

SUMMARY OF THE DISCUSSIONSSession IV THERMOCHEMICAL ROUTES TO GASEOUS AND LIQUID FUELSRapporteur : R. OVEREND, CanadaSpeakers : W.P.M. VAN SWAAIJ, Netherlands
T. REED, USAChairman : K. ROBINSON, IrelandPoster Session : 16 papers presented

Biomass energy can only be realistically viewed as a holistic system encompassing the chain from land/water resource management to end use application. To separate out one set of conversion technologies from the context of the system (resource, straw/wood/animal residues, transport, conversion, delivery and end use application) results in the loss of perspective of both social costs and benefits to be gained from bioenergy utilisation. As a result of this distortion the session was rather inconclusive on the issue of thermochemical technologies for the EC or North America while being extremely definitive about the application of combustion and gasification or electricity generation in developing countries. The paradox resulting from this was disturbing; many audience members (their memories of world war II technologies somewhat blurred by the passage of time) suggested that these technologies, while not meeting the environmental "niceties" of the developed world, were quite adequate for the developing world !

The general impression gained was that the application of the combustion of difficult materials such as straw for on-farm applications or as a supplementary fuel with high sulphur coal and the coupling of wood fired gasifiers to boilers previously fueled on premium fuels, should be treated as demonstration projects to accelerate their introduction into the free market system.

Because not many discussed the current activities of national governments and the EC in accelerating the development of biomass derived syngas to methanol synthesis, it is evident that the role of land use strategies and scale effects on the economics of liquid fuels are not

*Ans**Energy from Biomass**E.C. Conference 1980*

receiving significant public consideration. The poster paper by Ader et al showed that at plant scales approaching those of modern pulp mills, an energy product (methanol) from either the yet to be proven technologies of steam or oxygen/steam gasification, is very close to commercial viability. This study is comparable to others in Canada and Sweden which draw similar conclusions, thus reinforcing the need for the construction of process development units of around 50-100 tons per day dry feedstock capacity to finally confirm cost and yield data.

While both session speakers stressed the antiquity of gasification technology Van Swaaij managed to convey clearly the lack of refinement of the technology that during MW II produced more than 1/2 million vehicle gasifiers. A concentrated program at Twente University on the co-current gasifier has resulted in the development of both a satisfactory technology along with an adequate chemical engineering design basis, thus enabling calculation of scale up/down parameters. The dark horse development in gasification is the fluidised bed which offers feedstock throughputs as high as 2 tons/m²/hr using air at atmospheric pressure. While not commercially viable below about 10 MW the evidence from experiments in Canada suggests that fluidised bed reactors with wood feedstock give high yields of saturated and unsaturated hydrocarbons (CH₄, C₂H₄, C₂H₆) with little tar. Poster papers 6,7 and 10 concerned with experiments using rapid pyrolysis rates of more than 200 C/sec and brief residence times followed by rapid quenching, indicate high yields of hydrocarbons at the expense of CO & H₂ yields. In the limit at heat fluxes more than 100 W/cm², Reed reported that more than 20% mass conversion to olefins are possible. Fast pyrolysis in fluidised beds evidently could lead to processes producing ethanol for example by the hydration of ethylene which would be far superior to current hydrolysis and enzymatic routes from wood.

Slow or traditional pyrolysis is still the subject of scientific interest despite the well-known difficulties in applying the data obtained to "fixed bed gasifier design". The general knowledge that slow heating rates result in less gas production with greater proportions of CO & H₂ as well as char are verified by papers 3 and 4. The influence on pyro-

lysis products of differing feedstock composition obtained by fractionating the plant material was demonstrated in papers by Richard and Gaudet. Much of the current thermochemical laboratory work and technology development is specific to dry feedstocks. To obviate the requirement to evaporate water with its attendant loss of energy before pyrolysis a paper by Bobleter discussed a hydrothermal treatment which offers the opportunity of fractionating the feedstock with the recovery of chemical feedstocks as well as energy products. A paper by Have outlined a combustion scheme that would effectively recover the latent heat of evaporation in drying feedstocks such as animal residue - the restriction being that only low grade (less than 80°C heat) would be available as a product though at relatively high efficiency.

Liquefaction by indirect methods such as syn-gas to methanol are seen as the near term opportunity while direct liquefaction is recognised as being some time away from even pilot plant demonstration. Syn-gas to methanol synthesis over selective catalysts is seen to be far more viable than Fischer-Tropsch type synthesis with its accompanying diverse product slate. Current technology is operating at high pressure requirement and even into less selectivity, thus producing a methyl fuel with higher alcohols will give significant gains in process efficiency. The paper by Masson suggests a promising route to lower pressure (and therefore process energy requirements).

The energy requirements for gasification to MJV (medium joule value) or LJV gas are less than 10% of that contained in the wood feedstock. For countries with significant non-fossil fueled electricity generation the use of electricity to provide this energy in gasification appears promising as a route to syn-gas or MJV gas, as discussed in the paper by Divry.

As a worker in the field I would like to make a plea concerning the gathering of experimental data. Biomass quantities should if at all possible be given on a dry mass basis. Where moisture is a significant parameter, the moisture content should if possible be stated as a total mass basis i.e. $\frac{ZH_2O}{\text{mass } H_2O + \text{mass Biomass}}$.

As far as possible SI units should be used rather than Btu or k Cal. The reporters of experimental data should take care to analyse their chemical products and close their mass balances - particularly with respect to the char produced. Deglise noted that the molecular weight of a 700 C pyrolysis char at 16.7 amu is considerable in excess of the theoretical value of 12 amu assumed in most studies. Likewise weight loss data presented in terms of Arrhenius factors ($A \exp(-E/T)$) presumes a mechanistic understanding which is just not available at this time. In fact the poster papers at this meeting clearly show our lack of understanding of fundamental factors in the process that we casually call pyrolysis. Feedstock variation, heat transfer and heating rates, moisture contents, thermal history, the immediate gaseous environment, etc., all are significant factors in this puzzle. Nevertheless, the meeting did show significant advances in the technologies of gasification despite the lack of fundamental understanding.

"GASIFICATION - THE PROCESS AND THE TECHNOLOGY"

W.P.M. VAN SWAAIJ

Twente University of Technology

The Netherlands

Summary and Conclusions

Thermochemical gasification of biomass can produce low, medium and high joule value gases. The characteristics, applications and potential of the different processes and reactor types are discussed. The introduction of biomass gasification on a large or intermediate scale for the production of power, SNG, methanol etc. will depend on developments in coal and municipal solid waste gasification and on the prices of biomass. Biomass and especially wood is a clean fuel and therefore its direct combustion using modern equipment will be a strong competitor for energy generation via gasification. Gasification is also attractive for small scale, power and power heat generation and developments necessary for its widespread acceptance are discussed. It is further concluded that, on the small and intermediate scale, new processes which require minimum feedstock preparation and preferentially producing M.J.V. gas without the use of oxygen, should be developed.

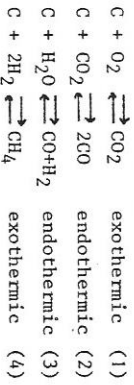
INTRODUCTION

Thermochemical gasification of solid fuels such as biomass, peat and coals has been studied and applied for about 140 years (1). A complete review would easily fill several textbooks. Therefore the discussion will be restricted to some of the fundamentals and the different types of technology used in the field of biomass gasification and will then concentrate on some applications which are expected to penetrate the energy market in the near future.

The aim of a gasification process is to transfer the combustion value of the solid fuel to a gaseous energy carrier, preferably in the form of chemical energy and not in the form of sensible heat. Gasification is performed because of the advantages of a gas over a solid fuel: gases are easy to clean, to transport and to combust with a low excess of air and there is little resulting pollution. Further, gases can be burned in an internal combustion engine (gasturbine, reciprocating engines) and can be easily applied in combined cycles.

Biomass gasification can also be carried out via biological gas generation. Thermochemical routes have the advantages of compact equipment due to the relatively short residence times required (1 - 10.000s), easy start-up and stable operation and there are no requirements on the nutrient value of the feedstock. Its disadvantages are that relatively dry feedstocks are required and that the ash produced has little value as fertilizer. We will only discuss the thermochemical routes further.

In the gasification process the biomass is successively heated up, dried and pyrolysed to produce gases and char. These products then react further in a complex way with a gasification agent which can be air, oxygen, CO₂, steam, mixtures of these gases of hydrogen. The reactions that take place between the char and the gasification agents can be described broadly speaking by the following equilibrium reactions:



The composition of the productgas is determined by the biomass feedstock and gasification agent used, and by process conditions such as pressure, temperature, residence time and heat loss or external heat input. The external heat source can be a nuclear plant (2), concentrated solar radiation or another chemical reaction (e.g. external combustion of part of the fuel, CO₂

acceptor process (3) etc.). Most gasification processes are autothermic however and we will consider only those cases. Gasification produces several types of gases and these can be roughly divided into three categories, according to their heat of combustion per m³ at ambient conditions (see table 1.)

	CO	H ₂	CO ₂	CH ₄	C _n H _m	N ₂	Joule value MJ/m ³
L.J.V. gas %	17.0	18.3	14.2	1.8	-	48.7	4.75
M.J.V. gas %	61.0	28.0	2.0	8.0	-	1.0	13.61
H.J.V. gas %	-	-	0.9	81.2	3.4	14.5	31.65

Table 1. Typical compositions of dry, clean product gases (vol.%).

Low Joule Value gas. (3.5 - 7 MJ/m³)

A typical production and application scheme is given in fig. 1.

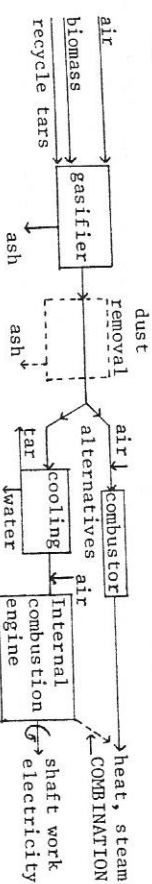


fig. 1., L.J.V. gas production and application.

Air is the gasification agent. In most cases it is simply a two stage combustion process but sometimes the gasifier is retrofitted to an existing gas/oil boiler, kiln or motor. The lower scheme is specially attractive if electricity generation can be combined with a useful application of the sensible heat of the exhaust gases (drying, heating, etc.). Due to the low specific energy content the product gas cannot be transported or stored economically.

Medium Joule Value gas. (9 - 15 MJ/m³)

Two typical production schemes are given in fig. 2 together with possible applications.

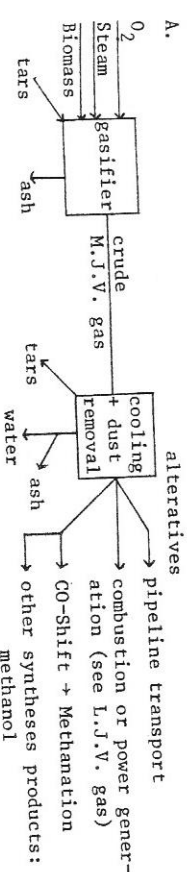


Fig. 2A.

