freising, Fed Rip Germany NTIS P.C. ALL/MF.AO/ File No. 87770134 (Nov.1985).

6. Knight J.A. and Bowen M.P. : Pyrolysis - A method of conversion of forest wastes to useful fuel report on pyrolysis. American Pulp Association, Atlanta, Ga, VTA (1975).

7. Knight J.A. : Pyrolysis of wood reduces with a vertical bed reactor in progress in biomass conversion vall. (K.V.Sarkannen and D.A. Tillman edt.) Academic Press, N. York. (1982)

8. Kulkarni A. and Saluja J : Coal Conversion and Biomass Conversion Final Report on VSAID/GOI. Alternative energy resource and development programme, Energy Abstracts for Policy Analysis. 14, 265 (1988).

9. Maheshwar Dayal : Energy Today and Tomorrow. Publishing Division, Ministry of Information & Broadcasting, Govt. of India, 2nd Ed., pp. 60-61 (1989).

10. Mayers R.A. (eds.) : Handbook of Energy Technology, John Wiley and Sons, New York (1983).

11. Milne T. : Pyrolysis the thermal behaviour of biomass below 600^{o}C. A survey of Biomass Gasification, Rep. No.TR-33-239. Solar Energy Research Institute, U.S.A. (1979).

12. Milne T. : Pyrolysis - The thermal behaviour of Biomass below 600^{o} In biomass gassification, Principal and Technology. Ed. T.B.Reed. 67, 91-118 (1981).

13. Naguhiro J., Nomura F. and Shimane K. : Manufacture of Fuel gas and Charcoal. Japanese Patent 61, 209, 293 (Sept.1986), File date 14 March, 1985.

14. Narinder Gauthm : Energy Plantation for Fuel Wood Crisis. Invention Intelligence, pp. 247-250, (July 1985).

15. Neepchand, Kassiap : A note on the pyrolysis behaviour of sugar cane fibrous products. Biological Wastes 20, 3, 203-8 (1987).

16. Paul S. : Biomass Char. Energy Digest. Vol.1, 11-5 (1982).

17. Peters W. : Biomass Pyrolysis System Final Report, Official Publications of the European Communities, Luxembourg, EUR-10112-OE 42 P (1985).

18. Prabhakar K., Maheshwar R.C. and Vimal O.P. : Pyrolysis of Coconut Shell and its Potential as Fuel. Centre for Rural Development and Appropriate Technology, Indian Institute of Technology, New Delhi, Agricultural Wastes, 17(4), 313-7 (1986).

19. Reger H. : Carbonization of Forestial, Agricultural and Agro-Industrial Waste as well as of Organic Municipal Waste and Practical Utilization of the Recovered Product (Char, gas, pyrolysis) Final Report. Official Publications of the European Communities, Commission of the European Communities, Luxambeurg. EUR-9974 -EU 112 p. (1985).

20. Shafizadeh F. : Chemistry of Pyrolysis and Combustion of Wood in Progress in Biomass Conversion. Vol.3 (K.V. Sarkanen, D.A.Tillman and E.C.John eds.) pp. 51-75 Academic Press, New York.(1982).

21. Summers and Mansson M. : Experimental Chemical Thermodynamics Combustion. Calorimetry Pergman Press Vol.1, Cha.II. (1979).

22. Vahrman M. : TheCharcoal in a Scientific Age : Production in Kilns and Quality of Twelve Charcoals. Caribbean Consultation on Energy & Agriculture. pp.302-33 (1980).

23. Venkataraman C., Raman P. and Kohli S. : Calorific Value Measurements for Biomass Fuel Energy. Environment Monitor No.061006, 3, 63-67 (1987).

24. Vimal O.P. and Tyagi P.D. : Energy from Biomass. Agrocale Publishing Academy, 203 Defence Colony Flyover, New Delhi,110024, India, pp. 375-440 (1984).

25. Vimal O.P. and Bhat M.S. : Wood Energy System. K.L. Publications, New Delhi 110052, pp. 50-52 (1989).

26. Wans E.I. and Simman J.A. : Biofuel Synthesis in Research Overview of Biological and Chemical Conversion Methods and Densification of Key Research Areas. SERI ITR-33-067. Solar Energy Research Institute, USA, 204 September (1978).

Yamba F.D. : Development of Charcoal Retart Pilot Plant in Zambia African Energy Programme Research Report, Series No.4, London Commonwealth Science Council, C.S.C. No.239, viii+ 491 (May 1988).