Fuels and Chemicals from Biomass

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Abstract

Biomass is the basis of all fossil fuels. It can also be the source of many chemicals. Because of the extraordinarily high rate of use of fossil fuels (in terms of a few human life span periods) in comparison to their rate of generation (on geological time scales), there is need to examine the use of bio-fuels in particular and chemicals as value addition to the use of biomass. While the methods to use biomass as a clean source of fuel for high grade heat or electricity have been largely mastered in recent times, in part by the work of the group at the author's laboratory, there is such an extraordinary variety in the possibility of chemicals from biomass that only a few familiar to the present author will be discussed. The rudimentary and widespread use of bio-residues as cooking fuel on grate, known to be pollution ridden in terms of gaseous emissions can indeed be upgraded into a clean combustion system through the use of a inverted downdraft gasifier stove. In this case a gaseous fuel - producer gas is being generated and burnt. Such a system has the advantage of fire and forget philosophy but limited to being a batch system. For continuous operation at power levels including MW level for either clean thermal energy or cleaner gas for mechanical/electric power, one needs to undertake thermo-chemical conversion with careful design aimed at burning all tars (complex oxygenated hydrocarbons) and reducing particulate content. These aspects for getting producer gas from atmospheric pressure air gasification will be described. The important feature of the approach taken to make the system design allow for multi-fuel operation including light agro-residues will be described. Examples of value added products in terms of activated carbon from biomass, more particularly from coconut shell and activated carbon as well as precipitated Silica from rice husk char will be discussed. The choice of these examples is due to their current relevance as industrial products.

Introduction

Biomass has been a known source of fuel energy for several thousands of years; however, the scientific study of these fuels for combustion got started only about a few hundred years ago. The fact that most users believe that they know how to use biomass in a traditional manner has posed difficulties for the acceptance of newer ideas of the use of these in a cleaner and upgraded manner. Modern use of biomass particularly in a form upgraded into electricity is perhaps only a few decades old and other ideas of efficient thermal use even for domestic cooking are only a few years old and hence, it is appropriate to classify what is being described here as non-traditional. The developments on using biomass as a clean domestic fuel, an industrial fuel for high-grade thermal applications and for electricity, and chemicals – activated carbon and silica in view of their industrial importance are described.

Biomass as a clean fuel

Traditionally grate combustion is used for burning odd pieces of collected biomass from tree fallings and the like. A small fire is lit on the grate and biomass is continuously added to generate combustion gases used for cooking. Somewhat similar procedure is adopted in large furnaces as well. Once in a while when power level goes down as measured by the steam pressure if the furnace is used for generating steam or some other parameter in other cases, the operator is expected to shove in the fuel. If one examines this process, it turns out that the thermal power level keeps fluctuating over a time. This is because, during the early period, the biomass will get heated and at this time power level actually goes down. Once the material is heated to 350 to 400 °C, it begins to loose volatiles. The power level at this stage may increase enormously to the point of being fuel rich due to the fact that biomass has 75 to 80 % volatiles (based on ash free condition). Once all the volatiles are burnt away, the power level again goes down. The issue is complicated by many features: size distribution of biomass, amount of moisture in the biomass, and its intrinsic density. This problem of combustion-on-grate does not affect the performance greatly if one were looking for steam generation from a boiler since the inertia of the system can accept variations in many features to a reasonable extent. If on the other hand, one were using the hot gases from the furnace to heat up air for drying purposes either directly or indirectly, then there will be variations in the hot gas temperature to the extent that one might find that the gases are too hot or cold compared to set or desirable value. This might actually create conditions of burn up of the product which is being dried or inadequately dried. To overcome this problem, one must have a mechanism of maintaining a constant thermal power from biomass, which is varying in size, moisture distribution and ash content. Gasification process provides such an alternative. In this process, one conducts the thermo-chemical conversion under sub-stoichiometric conditions. These are based on downdraft principle. Normal downdraft systems have biomass pieces moving down under gravity with air also being drawn in the same direction. At a point along the reactor, a high temperature zone is created initially by lighting the system and subsequently on its own through exothermic chemical reactivity. Reverse downdraft systems are cylindrical containers/reactors with air flowing from bottom to the top and biomass moving down. Figure 1 illustrates the reactors for two downdraft systems. The advantage with normal downdraft systems is that biomass can be continuously loaded from the top region; in reverse downdraft systems, the loading can be only at one point of time. Hence the design must include the specification of the burn time. Lighting the system in the first case calls for air nozzle (s) at which a wick flame can be brought for ignition to be started under conditions in which the air is drawn through the system by suction. In the latter case, one can light the fuel at the top. One cannot run the normal downdraft system unless a blower is used. In the latter case, one can possibly benefit from natural convection under certain conditions although with an emission performance inferior to one with blower. Also the power required to operate the blowers is indeed very small – about a thousandth (in electricity) of the thermal power delivered.