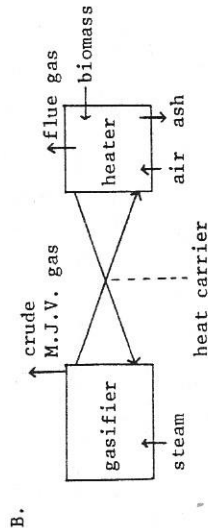


fig. 2B.

fig. 2., production and application of M.J.V. gas.

Scheme A is well known. However, Oxygen is usually expensive and scheme B avoids its use. The endothermic char-steam reaction is separated in location from the exothermic reaction (combustion with air). Solid reactants and/or heat carriers are circulated between the gasifier and the heater in the same way as in fluid bed catalytic cracking. To some extent it can be considered as a continuous variant of the old intermittent water gas process. This scheme B (4,5) has not yet been proven commercially. The M.J.V. gas can be economically transported over large distances and used for (combined) power/heat purposes. Furthermore the product gas (also called synthesis gas) can be used to produce a wide variety of chemicals and energy carriers such as methanol, H₂, gasoline, SMG, etc. High Joule Value gas. (20 - 36 MJ/m³) Mostly these gases are used to substitute or supplement natural gas. They are usually produced from M.J.V. gas (see fig. 2) but in a few schemes direct production by gasification is being developed (see fig. 3)

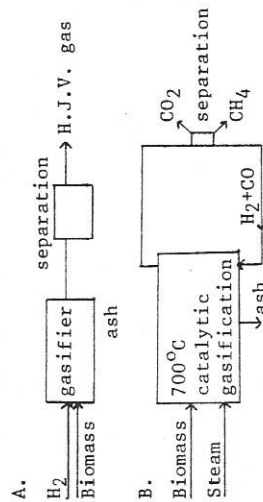


fig. 3., direct H.J.V. gas production by gasification.

Apart from gasification at high pressure with hydrogen (A) the EXXON (6) process for coal looks promising. The almost thermally neutral reaction: $2\text{H}_2\text{O} + \text{C} \rightarrow \text{CH}_4 + \text{CO}_2$ is realized at approximately 600-700°C utilizing K₂CO₃ as a catalyst. Methane is continuously separated from the recycle system by cryogenic distillation. However such processes are not yet commer-

cially available.

Most of these type of processes have been developed for coal or peat but some have also been tested for biomass or municipal waste. Biomass contains much more oxygen and hydrogen than coal, reducing the amount of steam necessary to effect gasification. Furthermore, its sulphur content is usually low. On the other hand, as produced, biomass often contains large amounts of water and after drying it will attract an equilibrium amount of water if not properly stored. Apart from energy losses in drying, this adds to the complexity of the process. The biomass is often in an inconvenient shape and unless the gasifier is specially adapted, extensive feedstock preparation may be required such as grinding or pelletizing. The cost of these operations can be considerable (up to \$ 25,- per ton (7)) and consume up to 10% of the heat of combustion of the biomass. Another important property of biomass is the dispersed nature of its production giving rise to important collection and transportation costs specially for large scale conversion processes. The different technical solutions proposed for the gasification reactors will now be discussed in relation with the properties of the biomass feedstock.

REACTOR TYPES

Most of the reactor types have already a long history. Fig. 4 gives the different principles together with temperature and conversion profiles. It should be realized that reactor properties do not necessarily reflect the process performance. Tars and heat can be recovered and recycled to the reactor. However this complicates the overall process.

The countercurrent moving bed reactor has the longest history and is widely used (1, 8, 9, 10) both with solid and liquid (10, 11) ash removal. Its advantages are its simplicity of operation, that no solids flowrate control is necessary and that there is internal heat exchange of the product gas with the biomass feedstock. ($T_{\text{out}} = 400^\circ\text{C}$). Its disadvantages are that large amounts of tars are produced, and that channeling due to sticking tar particles may occur, necessitating the use of rotating grids. Pelletizing may be necessary depending on the feedstock.

The co-current moving bed reactor (1, 12, 13, 14) is also simple to operate, produces an almost tarfree product gas but is more difficult to scale-up (see later). It has a higher product gas temperature (700°C) and can also require feedstock pelletization.

The fluid bed (15, 16, 17) reactor can handle a wide range of feedstocks but has a high product gas temperature (e.g. 900°C), and important

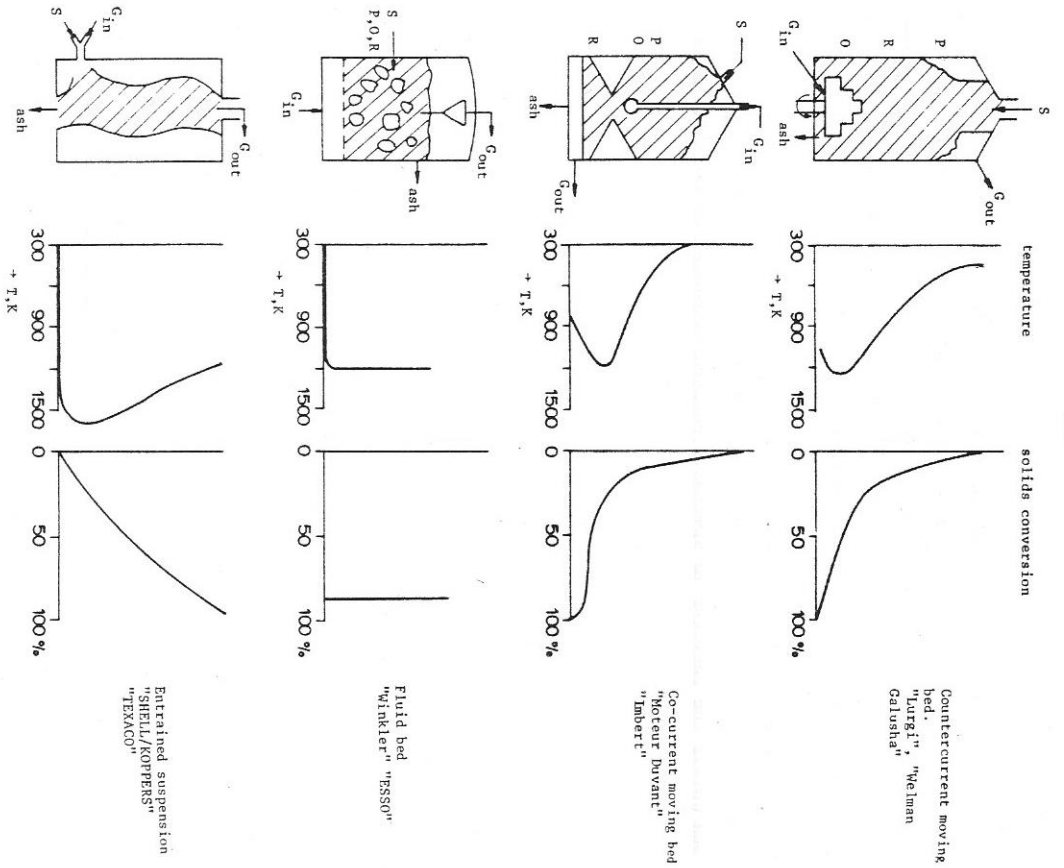


Fig. 4 - Gasification reactor types with temperature and solid conversion profiles

S = solids feedstock input, G_{in} = gasification agent input, G_{out} = product gas output, P = pyrolysis zone, O = oxydation zone, R = reduction zone

tar production, limited solidsconversion, severe particle entrainment and is more difficult to operate (solids flow rate control etc.).

Also, the entrained bed reactor (1, 18, 19, 20) is omnivorous, operates tar free and with molten ash due to the prevailing high temperatures. However the process is complex in operation, requires powdered biomass and extensive heat exchange. We shall not consider here the molten salt (21) and molten iron processes (22) as the conversions and temperatures of these processes are somewhat simular to the fluid bed process. Also rotary kilns are used for co- and counter current operation. Furthermore intermediates between co- en counter current operation existed; double shaft and double fire gasifiers (see (1), (12)).

PROSPECTS FOR BIOMASS GASIFICATION

The important factors for all gasification processes are the gasification agent, the operational pressure and the unit capacity. Fig. 5 gives a general picture of the situation as seen by the author.

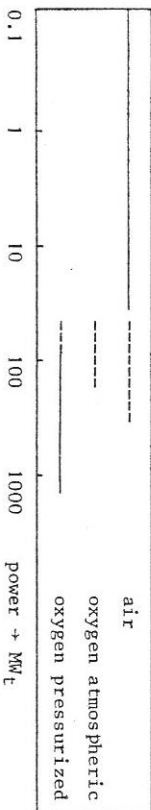


Fig. 5., application of biomass gasification processes.

With regard to large scale biomass units (>100 MW_t) if feasible the criteria for process selection are not unlike those of the coal gasifiers and pressurized gasification with oxygen seems logical. Process pressures will be 30 Bar or higher in relation to the subsequent syntheses process (methanol, SNG, etc.). For coal gasification only the LURGI process (8) has reached the commercial stage here but many others (Texaco (19), SHELL/KOPPERS (18)) are in an advanced stage of development. For electricity production from coal, air gasification at e.g. 30 Bar is often proposed (23). With biomass gasification the problem of sulphur removal is far less important (or absent) and therefore direct combustion (e.g. in powder flames) seems more likely. The situation may change if high efficiency power units (combined cycles) based on gasification of coal can attract widespread use.

For the intermediate scale (10-100 MW_t) the situation is not yet clear. Direct combustion in powder flames or (fast) fluid beds (24) are strong competitors to gasification. The preference for gasification depends much on the existing site facilities, feed preparation requirements and heat/work demands of the applications. It is very difficult to give general rules but

sure many more technical/economical data are required. Gasifiers for municipal waste based on oxygen (25) or air (26) (27) gasification are slowly finding application and similar biomass gasification may become more attractive.

Retrofitting existing boilers, kilns etc. previously fired by coal, gas or oil is widely discussed in the literature (28, 29, 30) especially in relation to wood. No derating is necessary if M.J.V. gas is produced. However the system requires expensive oxygen or processes still to be made commercially available. Derating becomes important with air gasification if the heating value of the product gas is below 7.4 MJ/m³. (28). An important factor in air blown gasifiers can be the conservation of the sensible heat of the product gas by fitting the gasifier directly to the boiler. Increasing the joule value or dual fuel firing may also counteract derating.

For small and medium scale power generation 0,1 - 20 MW_t the set up given in fig. 1, is very attractive and it is likely that gasifiers in connection with dual fuel diesel engines or gas engines for combined power/heat generation will capture an important slice of the market in the near future. These plants have a relatively high efficiency at different loads and are basically simple. Several manufacturers are marketing such systems (31, 32) and some units are already operating or are in the construction phase. Some units operate in the countercurrent mode but for smaller plants co-current operation seems to be particularly attractive because of its low tar production. We will discuss these units in more detail.

CO-CURRENT MOVING BED GASIFIERS

Although these gasifiers have been known for more than 100 years only approximate descriptions of the reactor and only purely empirical design rules can be found in literature. Groeneveld et al (13, 33) recently studied the reactor mechanics in more detail. (see fig. 6). The solid feedstock enters the top of the gasifier and the pyrolysis zone is situated above the hottest zone i.e. the oxidation zone. A critical requirement is that tars and other pyrolysis products should pass the hottest zone and not escape via the reduction zone into the product gas. In the reduction zone oxygen is absent and due to the endothermic reactions (2) and (3) the temperature is relatively low. Therefore the reaction time for the gas phase is not sufficient for tar conversion in this zone. It was found that for tar free operation a double vortex induced by the incoming airflow should fit into the throat geometry. With this in mind and knowing the time required for complete pyrolysis of the particles it is possible to understand to some extent the empirical rules for throat design found in the

LITERATURE (13)

The product gas composition and the temperature can be estimated by using simple heat and mass balances, the estimated methane formation (mainly in pyrolysis zone (34)) and assumptions on heat loss and "equilibrium" temperature (see e.g. Schläpfer model (35)). Although the concept of equilibrium cannot strictly be applied to this process, these simple models give good results once fitted for a specific unit. Groeneveld et al (33, 13) have made an approximate kinetic/transport model for the processes occurring in the reduction zone. From this model the relationship between reactor volume conversion, particle size, carbon conversion profile in the particle, solids flow, gas composition and temperature can be understood (see fig. 7). This model can be used as an additional guide for design and gives some background information about the limits of the simple "thermodynamic" models.

A very critical design problem concerns the scaling up of the throat without increasing tar production. A possible solution might be the use of a cylindrical annular throat (34). The problem might also be solved by recycling of pyrolysis gas over the top of the gasifier, possibly via an external combustion chamber to the air inlet. However this increases the complexity of the system. Such systems have been in operation for some years (1, 12) and is now being used in designs of "Moteur Durant" (32). An additional advantage of this system could be a lowering of the highest oxidation zone temperature and thus reducing the risk of ash fusion. However the exact description of the highest solid temperature in the oxidation zone specially in relation to pyrolysis gas recycle needs more investigation.

Although the future for the small scale units appears bright, new demands concerning automation, safety, flexibility and environmental protection have been imposed on these units as compared to former applications. In designing modern units we must consider the following: a. automation of solid preparation and feeding, start up, stand by, turn down, control of dual fuel ratio and speed control. b. problem free heat exchangers and residual tar soot and ash removal. c. safety with respect to CO and to the danger of explosions of gas/air mixtures. d. environmentally acceptable solutions for the condensate containing compounds such as sulfides, cyanides ash, traces of organic compounds (phenolic compounds, etc.).

Another important factor is the selling/buying policies of electricity companies which will influence the economics of all decentralized electricity generation units. Furthermore feed preparation steps may be too

expensive in some cases. (drying, pelletizing). Drying should be integrated as far as possible with exhaust heat recovery and for extremely wet feedstocks compression drying or other special upgrading processes may be required. Because feedpreparation is so costly (7) more complicated techniques (fluid bed reactors in combination with new type heat exchangers) may gain preference over the simple moving bed system. The application area can be extended to much larger capacities if intergration with gas turbines can be realized. Also small scale units (30 - 50 kW) might become economically attractive for individual energy provision for farms, homes and for villages in developing countries. In a Dutch-Tanzanian development cooperation program (12, 36) 40 kW units running on maize cob spills and used for maize mulling in the villages are being tested for the technical economical and social viability of this concept.

On the long term even small scale production of pure H₂ via shifting and separation could become attractive depending on possible developments in e.g. fuel cell and hydrogen storage technology. Generally the production of syntheses gas from L.J.V. gas deserves more attention in research programs.

References

- (1) Meunier, J. Vergasung feester Brennstoffen Verlag Chemie GmbH, Weinheim (1962).
- (2) Peters, M., Junzgen, H. and Van Heek, R.H. Chemical Engineering in a Changing World. Elsevier Amsterdam (1976) 285-299.
- (3) Dravo Corport; Handbook of Gasifiers and treatment systems; NTIS, FE 1772-11 Feb. (1976).
- (4) Jackson, F.R. Energy from Solid Waste Noyes data Corp. New Jersey U.S.A. (1974) 106-120.
- (5) Feldman H.F. Energy from Biomass and Wastes. I.G.T. symp. Washington D.C. (1978) 537-557.
- (6) Gallagher, J.F. and Marshall, R.A. Coal Process Techn. V (1979) 199-204.
- (7) Jones, D. and Jones, J. Energy from Biomass and Wastes. I.G.T. symp. Florida (1980) 223-249.
- (8) Pollaert, T.J. C.E.P. aug. (1978) 95-98.
- (9) Ham, O.J. Fuel Process. Techn. 2. (1979) 1-16.
- (10) Davidson, P.E. and Lucas, T.W. A.S.C. symp. series 76 (1978) (ISSN0097-6156).
- (11) Aubo, J.C. and Glaser, D.P. Energy from Biomass and Wastes IV. I.G.T. symp. Florida (1980) 387-401.
- (12) Groeneveld, M.J. and Van Swaaij, W.P.M. Applied Energy 5 (1979) 165-179.
- (13) Groeneveld, M.J. Thesis Twente University of Technology (1979)
- (14) Hes, J.J., Groeneveld, M.J., Van Swaaij, W.P.M. Energy from Biomass and Wastes IV I.G.T. symp. Florida (1980) 333-351.
- (15) Franke, F.H. V.G.B. Kraftwerktechnik 59, H.9 sep. (1979) 697-702.
- (16) Keatins, D.L. AIChE Symp. Series No. 156 vol 72 (1977) 103-116.
- (17) Beck, S.R. and Wang, N.J. Ind. Eng. Chem. F.D. 12 No. 2 (1980) 312-317.
- (18) Vogt, E.V. and V.d. Burgt, M.J. C.E.P. March (1980) 65-72.
- (19) Cornils, B. Chem. Ing. Tek. 52 No. 1 (1980) 12-19.
- (20) Levy, S.J. Proc. CIP conf. (1975) Montreux, Swiss (1975) 226-231.
- (21) Kohl, L. C.E.P. Aug. (1978) 73-79.
- (22) La Rosa, P.J. Symp. Clean Fuels from Coal. Coal. I.G.T. Chicago (1973).
- (23) McCallister, R.A. and Ashley, G.C. Proc. Am. Power Conference, 36 (1974) 292-299.
- (24) Engstrom, F. and Ahlstrom, O. Energy from Biomass and Wastes IV I.G.T. symp. Florida (1980) 555-566.
- (25) Chermisthoff, P.N. and Morresi, A.C. Energy from Solid Wastes; M Dekker Inc. New York (1976) 168-177.
- (26) Mark, S.D. Energy from Biomass and Wastes IV I.G.T. symp. Florida (1980) 577-589.

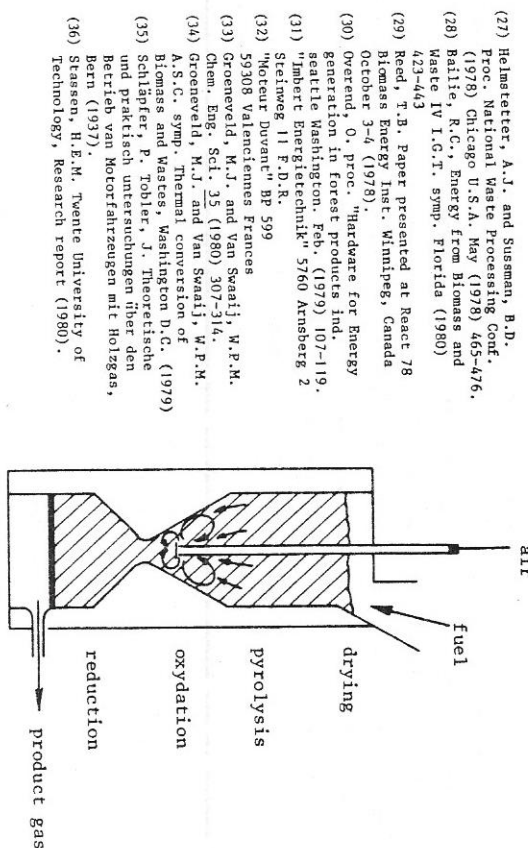


fig. 6. Typical Co-current moving bed gasifier.

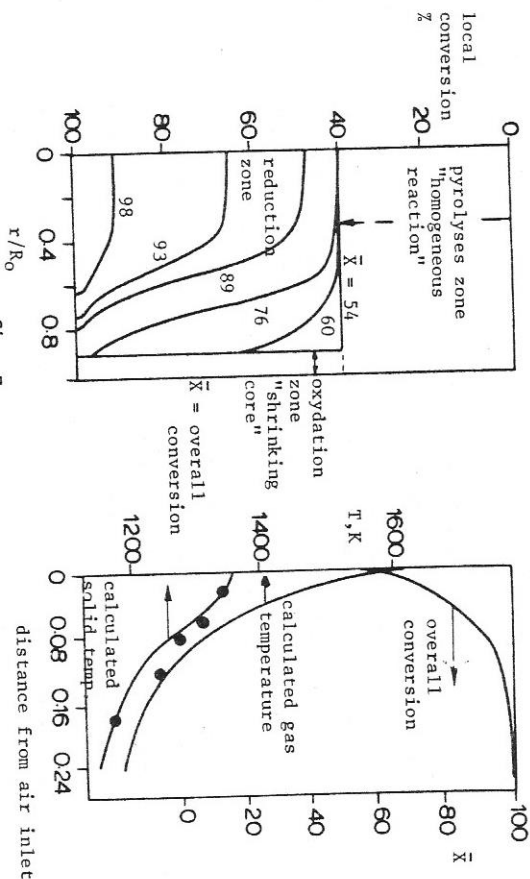


fig. 7. Co-current moving bed gasifier

Typical local conversion inside a wood particle of initial radius $R_0 = 12,4 \times 10^{-3}$ m (Groeneveld (13)).

Typical profiles observed by thermocouple readings

THE COMBUSTION, PYROLYSIS, GASIFICATION AND LIQUEFACTION
OF BIOMASS

T. B. Reed

The Solar Energy Research Institute (SERI), Golden, Colorado

Summary

We can provide all the products now obtained from oil by thermal conversion of the solid fuels biomass and coal. As a feedstock, biomass has many advantages over coal and has the potential to supply up to 20% of U.S. energy by the year 2000 and significant amounts of energy for other countries. However, it is imperative that in producing biomass for energy we practice careful land use.