The principal feature of the gasification based power generation system is that the power output remains near constant and can be controlled over a wide range. The reason why this happens to occur is that the sub-stoichiometric exothermic chemistry leads to gases which react further with hot charcoal so that endothermic conversion of the gases into combustible gases like CO, H_2 and

CH_4 takes place. These combustible gases carry most of the energy. Only about 6 to 8 % of the energy is in the heat of the hot gases. In fact, the cold gas captures about 80 to 85 % of the calorific value of the input material. Thus the generation point of energy and station where it is used can be separated over considerable distance. The fact that the energy is in the gas lends itself to use in more compact combustion equipment, more economically arranged than otherwise.

The Gasifier Stove

Figure 2 shows the schematic of a new kind of biomass stove. It is a twin walled chamber, the inner chamber containing a grate towards the bottom, holes towards the top connecting the inner and the outer chamber. A small tube at the bottom with variable area control is expected to help control the power level. The chamber is filled with pieces of biomass of almost any kind albeit with a moisture fraction less than 15 % (sundry biomass has moisture fraction between 8 to 10 %). The filling should be up to a level below the air holes. After light up at the top, the high temperature zone above the air holes will cause free convective pumping action on atmospheric air which will be drawn through the annular space. If a small capacity blower is available, the air flow can be set and this would make the combustion quality in the space above the air nozzles very good. Notwithstanding the deficiency in combustion quality in the absence of blower, the power level will be near constant. If higher power is required, part of the air from the blower needs to be put through the bottom tubing to enhance the rate of gasification. A typical Power vs. time trace is shown in Figure 3.

Downdraft Gasifier for power generation

The gasifier for power generation has three primary elements – reactor, cooling and cleaning. The primary aim of the gasifier is to produce cool and clean gas of high calorific value (as high an energy retention as possible compared to the biomass fed into the system – another way of stating this is that one should aim at high gasification efficiency). The role of the reactor is to generate not only a combustible gas but to do so by cracking tars as much as possible. The requirement that dust level in the gas also should be low calls for the use of solids with relatively high structural integrity to prevent break-up into fine pieces, ultimately into powder. One cannot expect to tailor make this requirement at all. One may have to accept whatever one gets from natural biomass as it were excepting that one need not size the biomass. However, if one were to use briquetted biomass, one needs to insist on good structural integrity, perhaps by looking for briquettes from screw press instead of ram press to help ensuring retention of structural integrity till as late a stage in the conversion process as possible. The reactor shown in Fig. 1b has several air entry zones – one from the top and another from the side air nozzles and/or a central air nozzle located at an appropriate distance above the side air nozzles. While the air from the top ensures the gasification process occurs more uniformly, the air from the other two zones will ensure better tar crack up and hence gas with little tar. Also it is possible to manage the operation of the reactor with top closed and air nozzles open. In this case the operation of the system will approximate the closed top World war II class gasification system. The flow and thermal non-uniformity in the azimuthal direction is often suggested to be the cause of higher tar levels in such systems, certainly at part load. Such problems are less severe in the case of open top systems. This subject is also connected to char conversion. If only the top is open and the side as well as central air nozzles are closed, the char conversion will not take place and the entire reactor will be slowly converted into a char bin. In order to cause the char conversion, it is necessary to allow air at a location where char is already formed in the reactor. This process will also help tar reduction since biomass char is known to be reactive at the high temperatures experienced in this zone (700 to 900 °C).