Combustion is the simplest method of producing heat from biomass, using either the traditional fixed-bed combustion on a grate or the fluidized-bed and suspended combustion techniques now being developed. Pyrolysis of biomass is a particularly attractive process if all three products--gas, wood tars, and charcoal--can be used. Gasification of biomass with air is perhaps the most flexible and best-developed process for conversion of biomass to fuel today, yielding a low energy gas that can be burned in existing gas/oil boilers or in engines. Oxygen gasification yields a gas with higher energy content that can be used in pipelines or to fire turbines. In addition, this gas can be used for producing methanol, ammonia, or gasoline by indirect liquefaction. Fast pyrolysis of biomass produces a gas rich in ethylene that can be used to make alcohols or gasoline. Finally, treatment of biomass with high pressure hydrogen can yield liquid fuels through direct liquefaction.

1. COAL VS. BIOMASS - THE PAST AND FUTURE ROLE OF SOLID FUELS

Until a little over a century ago, mankind relied on the solid fuels--biomass (mostly wood) and coal--to supply space and industrial heat, energy for transportation, and power. With the discovery of plentiful, convenient, low cost oil and gas, the use of solid fuels greatly diminished. Now that shrinking gas and oil reserves necessitate a return to the traditional solid fuels, several new factors which favor the use of biomass must be considered in choosing between biomass and coal for various uses.

Wood was the principal fuel of mankind until about 1800, when many nations began to use coal for a variety of reasons. In some cases (England) the wood supply was exhausted by overharvesting. In other countries (the United States) coal was plentiful and could be obtained more cheaply than wood. Coal also has the advantage of being a denser fuel than wood, and it can be stored and transported more conveniently.

Now that we are turning back to solid fuels (reluctantly), this past experience suggests that where possible we will choose coal rather than biomass. However, a number of technical and social factors have changed and can tilt this decision toward wood and other forms of biomass. Coal is now less desirable because we are less willing to tolerate the despoilation of the land associated with mining. We are concerned about contamination of our air and water by the sulfur in coal. We also recognize the possibility that continued use of fossil fuels may upset the CO₂ balance of the atmosphere and our climate. Finally, the race of men willing to toil and toil in the bowels of the earth for pennies a day has disappeared during the era of low cost oil energy.

Biomass, on the other hand, can be obtained on a renewable basis with actual improvement of the land. The techniques for planting and harvesting biomass for fuel are similar to those used for agriculture and forestry; biomass can be produced continuously on a renewable basis as we now produce food, lumber, and paper. Biomass production can be a source of revenues for land improvement. Table I lists six areas where biomass production has resulted in the improvement of the environment.

In the past biomass production has often resulted in land destruction, and Table II is a cautionary list of examples of the destruction caused by unregulated use of biomass for food, lumber, paper, or fuel production. Thus, biomass is a two-edged sword for mankind, and we must learn to produce it only on a renewable basis (1,2).

TABLE I. EXAMPLES OF LAND RESURRECTION

REGION	DATE BEGUN	ACTIVITY	RESULT
Jordan, Syria,	1970	Dam construction, irrigation, sprinkling	Agriculture being reestablished
Israel	1900	Drainage, irrigation, terracing	Productive farms, orchards and forests
China	1950	7% reforestation, shelterbelts halt "sanddragon"	Decreased silting, dust storms reduced, improved forestry
England, Holland	1300	Dyking, pumping	Productive farmland
France (Provence)	1910	Reforestation	Forestry, farming, industry, towns
United States (Kans., Nebr., Colo., Okla.)	1935	Contour plowing, crop rotation, windbreaks	Productive farmland

Biomass is a desirable fuel ecologically because it contains very little sulfur and generally much less ash than coal. With the new agricultural and forestry machines now available, its production is no longer as labor intensive as it was a century ago and the work is certainly less hazardous than mining.

In the past, the principal form of biomass burned for energy was wood because of its relatively high density and availability. The process of densification, in which biomass residues (sawdust, straw, food processing wastes) are compressed into pellets, briquettes, or logs, promises to make other biomass forms, now wasted, equally attractive (3). These processes produce a fuel that has approximately three-fourths of the energy of coal, both on a mass and volume basis, and thus densified biomass could be called "instant coal". A number of plants are now operating in the United States to produce densified biomass.

Thus, though coal will no doubt be the staple solid fuel in many countries, recent technical and social developments favor biomass, and ultimately, when the supply of coal is depleted, mankind will have to learn to

TABLE II. EXAMPLES OF LAND DESTRUCTION

REGION	DATES	ACTIVITY	RESULT
Mesopotamia (Iraq, Syria)	6000 BC to 1200 AD	Canal irrigation and intensive agriculture	Silting and salting - 20 M population at peak, now 3.5 M.
Israel	3000 BC to 100 AD	Agriculture, terracing, grazing	Soil loss through erosion, overgrazing, created hardpan
Phoenecia	4000 BC to 400 AD	Lumbering	Deforestation, erosion
China	3000 BC to 1950 AD	Deforestation, intensive agriculture	Silting, flooding, dust storms
North Africa (Tunis, Algeria)	0 to 600 AD	Corn, wheat, olive production	Erosion, desertification
England	1500 AD to 1700 AD	Lumbering, charcoal manufacturing	Hardpan formation leading to moors, few forests
France (Provence)	1800 AD to 1900 AD	Charcoal manufacture to support steel industry	Hardpan formation, high moors
United States (Kans., Nebr., Colo., Okla.)	1900 AD to 1934 AD	Wheat farming	Dust bowl, wind erosion, soil depletion, overgrazing

live on its "energy income" because its "energy capital" will be exhausted. A recent analysis of possible energy futures for Sweden suggests that she could rely solely on renewable energy sources, primarily various forms of biomass, and maintain her current standard of living (4). A recent evaluation of U.S. biomass resources suggests that 12 to 17 x 10¹⁵ KJ (12-17 quads) could be obtained from biomass by the year 2000 (2). The potential for biomass production in many other countries is also enormous.

2. COMBUSTION OF BIOMASS

In the past, energy has been produced from wood by simple combustion to produce heat. Combustion now provides about 1.5×10^{15} kJ (1.5 quads) of energy in the United States, primarily from waste liquors from the Kraft paper process, but increasingly from combustion of wood wastes and in home stoves. This combustion is most familiar in the form of a fixed bed of fuel on a grate (or andirons), but we are increasingly turning to fluidized-bed combustion or suspended combustion, which permits cleaner, more automatic combustion in a smaller volume and allows the use of fuel particles as small as sawdust (5). Figure 1 shows a variety of such combustion devices.

3. PYROLYSIS OF BIOMASS

The combustion of wood produces only heat directly (and power indirectly through steam). However, pyrolysis and gasification make possible the production of more refined fuels, which can be used to produce power directly in engines and turbines or for the synthesis of the liquid fuels such as methanol or gasoline on which we have become so dependent.

A familiar experiment in the chemistry laboratory is the heating of a wood splint in a test tube to pyrolyze (rearrange by heating) the wood. A clean combustible gas issues from the mouth of the tube, a brown oil (pyrolysis oil) collects near the cool mouth of the tube, and charcoal remains in the lower portion. In situations where all of these products are needed, pyrolysis processes such as this, on a larger scale, are highly recommended because they are very simple and have a high throughput. A number of pyrolytic processes are being developed (6). Unfortunately, the oil that is produced is corrosive and presents handling problems. Yet ultimately, when we learn how to separate the valuable components of this oil, we may look on it as the most valuable product obtainable from biomass.

The amount of charcoal produced by pyrolysis depends strongly on the rate of heating. If the heat is supplied fast enough, little or no char results, greatly simplifying the subsequent processing. "Fast pyrolysis" processes are discussed in Section 5.

4. GASIFICATION OF BIOMASS

Gasification is the process of treating biomass so that only gas (and sometimes oil vapors) are produced. The charcoal resulting from pyrolysis is converted to gas by partial combustion with oxygen or steam:

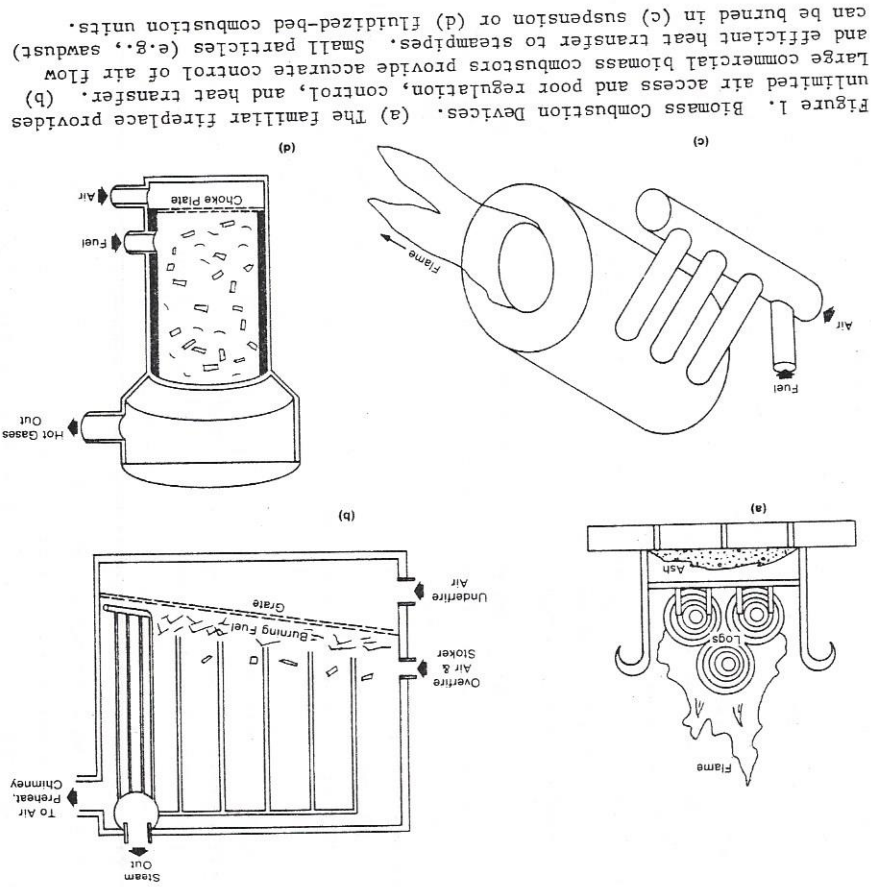
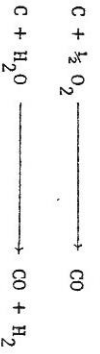


Figure 1. Biomass Combustion Devices. (a) The familiar fireplace provides unlimited air access and poor regulation, control, and heat transfer. (b) Large commercial biomass combustors provide accurate control of air flow and efficient heat transfer to steam pipes. Small particles (e.g., sawdust) can be burned in (c) suspension or (d) fluidized-bed combustion units.



This can be accomplished in the updraft, downdraft, fluidized-bed, or suspension gasifiers shown schematically in Figure 2 (6).