In trying to build these systems for agro-residues, one needs to account for ash content much higher than in wood (which is <1 % compared to rice husk with ash content of 20 %) implying the need for continuous ash extraction systems.

The subject of cooling and cleaning is also intricate; they have been addressed in earlier papers from our laboratory (one can see more details on the home page at http://144.16.65.129/~mukunda/home.html). They are not discussed here due to weak relevance to the subject under discussion.

One of the interesting features of the gasification process is that the gasification efficiency and the reduction in tar content improve with the reduction in moisture fraction of the biomass based reactors.

Bio-liquid fuels

From the above discussion and the work done in India, it is possible to imagine that gasification route will meet stand alone small power generation requirements at bio-pit heads, namely, the villages and bio-plantations and also for grid synchronization at power levels of a MWe or so. There is however, a serious problem for transportation, which now depends heavily on diesel. One area in which scientific work has led to clear conclusion of practical relevance is the use of bio-oils like rapeseed oil in some western countries and the possible use of non-edible oils in India. Yet, there has been a serious thrust on the production of pyrolitic oils from biomass in many countries – Canada, Spain and Italy to enable their use in reciprocating engines. Several studies have shown that pyrolitic oils have problems related to their acid content and water – ignition and performance in reciprocating engines. Gas turbine engines using this oil seem to show less problems of ignition and combustion since these are continuous combustion devices. One serious question to be debated is the relative importance given to the two routes –

(a) pyrolitic oils and their refinement and (b) non-edible oils and their refinement to enable use in reciprocating engines (the main focus of developing country alternative for small power generation will be reciprocating engines).

In several developing countries, there is need to enhance biomass productivity because the existing stock is removed for industrial (major) and domestic purposes with inadequate thought to replantation. The efforts to generate such plantations under social forestry and other programs supported in part by international aid has focused attention on traditional species like Subabul, Acacia arabica, Eucalyptus and the like all of which generate an annual output of 5 to 8 dry tonnes per hectare. These amount to an income of Rs. 10,000 to 16,000 / hectare (250 to 400 US $ / hectare). If on the other hand, one conceiveds of a high value product like fruits (coconut, for instance), or non-edible oil seeds to grow even on degraded lands, one could conceive of an output – the fruits or oil seeds in addition to bioresidues. For instance, in the case of coconut tree, one gets 10,000 to 30,000 nuts/year/hectare and residues of 5 to 7 tonnes shells and 8 to 10 tonnes fronds/hectare/year. The net revenue from one hectare of coconut plantation is 50,000 to 120,000 Rs (1250 to 3000 US $) for the food product and 15,000 to 20,000 Rs. (400 to 500 US $) per year equivalent of residues. Similarly if one were to take the plantation of Jatropha, one can get seed yield of 4 tonnes/hectare/year and bioresidue yield of 5-6 tonnes/hectare/year and these are equivalent to 2 tonnes/hectare/year oil, 2 tonnes/ hectare/year cakes suitable for use in biogas plants and later as fertilizers or directly as fertilizers. A gasifier based compression ignition engine can operate on producer gas from solid bioresidues and oil from these sources in a dual-fuel mode. Also, if the esterified liquid fuel can be generated, then one of the issues related to maintenance problem, namely, gumming of the fuel injectors can be avoided. Thus it is not obvious if the research into pyrolitic oils should be relevant immediately to developing countries in terms of energy mix from bioresidues.

The important issue that needs to be tackled is the growing of these plants/trees. The advantageous point is that there is a lot of waste (or wasted) land that has been allowed to become fallow can be used to grow these trees (the estimate of waste lands in the country is between 70 and 130 million hectares), the selection of the species dependent on agro-technical considerations, and the land can be made to become green and yield oil and bioresidues for various uses. These require governmental (both centre and states) interventions in terms of policy. One sector, which has not been tapped for this purpose adequately, is the industrial sector in establishing a relationship between their needs and the biomass option. Bringing industry (say, the confederation of engineering industries), the government – the ministry of forests and environment as well as non-conventional energy sources and the corresponding state governmental agencies would be vital to the development in this area.