In an updraft gasifier for biomass or coal, air or oxygen is injected under a grate supporting charcoal causing combustion and reduction of the gases. The resulting hot gases then rise through the incoming biomass at the top of the shaft furnace of Figure 2, producing oils and water by pyrolysis and drying. The resulting gas must be burned directly (close coupled) because the tars are difficult to remove. Updraft gasifiers are especially appropriate for retrofitting existing gas- or oil-fired boilers. There are now several dozen manufacturers of updraft and downdraft gasifiers in the United States (7).

In the downdraft gasifier air or oxygen is injected above the char mass, causing pyrolysis of the incoming biomass and producing char and oils. These oils then pass over the hot char and are cracked to gases; as a result, very little oil is produced. For this reason, downdraft gasifiers are particularly suitable for running internal combustion engines and over a million were used in Europe during World War II (8).

Although not as well developed, fluidized beds for biomass gasification offer a number of theoretical advantages over the fixed-bed gasifiers discussed above. Because of their very high recirculation rates, fluidized beds have a high heat transfer rate and high throughputs. They are also able to process a wide range of biomass sizes. However, because the contact time is short, they are not as efficient as downdraft gasifiers in consuming char or cracking the oils and tars. There is also a tendency for the light biomass fraction and lighter char fractions to separate from the bed prematurely. Even less well developed is suspended gasification, though again the suspension gasifier offers high throughputs and the processing of small particles as potential advantages.

When air is used for biomass gasification, a low energy gas [typically 5200 kJ/nm³ (150 Btu/scf)] results because of the nitrogen dilution. Though suitable for operating engines or close coupling to boilers, it is not economical to distribute this gas in pipelines. When oxygen is used for biomass gasification a "medium energy gas" [typically 10,400 kJ/nm³ (300 Btu/

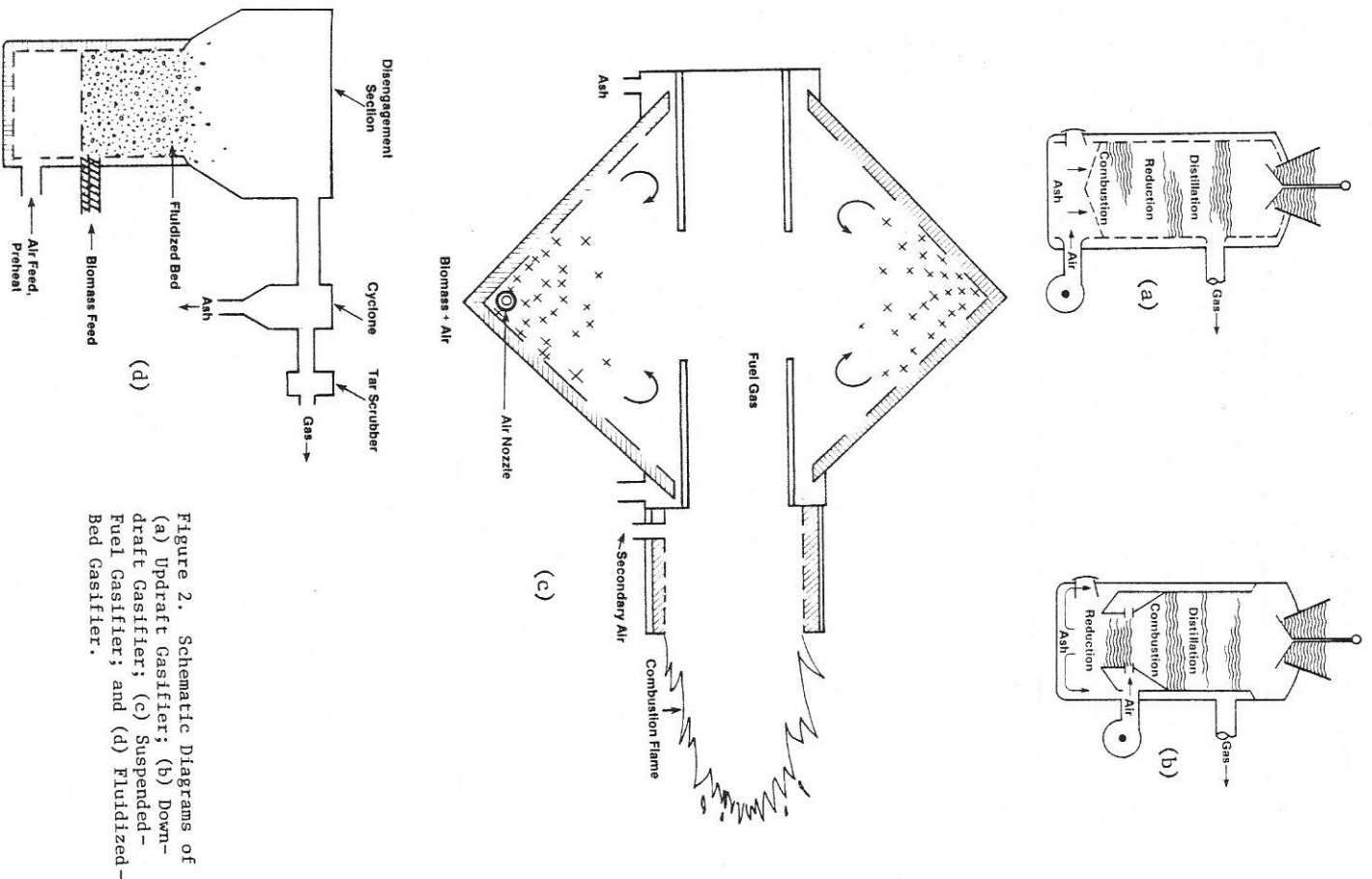


Figure 2. Schematic Diagrams of (a) Updraft Gasifier; (b) Downdraft Gasifier; (c) Suspended-Fuel Gasifier; and (d) Fluidized-Bed Gasifier.

scf)] is produced that can be distributed in pipelines and can be used to power turbines or to synthesize chemicals. We are presently testing the high pressure, downdraft gasifier shown in Figure 3, using oxygen to produce a very clean gas composed of only hydrogen and carbon monoxide.

5. INDIRECT LIQUEFACTION

In many situations gaseous fuels are desirable because they can be distributed by pipeline and are most easily burned with minimum emissions and maximum efficiency; however, gaseous fuels are difficult to store. We will probably require liquid fuels at least for transportation fuels and possibly (depending on cost) for turbine and power plant operation in isolated locations where pipeline costs make gas transport too costly.

Methanol (wood alcohol) was originally made by the destructive distillation of wood, but yields were typically several percent and the major product was charcoal and other chemicals. Now the following reaction is used to make methanol from synthesis gas:



The synthesis gas is compressed to 50-200 atm and passed over a chromium or copper oxide catalyst at 250°-350°C. Synthesis gas is likely to be the key industrial chemical of the post-oil era because, once obtained by gasification of biomass (or coal), it can be used to make methanol, ammonia, gasoline, and many other chemicals and fuels. The gasifier shown in Figure 3 is being developed at SERI especially for the production of fuels and chemicals from biomass.

Other important gases for chemical synthesis are ethylene and other olefins (primarily propylene and butylene). The slow pyrolysis discussed in Section 3 produces oxygenated tars and methane gas. However, it has recently been recognized (7,8,9) that sufficiently high heat transfer rates (typically in excess of 100 W/cm²) induce fast pyrolysis, producing high yields of olefins and often no charcoal at all. Such a process was initiated at the Naval Weapons Center, China Lake, and now is being developed at the Solar Energy Research Institute. High yields of olefins are produced from biomass (typically over 14%). These olefins can in turn be made into plastics (by polymerization), gasoline (by thermal polymerization), or alcohol fuels (by hydration).

SERI Oxygen Biomass Gasifier

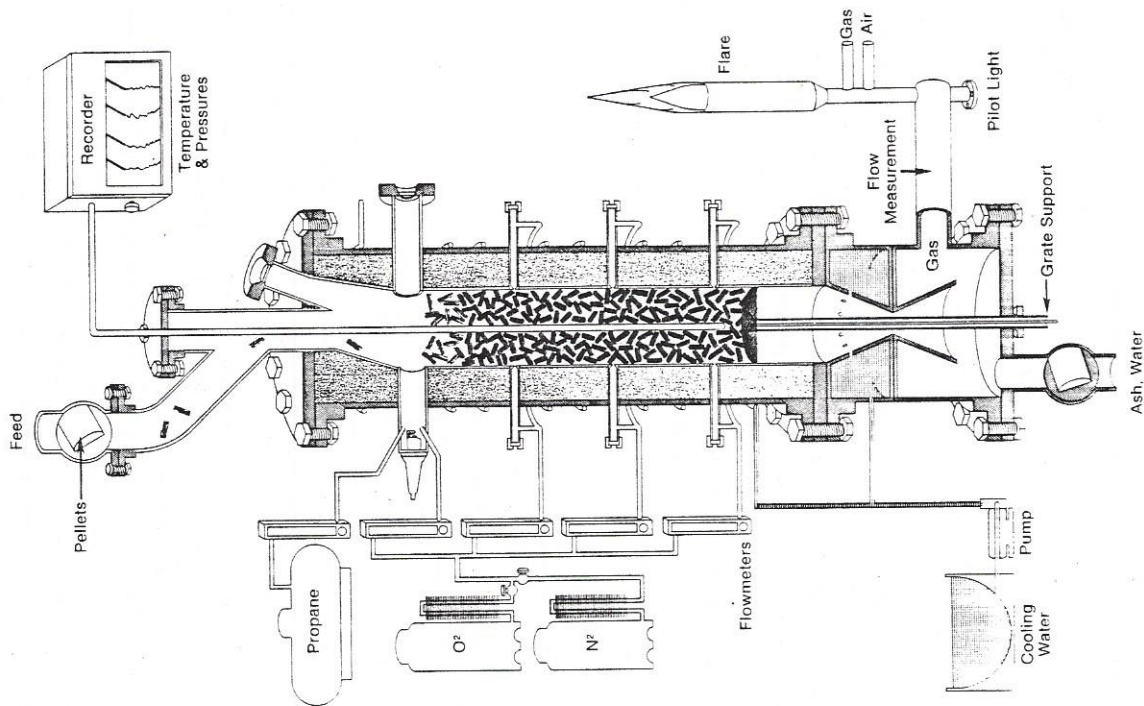


Figure 3. SERI Oxygen Biomass Gasifier

6. DIRECT LIQUEFACTION

It is desirable to be able to convert biomass directly to a liquid fuel, bypassing the gaseous intermediate. In work undertaken during World War II it was demonstrated that alcohols and hydrocarbons could be produced in significant yields by the direct, high pressure hydrogenation of wood or lignin over a catalyst (see Table III)(10). Work along these lines is being pursued now in Canada (11,12). Up to 50 (weight)% of biomass has been converted to oxygenated oils using nickel carbonate catalysts.