Experience on the use of one of the non-edible oils namely, Honge-oil (Pongomia Pinnata) as a fuel in running diesel engines has been obtained under a MNES funded project by Prof. U.Shrinivasa, of the Mechanical Engineering department at Indian Institute of Science, Bangalore. The essence of the experience in the running of a single engine over about 1500 hours and several engines together over 3000 hours is as follows.

1. The oil as obtained from the expeller requires thorough cleaning.
2. The engine can be both started and run on Honge oil continuously whenever the engine itself is in good condition.
3. The engine exhaust appears clean during visual inspection.
4. The engine fuel consumption increases by 10 per cent by volume as compared to diesel.

Initial estimates and assessments suggest that at least in the semi-arid areas enough Honge trees can be grown to enable most villages to operate local power stations using this oil, at the rate of about 0.5 kW per capita. This will allow villages to feed surplus power to grid instead of being consumers of grid power as is the situation at present. It will also make available to the villages electricity in sufficient quantities from one of the most inexpensive of the renewable energy options. Since India has more than 300 varieties of tree species whose seeds yield oil, the twin problems of need for adequate energy resource and the need for requisite tree cover in the semi-arid rural areas could be overcome by propagating seed oil based electricity generation. Needless to state that the proposed path will be both environmentally and ecologically sound, would meet international obligations in reducing CO_2 emissions and will provide energy security to the rural areas. The by-products of such a scenario, being the tree residues, leaf litter and oil cakes, will create additional opportunities for appropriate use in the rural areas. The real question today is how to make progress in achieving these eminently feasible objectives.

Chemicals from Biomass

While the chemicals that can be extracted from biomass are many including those with medicinal properties, only two chemicals which can be obtained from biomass namely, activated charcoal and silica are considered here because of large scale and wide industrial applications. Almost any biomass can be used to obtain Activated charcoal; Silica can be profitably obtained from rice husk ash since 95 % of the rice husk ash is Silica.

Activated carbon is being manufactured by about fifty industries in India. A large part of this is from charcoal generated out of coconut shell. Only a few industries produce activated carbon from hardwood and pine. Activated charcoal is used in the form of powder as well as granules/pellets. In most cases, the activation stage is separated from the char generation. The char is subject normally to steam activation at temperatures between 500 to 1000 °C to generate high surface area char whose quality is characterized by Iodine value, Methylene blue value, and some times Benzene absorption value. Typical Iodine absorption number is 600 to 900 mg/gm (Methylene blue value between 80 to 280 mg/gm) of the activated char. This amounts to total internal surface area of 500 to 1000 m^2/gm. Typical selling prices of these vary from Rs. 30 to 240 depending on the quality as defined in specifications; these are dominated by the Iodine value or Methylene blue value. The process of making the charcoal from biomass is largely in the unorganized sector and is done by the pit method which is both unclean and unhygienic. In some instances, court rulings have banned the use of this technique. In our country, the reach of courts some times is limited and leads to illegal manufacture in remote places including forests and the only visible impact would be raised costs of the product. It is now possible to combine power generation with activated char manufacture in an economically and environmentally meaningful manner. Recent measurements of the charcoal drawn from the exit of the gasifier after partial operation or the fine pieces which have come out of the grate dried at temperature beyond 110 °C show values of Iodine number between 550 and 800. Hence possibility of converting the entire process of manufacture by combining it with power generation seems industrially interesting. One such plant is currently in the process of being built in Tamilnadu with the technology provided from IISc.

Silica is industrially produced from sand in relatively large industrial infrastructure using high temperature melting process. This technology is becoming more and more dependent on the scale of operations demanding higher capacity ratings for being economically viable. This allows for alternate low temperature processes to be economically viable. One of the generally known processes is to treat the cleaned rice husk ash with dilute HCl to eliminate most of the soluble impurities and then with caustic soda to generate Sodium leaving behind carbon. Sodium silicate thus produced is diluted and reacted with carbon dioxide at 95 °C and a pH of 10 ± 0.5 leading to the precipitation of Silica particles of about 25 μm. This Silica is filtered and re-slurried to pH of 7 and washed; the precipitated Silica so formed has moisture which is dried in a spray drier and later processed to desired physical requirements. Sodium carbonate solution is causticized with lime to get back treated caustic soda for reuse. The typical process path is illustrated in Figure 4. The essentials of the process and the quality of Silica produced have been tested out at 1 kg/hr in the laboratory and the product quality verified to be reproducible. The typical properties are as follows:

SiO_2 on dry basis : 99.7 %; Sodium as Chloride, Sulfate : < 1100 ppm; Fe_2O_3 : 150 ppm; Surface Area : 190 m^2/gm; Loss on drying : 6 %; pH : 6.3; Density : 2 gm/cc; Bulk density before tapping : 0.202 gm/cc; Tapped density : 0.322 gm/cc

These properties are much better than required for tyre industry. The process parameters have been scaled for production of 1200 tonnes per year and the techno-economics of the process has been worked out. The production cost of silica from the present process has been compared with that of the current processes based on sodium silicate. Whole the current production costs are around Rs. 19/kg, those from the existing processes are around Rs. 33/kg (after accounting for loan repayment, depreciation, etc.). The investment for this plant a 1200 T/year plant based on the current process is Rs. 385 million and the annual sales revenue is Rs. 457 million from 1200 tonnes of Silica at a sale price of Rs. 35 /kg and calcium carbonate of 622 tonnes at Rs. 6/kg. The pay back period for this project is 3 years using standard financial criteria for the assessment. The actual market prices of Silica as assessed from one industry (a tyre industry) appears to be around Rs. 55 per kg and in this case the economics is even better. Currently efforts are going on along with a marketing and engineering consultant to put up one large plant in South India.

Figure 1 The schematic of normal and reverse downdraft combustion system

Figure 2 The gasifier stove – internal details.

Figure 3 Power vs time of a typical gasifier stove

Figure 4 Process chart for Precipitated Silica plant.