TABLE III. EARLY WOOD LIQUEFACTION RESULTS

PROCESS	FEEDSTOCK	PRODUCTS
Hydrogenation	Wood	5% methanol, 15% propanol, 40% pulp
Hydrogenation	Lignin	8% methanol, 13% alcohols, 23% hydrocarbons

More recently, an attempt has been made to apply the methods developed for coal liquefaction to biomass in the "Albany, Oregon" biomass liquefaction process (13). In this process, 30 wt% of biomass is slurried with anthracene oil and heated to 370°C in high pressure (160 atm.) hydrogen or carbon monoxide. A number of difficulties have plagued this pilot plant because the oil does not allow high concentrations of wood to be injected into the reactor. An aqueous pretreatment has permitted higher concentrations of more reactive wood to be used in the reactor and several barrels of oil have been produced with a relatively low oxygen content (13).

Thus it can be seen that the thermal conversion of biomass can follow the various routes outlined here to provide the heat, power, fuels, and chemicals currently produced from petroleum.

REFERENCES

1. Reed, T. 1978. "Biomass Energy: A Two-Edged Sword." Paper presented at the International Solar Energy Society (ISES); Denver, CO; 28 Aug. 1978. SERI DDS-011. Golden, CO: Solar Energy Research Institute.
2. T.E. Bull, Project Director. 1980.
2. Energy from Biological Processes. Office of Technology Assessment.

3. Reed, T.; Bryant, B. 1978. Densified Biomass: A New Form of Solid Fuel. SERI-35. Golden, CO: Solar Energy Research Institute. 1980.
4. Lonnroth, M.; Johansson, T.B.; Steen, P. "Sweden Beyond Oil: Nuclear Commitments and Solar Options." Science. Vol. 208: p. 557.
5. See, for example: (a) O'Grady, M.J. 1979. "Grate, Pile, Suspension and Fluid Bed Burning." Wood Fuel for Small Industrial Energy Users. Conference Proceedings; North Carolina State University, Raleigh, NC; 2-3 Oct. 1979. (b) Zerbe, J.I. 1979. "Wood Processing, Forestry and Agricultural Wastes." New Fuels and Advances in Combustion Technologies. Symposium sponsored by the Institute of Gas Technology; New Orleans, LA; 26-30 Mar. 1979. (c) Bio-Energy Council. Bio-Energy Directory. Washington, DC. pp. 515-526.
6. Reed, T. 1979, 1980. A Survey of Biomass Gasification. SERI/TR-33-239. 3 Vols. Golden, CO: Solar Energy Research Institute.
7. Solar Energy Research Institute. 1979. Retrofit '79: Proceedings of a Workshop on Air Gasification. Seattle, WA; 2 Feb. 1979. SERI/TR-49-183. Golden, CO: Solar Energy Research Institute. 1979.
8. Solar Energy Research Institute. 1979. Generator Gas: The Swedish Experience from 1939-1945. SERI/SP-33-140. Translation of Gengas, published by the Swedish Academy of Engineering; 1950. Golden, CO: Solar Energy Research Institute.
9. See, for example: (a) Diebold, J. 1980. Research into the Pyrolysis of Pure Cellulose, Lignin, and Birch Wood Flour in the China Lake Entrained-Flow Reactor. SERI/TR-332-586. Golden, CO: Solar Energy Research Institute. (b) Solar Energy Research Institute. Forthcoming. Specialists' Workshop on Fast Pyrolysis of Biomass. Copper Mountain, CO; 20-22 Oct. 1980. Golden, CO: Solar Energy Research Institute.
10. Stern, A.J.; Harts, E.F. 1953. The Chemical Processing of Wood. New York: Chemical Publishing Co.
11. FMC Inc. Engineering Analysis. 1979. "A Study on the Design and Optimization of Biomass Liquefaction Processing Units." 2 Vols. For Project C-69, Dept. of Canadian Forestry Service.
12. Boocock, D.G.B.; Mackay, D. 1980. "The Procession of Liquid Hydrocarbons by Wet Hydrogenation." Energy From Biomass and Wastes.

IGT Symposium; Lake Buena Vista, FL; 21 Jan. 1980. p. 765. See also Boocock, D.G.B.; Mackay, D.; Franco, H. 1980. "The Direct Liquefaction of Wood Using Nickel Catalysts." Thermal Conversion of Solid Wastes and Biomass. Jones and Radding, eds. ACS Symposium Series #130. Washington, DC: American Chemical Society.

p. 363.

13. See, for example: (1) Ergun, S. "An Overview of Biomass Liquefaction" and following papers in 3rd Annual Biomass Energy Systems Conference Proceedings. 5-7 June 1979. SERI/TP-33-285. Golden, CO: Solar Energy Research Institute. (2) Ergun, S.; Schaleger, L.; Seth, M. 1980. "Albany Biomass-to-Oil Project." Design and Management for Resource Recovery. Vol. I. T.C. Frankiewicz, ed. Ann Arbor, MI: Ann Arbor Science.

PYROLYSIS AND COMBUSTION OF WOOD IN RELATION
WITH ITS CHEMICAL COMPOSITION

H. MELLOOTTEE and J.R. RICHARD

C.N.R.S., Centre de Recherches sur la Chimie de la Combustion
et des Hautes Températures,
Orléans, France

and

B. MONTIES

I.N.R.A., Laboratoire de Chimie Biologique et de Photophysologie,
Grignon, France

Summary

Pyrolysis and combustion of wood has been investigated by thermogravimetric analysis (TGA) and by thermogravimetric analysis (TDA) in view to correlate the pyrolysis kinetic and thermal data to the physico-chemical characteristics of wood. Different parts of the wood such as the bark, the sapwood and the core of different species (e.g. poplar, pine, oak and beech) were compared. The study was also extended to the different constituents comprising wood : lignin, cellulose, holo-cellulose and parietal residues.

The behaviour of the different samples which were studied (on the form of sawdust or fine powder) was characterized by two heating rates (10 and 20°C/min) and under four different atmospheres ranging from air to pure nitrogen. One of the main results obtained points to distinguish two stages in the degradation process, one at temperatures ranging between 180 and 350°C and another one at temperatures higher than 400°C. In the first stage, the oxygen content in the oxidizer does not affect perceptibly the behaviour whereas the influence of oxygen becomes significant at high temperature.

The differences which were observed on the various samples studied should contribute to making a better choice in the application of the pyrolysis of biomass materials as an alternative source of energy.

1. INTRODUCTION

La valorisation énergétique de la biomasse passe par le développement des études sur l'augmentation des quantités disponibles et mobilisables de bois et sur le comportement en combustion et pyrolyse des bois dans des conditions appropriées à la valorisation recherchée. Dans ce domaine, il importe en particulier de caractériser la nature et la quantité des gaz dégagés au cours des traitements thermiques, la cinétique des dégradations, les effets thermiques. C'est à ces deux derniers aspects qu'est consacrée la présente étude.

Les corrélations entre cinétique de dégradation, effets thermiques et propriétés physico-chimiques du bois ont été recherchées. Les échantillons étudiés ont été non seulement diverses espèces, telles que peuplier, sapin, chêne et hêtre, mais aussi des fractions telles que l'écorce, l'aubier ou le coeur. En vue de permettre l'interprétation des résultats, le rôle de la constitution chimique des échantillons de bois peut être évoqué. Aussi les mêmes études cinétiques et thermiques ont-elles été appliquées aux fractions constitutives principales des bois, lignines (extraites au dioxane), cellulose, holocellulose, résidu pariétal.

2. PARTIE EXPERIMENTALE

Tous les essais ont été réalisés dans une thermobalance, équipée d'un analyseur thermique différentiel simultané. La montée en température est programmée, à la vitesse de 10 ou 20°C/mm. Quatre compositions de l'atmosphère ont été utilisées : air, azote, mélanges N_2/O_2 à 5% ou 10% d'oxygène. Le système permet l'analyse des gaz émanants, mais les résultats obtenus ne sont pas rapportés ici.

Les échantillons ont été employés sous forme de sciures pulvérulentes de 0,5 mm de diamètre environ, ou dans le cas des lignines, cellulose, holocellulose, résidus pariétaux de poudres fines de granulométrie moyenne 20 - 50 μ m. Les bois n'ont pas subi de traitement préalable particulier avant leur emploi.

3. RESULTATS

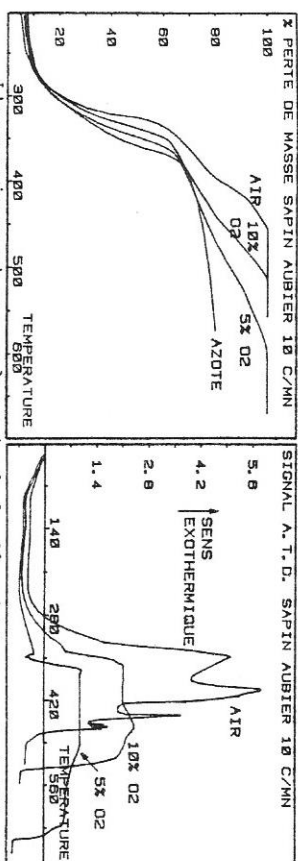
Les résultats donnés ci-dessous concernent le pourcentage de perte de masse des échantillons, les effets thermiques et les paramètres cinétiques de la dégradation en fonction de la température. Quelques exemples significatifs

de l'influence des divers paramètres expérimentaux sont proposés.

Dans tous les cas, les bois, fractions ou constituants des bois s'oxydent en deux étapes. Une première étape se situe vers 180 - 350°C. A la fin de cette étape, la perte de masse est comprise, selon les cas, entre 50 et 70% et s'é élève pour la cellulose à plus de 80% de la masse initiale. Une seconde étape se situe au dessus de 400°C. Si la dégradation a lieu sous azote, seule la première étape apparaît. Les paramètres cinétiques de cette première étape sont voisins, quel que soit le gaz utilisé. Il s'agit donc d'une étape de pyrolyse essentiellement. L'étape de haute température, plus sensible à la nature du gaz de traitement, est une étape d'oxydation.

3.1. Influence du gaz de traitement

Les courbes ci-dessous montrent cette influence dans le cas de l'aubier de sapin, à la vitesse de montée en température 10°C/mm.



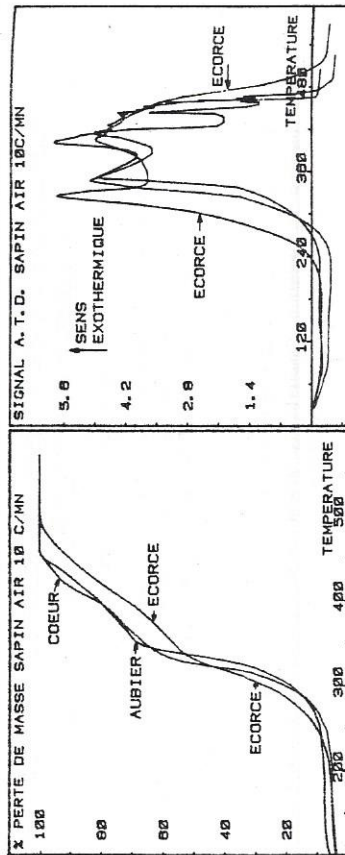
L'appauvrissement en oxygène retarde la dégradation, surtout l'étape d'oxydation, et reporte vers les hautes températures l'effet thermique, dilaté dans l'échelle des températures et donc moins intense. Les maximums de vitesse des deux étapes sont aussi déplacés vers les hautes températures (basse température : 325° pour l'air, 365° pour l'azote; haute température: 406° pour l'air, 507° pour 5% d'oxygène).