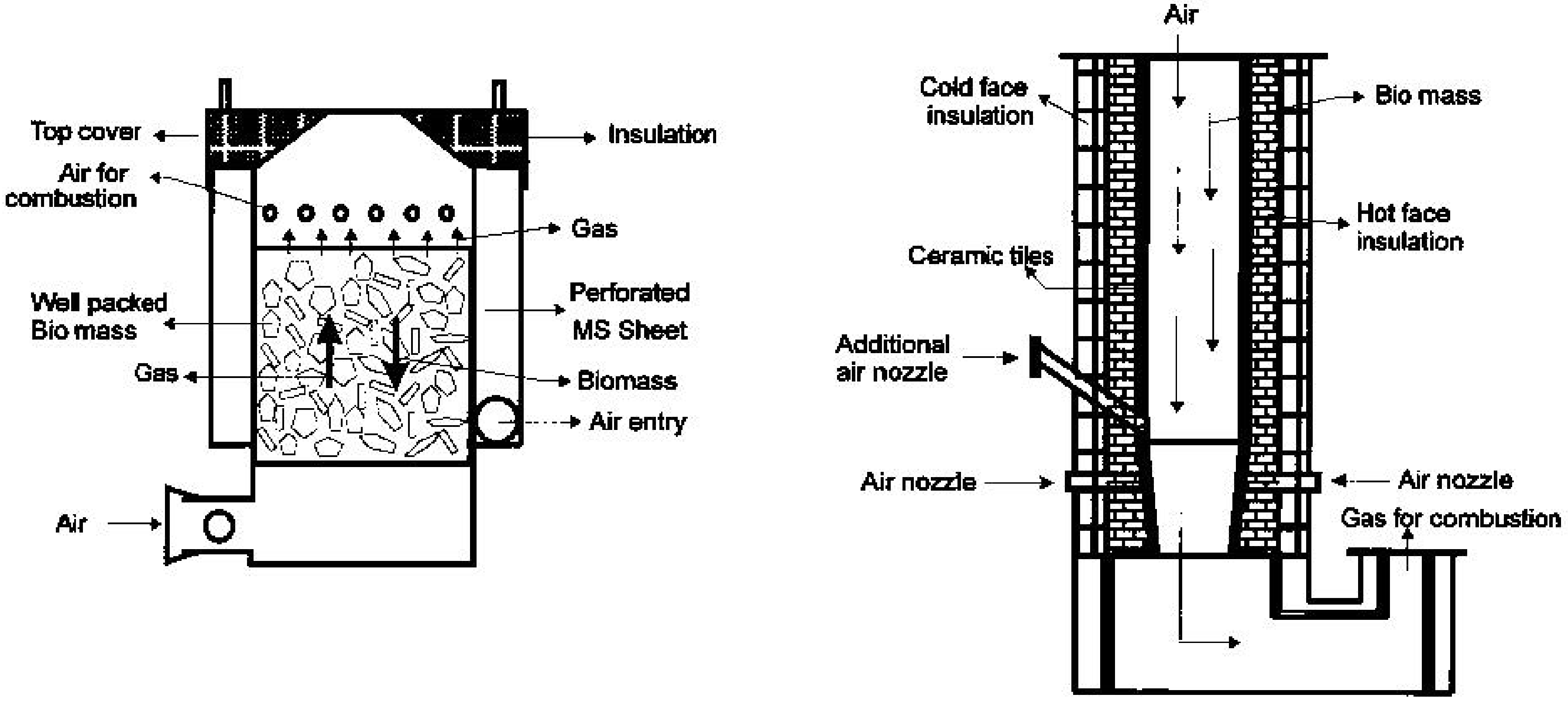

Fig 1a) Stove
(Reverse downdraft combustion system)

Fig 1b) Gasifier reactor
(downdraft gasification system)

Figure 1: Schematic of normal and reverse downdraft combustion system.

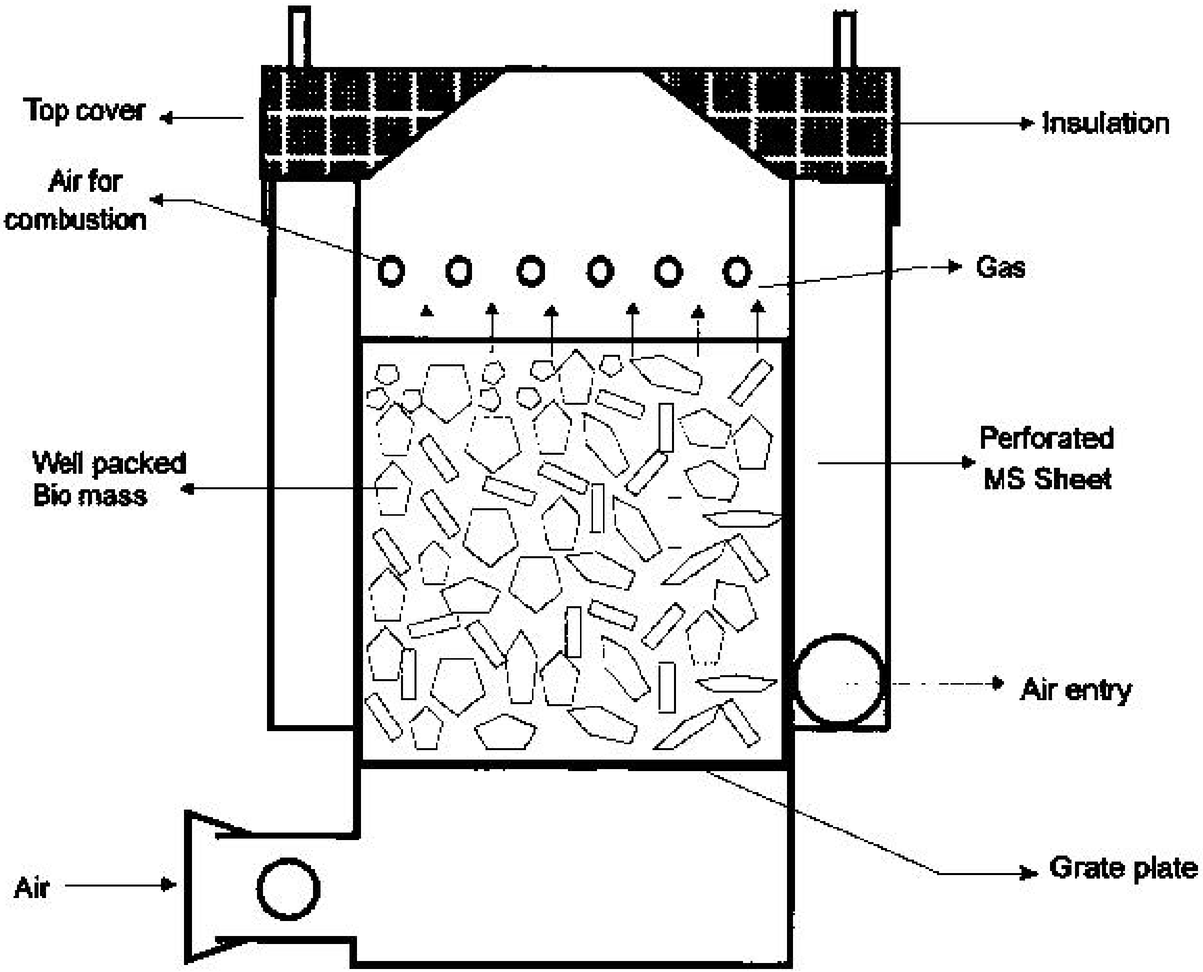

Fig 2: Internal details of Gasifier stove

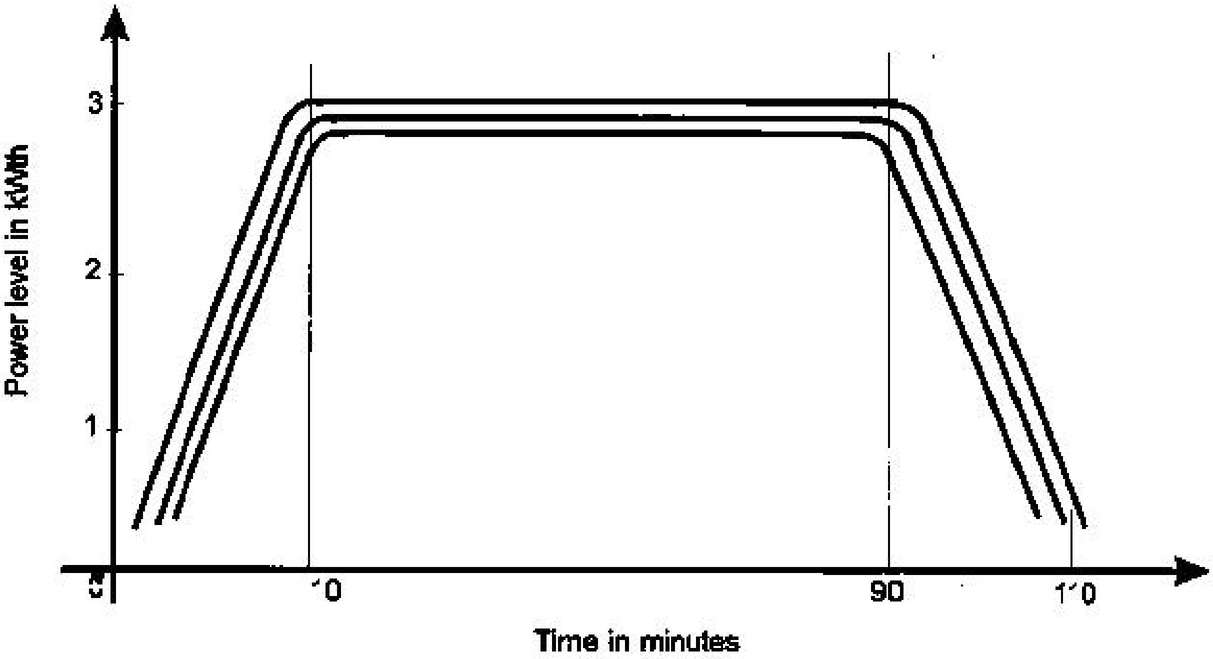