Paramètres cinétiques d'ordre 1	Air		10% O ₂		5% O ₂		Azote
	B.T.	H.T.	B.T.	H.T.	B.T.	H.T.	B.T.
Energies d'activation kcal/mol	30,6	34,5	23,3	23,8	21,3	18,3	20,9
log A (A en s ⁻¹)	9,1	8,9	8,1	4,7	7,1	2,5	6,8

3.2. Influence du prélèvement sur une même espèce (coeur, aubier, écorce)

Les courbes ci-dessous montrent une telle influence dans le cas du

sapin, sous air, à la vitesse de montée en température 10°C/mn.



Aubier et coeur se comportent sensiblement de la même façon, tandis que l'écorce se distingue en se dégradant à plus basse température et plus lentement à haute température. Les maximums de vitesse sont situés aux mêmes températures pour l'écorce et l'aubier (323°), décalés vers les hautes températures pour le coeur (337°).

Paramètres cinétiques d'ordre 1	Coeur		Aubier		Ecorce	
	B.I.	H.I.	B.I.	H.I.	B.I.	H.I.
Energies d'activation kcal/mol	31,6	28,8	30,6	34,5	20,8	13,2
log A (A en s ⁻¹)	9,2	6,8	9,1	8,9	5,3	1,7

L'écart entre l'écorce et les autres fractions du bois apparaît nettement sur le tableau des paramètres cinétiques.

3.3. Influence de l'espèce du bois (étude sur l'aubier à 10°C/mn)

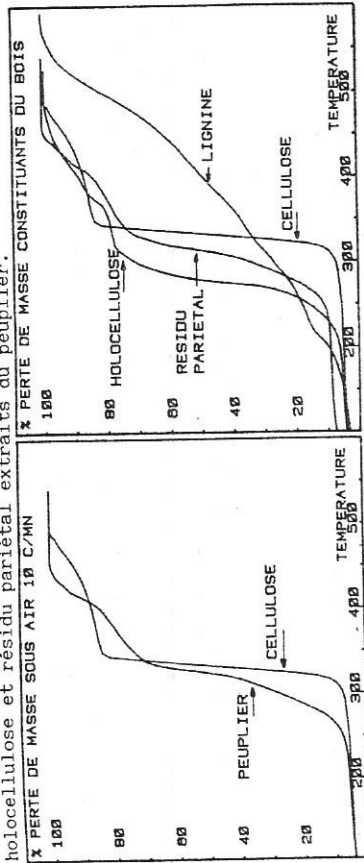
Sous air, les résultats sur les quatre espèces étudiées (chêne, sapin, hêtre, peuplier) montrent une grande similitude entre le hêtre et peuplier, un comportement voisin du sapin, un comportement différent du chêne (à basse température, sa dégradation commence plus tôt et est plus rapide jusque vers 320°, plus lente ensuite).

Paramètres cinétiques d'ordre 1	Hêtre		Peuplier		Sapin		Chêne	
	B.I.	H.I.	B.I.	H.I.	B.I.	H.I.	B.I.	H.I.
Energies d'activation kcal/mol	26,9	31,5	26,9	26,5	30,6	34,5	30,3	36,4
log A (A en s ⁻¹)	7,7	8,1	7,7	6,4	9,1	8,9	9,3	9,5

Le chêne a effectivement des énergies d'activation élevées, en particulier à haute température.

3.4. Influence des parties constitutives du bois

Une comparaison entre les dégradations de l'aubier de peuplier et de la cellulose sous air à 10°C/mn montre la différence des comportements. On constatera des différences encore plus grandes entre cellulose, lignine, holocellulose et résidu pariétal extraits du peuplier.

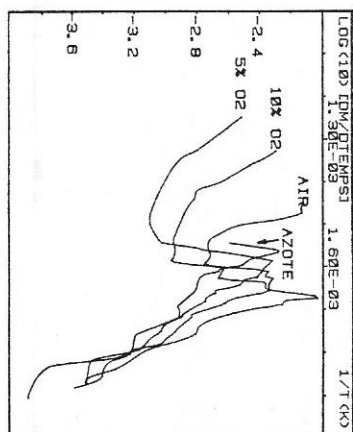


Les mécanismes de basse température sont simples et conduisent à des grandeurs cinétiques du premier ordre nettes, sauf pour la lignine. Les mécanismes de haute température sont généralement plus complexes et sont une succession et superposition de plusieurs réactions. Seule la réaction de haute température de la lignine apparaît avoir un mécanisme simple. Pour les autres corps étudiés, la cinétique du 1er ordre n'est, à haute température, qu'une représentation approchée.

Paramètres cinétiques d'ordre 1	Lignine		Cellulose		Holocellulose Rés. pariétal	
	B.I.	H.I.	B.I.	H.I.	B.I.	H.I.
Energies d'activation kcal/mol	4,9	22,1	93,6	33,5	25,9	32,2
log A (A en s ⁻¹)	0,1	2,8	19,5	6,4	9,0	3,5

4. DISCUSSION ET CONCLUSION

Il existe de nombreuses méthodes permettant d'obtenir les paramètres cinétiques. Dans ce travail, ils ont été calculés à partir de l'équation $dm/dt = -km$ où m est la masse actuelle et k est de la forme $A \cdot \exp(-E/RT)$. La figure ci-dessous donne un exemple de l'exploitation cinétique des résultats, où le logarithme de $(1/m)(dm/dt)$ est exprimé en fonction de $1/T$ (diagramme d'Arrhénius). Il s'agit dans le cas présent de l'aubier de sapin à différentes compositions de l'atmosphère de traitement.



On aura remarqué les écarts sensibles entre les deux mécanismes de basse et haute température, celui-ci correspondant à un phénomène d'oxydation.

L'étude a mis en évidence le très grand rôle de la composition de l'atmosphère de traitement, le comportement particulier de l'écorce par rapport à l'aubier, les différences sensibles selon l'espèce du bois. Elle a montré en outre les écarts importants de comportement entre le bois et ses constituants, cellulose et lignine en particulier.

Deux orientations se dégagent pour l'avenir. Le couplage des mesures d'ATG et ATD avec les analyses de gaz doit compléter les critères de choix de matériaux les plus aptes à une valorisation de la biomasse. On peut en outre espérer modéliser le comportement des bois en les considérant comme des associations en proportions variables de leurs constituants principaux.

ON THE INFLUENCE OF THE DIFFERENT PARTS OF WOOD ON THE PRODUCTION
OF GASEOUS COMBUSTIBLE PRODUCTS BY PYROLYSIS

J. R. RICHARD and M. CATHONNET
Centre de Recherches sur la Chimie de la Combustion
et des Hautes Températures
C.N.R.S. - 45045 ORLÉANS CEDEX - France

The aim of the present work has been to determine the optimum conditions leading to gaseous combustible mixtures by pyrolysis of different varieties of wood and its different parts.

The following parameters were especially studied

- Wood sample : cellulose, fir tree, poplar and beech - Different parts of the wood, i.e., sapwood, bark.
- Temperature : ranging from 400°C to 900°C.
- Pyrolysis method :
 - Slow, at atmospheric pressure,
 - Rapid, at low pressure.

The main results point to the following :

- A - Overall yield in gaseous products
 1. The percentage of solid residue is lower in the case of sapwood compared to bark. Cellulose leads to an even smaller percentage of residue. Concurrently gaseous products yields are higher for sapwood than for barks.
 2. At higher temperature the percentage of solid residue decreases and the yield in gaseous product increases.
 3. Higher gas phase yields are favoured by rapid pyrolysis.
- B - In so far as the distribution of gaseous species is concerned (CO , CO_2 , H_2 , CH_4 , C_2H_4 , C_2H_6) the following is noted :
 1. Whatever type of pyrolysis is used, sapwood produces more CO than bark wood. Yields in C_2H_4 and C_2H_6 are the same.
Low pyrolysis at 700°C yields more CH_4 in the case of sapwood than in that of bark wood.
Rapid pyrolysis shows that sapwood produces more hydrogen and less CO_2 than bark wood.
 2. All yields tend to increase with temperature except in rapid pyrolysis for that of CO_2 .
 3. Rapid pyrolysis increases the yield of CO but decreases those of CO_2 and CH_4 .

In conclusion the production of gaseous species is favoured by an increase in temperature. Their distribution can be controlled by the pyrolysis regime. In all cases sapwood and especially poplar sap appears to be the best generator of combustible gaseous mixtures.

I - INTRODUCTION

Le présent travail vise à déterminer les conditions expérimentales de la pyrolyse de matériaux celluloseux susceptibles de conduire à un mélange gazeux combustible.

On considère généralement que durant une pyrolyse, les matériaux celluloseux se comportent de façon à peu près identiques quelle que soit l'origine du produit.

Cette étude a pour but de rechercher les différences qualitatives et quantitatives éventuelles des produits obtenus par pyrolyse de différentes variétés de bois et de ses diverses parties constitutives.

Les méthodes expérimentales utilisées ont permis de déterminer :

1. la stabilité thermique des différents échantillons ;
2. la nature des produits gazeux obtenus et leur proportion respective.

Les paramètres suivants ont été étudiés.

- nature de l'échantillon: cellulose, sapin, hêtre, peuplier
- température variant de 400 à 900°C
- méthode de pyrolyse : lente à pression atmosphérique rapide à basse pression.

II - METHODES EXPERIMENTALES

Diverses techniques expérimentales ont été mises au point pour déterminer la résistance à la dégradation thermique d'une part et la nature et la proportion des espèces gazeuses libérées au cours de la pyrolyse d'autre part.

A) Analyse thermogravimétrique isotherme

Il s'agit de porter l'échantillon dans un délai minimum de la température ambiante à la température choisie dans une atmosphère contrôlée.

Un four mobile, maintenu en permanence à une température choisie, recouvre une nacelle porte-échantillon reliée à une balance monoplateau. L'évolution de la perte de masse en fonction des paramètres imposés est suivie en continu.

B) Analyse de la phase vapeur

a - Pyrolyse lente à pression atmosphérique

Il s'agit, après avoir déterminé le bilan massique de chacune des frac-

tion (résidu, phase liquide, phase gazeuse) après pyrolyse, d'analyser la nature et la composition de la phase gazeuse libérée.