Fig 3: Power vs time for a typical gasifier stove

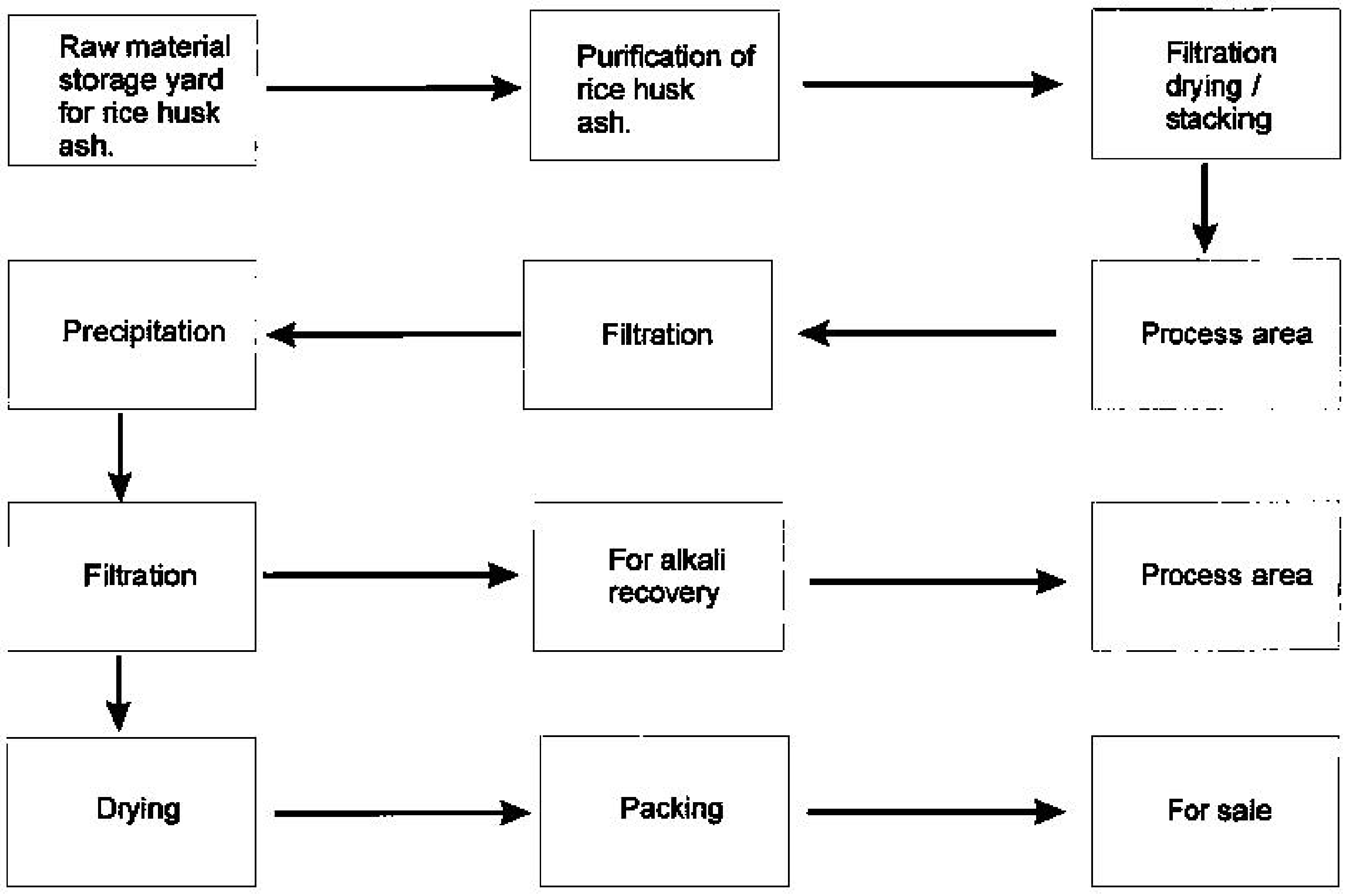

Fig 4 : Process chart for precipitated Silica plant.