Une nacelle porte-échantillon placée au bas d'un four vertical est portée à une température choisie, les produits pyrolysés sont entraînés par un écoulement de gaz et traversent dans la partie supérieure du four une zone de température isotherme où ils subissent une post-pyrolyse sur environ 50 cm.

La composition de la phase gazeuse est déterminée au moyen d'une sonde de prélèvement mobile dans le four. Les échantillons sont analysés par chromatographie en phase gazeuse.

Les fragments de bois utilisés en pyrolyse lente ont une taille moyenne de 0,5 mm. Le poids de l'échantillon est de 2g. La vitesse de montée en température de l'échantillon est voisine de 250°C/mn. Les produits gazeux de pyrolyse sont entraînés dans un courant d'azote ayant une vitesse voisine de 1cm/s.

b - Pyrolyse rapide à basse pression

Un tube en quartz fermé à une extrémité est placé dans un four et relié à un ballon par l'intermédiaire d'un piège à azote liquide ; le vide ayant été fait dans l'appareil, l'échantillon est porté à la température désirée. Les produits de pyrolyse sont recueillis dans le piège et dans le ballon. Après réchauffage du piège les produits gazeux sont analysés par Chromatographie en Phase Gazeuse.

La masse des échantillons utilisés, en pyrolyse rapide est de 100 mg. Ils sont placés dans une zone du four maintenu à 500°C environ, les produits de pyrolyse traversent une zone à 800°C ou 900°C sous une pression de 5 à 20 torrs avant d'être recueillis.

III - RESULTATS

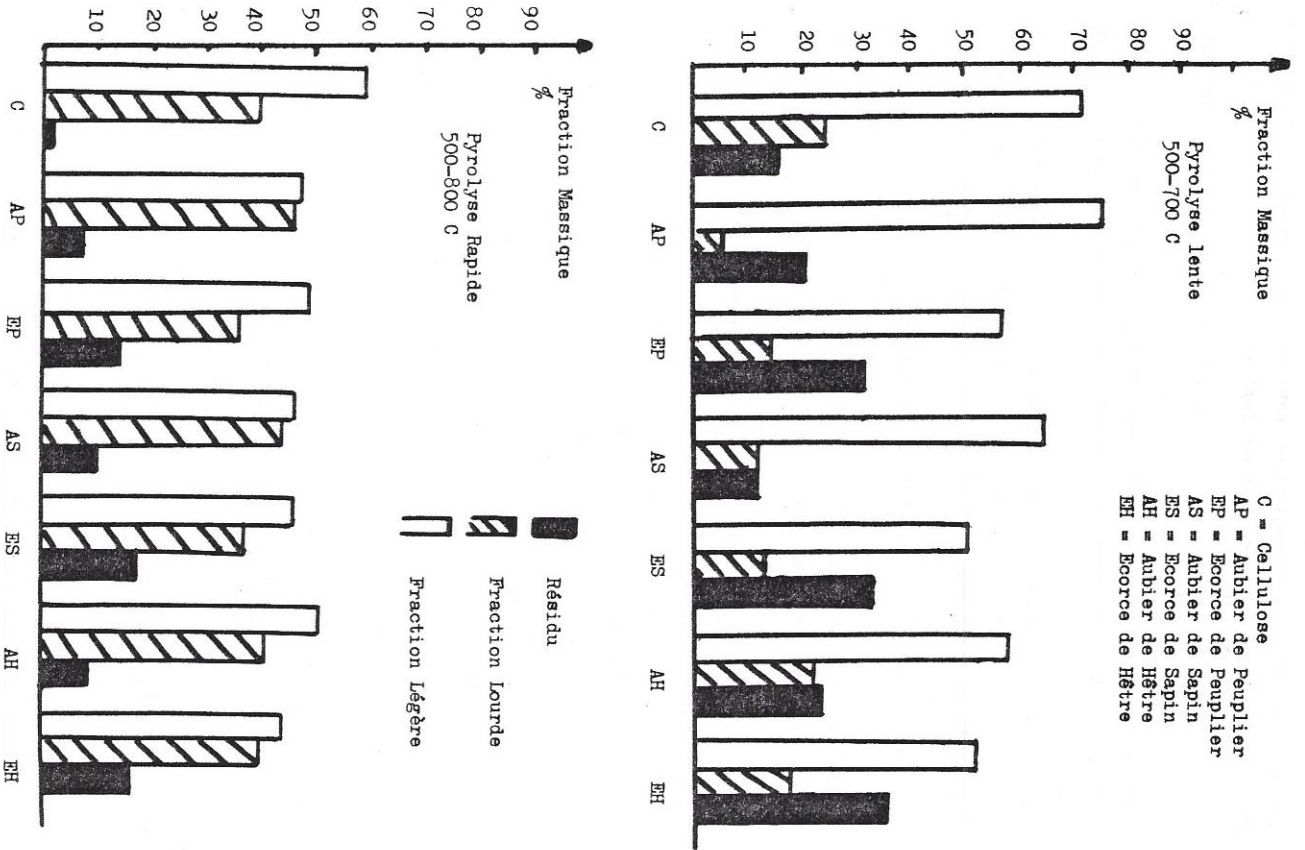
A) Analyse thermogravimétrique isotherme

Par analyse thermogravimétrique nous avons déterminé les pourcentages de résidu recueilli après pyrolyse.

On note que lorsque la température augmente les pourcentages de résidu diminuent.

Ainsi, le pourcentage de résidu pour l'aubier de peuplier passe de 30% à 400°C à 15% à 700°C.

Dans tous les cas étudiés, les écorces sont plus stables que les au-



biens. Les expériences effectuées avec la cellulose conduisent à une stabilité plus faible que n'importe quelle autre partie de bois.

B) Répartition des produits de pyrolyse lente

Pour chaque échantillon et pour des températures de post-pyrolyse variant de 450 à 700°C nous avons caractérisé les trois phases.

- 1) fraction légère ;
- 2) phase condensable ;
- 3) résidu de pyrolyse

Comme l'indique les schémas précédents, les produits gazeux légers sont plus abondants pour les aubiers que pour les écorces en pyrolyse lente. La différence est moins marquée pour aubiers et écorces dans le cas de la pyrolyse rapide où les produits lourds sont nettement plus abondants.

Dans tous les cas les pourcentages de résidu sont plus faibles en pyrolyse rapide.

C) Analyse de la phase gazeuse

L'analyse par chromatographie de la phase légère permet de déterminer l'évolution de chacune des espèces analysées, CO₂, H₂O, CO, H₂, CH₄, C₂H₆, C₃H₈, CH₃OH, CH₃CHO.

Une méthode de calcul a été mise au point ; elle permet de déterminer la fraction massique de chaque espèce à tout instant de la pyrolyse connaissant les fractions volumiques de chaque espèce recueillie.

Masse de produits gazeux libérés pour 100 g. de produit initial pyrolyse lente

	Peuplier		Sapin		Hêtre		Cellulose	
	aubier	écorce	aubier	écorce	aubier	écorce	500	700
H ₂ O	500	700	500	700	500	700	500	700
CO ₂	1,05	7,85	1,20	4,14	0,95	5,70	1,00	6,40
CH ₄	10,90	26,70	5,20	15,90	10,75	19,90	6,50	14,60
CO	27,20	35,15	25,70	27,50	26,50	34,70	15,50	31,30
CO ₂	4,10	1,10	3,15	1,15	3,05	1,25	3,30	1,10
C ₂	0,15	0,65	0,05	1,00	0,15	0,60	0,15	0,60
H ₂								

A partir des tableaux et schémas, on peut faire les remarques suivantes :

	Peuplier		Sapin		Hêtre		cellulose
	aubier	écorce	aubier	écorce	aubier	écorce	
T(c)	800	900	800	900	800	900	800 900
CH ₄	2,50	3,60	2,30	3,40	2,50	3,90	2,50 2,60
CO	31,00	39,50	23,00	25,40	27,20	35,80	21,20 28,20 29,50 39,50 21,80 22,80 34,00 54,70
CO ₂	6,40	4,30	14,00	8,10	6,20	4,30	9,50 7,60 5,50 4,80 10,50 6,80
C ₂	3,80	4,70	5,30	5,60	3,20	7,40	3,90 5,30 3,40 4,70 3,80 4,20
H ₂	0,40	0,70	0,34	0,50	0,35	0,60	0,30 0,50 0,40 0,50 0,30 0,70

pyrolyse rapide

Pour les deux méthodes, la température de pyrolyse de l'échantillon est de 500°C. On constate que le résidu solide est plus faible en pyrolyse rapide qu'en pyrolyse lente. Les rendements en produits gazeux augmentent avec la température de traitement des produits pyrolysés. Dans la fraction pyrolysée, les produits gazeux légers sont plus importants en pyrolyse lente qu'en pyrolyse rapide bien que la température de traitement de cette fraction soit moins élevée. Ceci s'explique par un temps de séjour beaucoup plus long. Quelle que soit la méthode de pyrolyse utilisée, l'aubier produit plus de CO que les écorces. Les fractions de C₂H₄ et C₂H₆ sont très comparables. En pyrolyse lente le CH₄ est plus abondant pour l'aubier que pour l'écorce. En pyrolyse rapide, l'aubier produit plus d'hydrogène et moins de CO₂ que l'écorce. Les rendements en CO augmentent alors que ceux de CO₂ et C₂H₄ diminuent.

IV - CONCLUSION

Les résultats obtenus ont mis en évidence les différences de comportement de chaque échantillon sous l'action d'une élévation de température en fonction de la méthode de pyrolyse étudiée et des parties où ont été prélevés ces échantillons. On a noté que la production d'espèces gazeuses, dans la gamme de températures utilisées, est favorisée par une élévation de température et leur distribution peut être contrôlée par le régime de pyrolyse.

Dans tous les cas l'aubier et plus particulièrement l'aubier de peuplier apparaît comme le meilleur générateur de mélange gazeux combustible.

THE PYROLYSIS OF TROPICAL WOODS : THE INFLUENCE OF THEIR CHEMICAL COMPOSITION ON THE END PRODUCTS

by G. PETROFF and J. DOAT

Centre Technique Forestier Tropical

Summary

Six samples of wood were pyrolysed at the laboratory scale :

- Three tropical mixtures consisting of woods :
 - . rich in lignin
 - . rich in extracts
 - . rich in carbohydrates
- Two reafforestation species :
 - . Gmelina arborea
 - . Eucalyptus
- A mixture of French hardwoods as a reference

It was observed that tropical woods gave slightly less pyrolygneous products than temperate zone woods. Furthermore, the products obtained seem linked with the chemical composition of the wood :

- . a high lignin content is reflected in a higher charcoal yield.
- . a high percentage of pentosanes gives more acetic acid and acetates.
- . a high cellulose content results in more methanol.
- . woods containing large amounts of alcohol benzene extractives may cause tarry deposits in the circuits.

From a practical point of view, it seems possible, without too great a risk, to replace temperate hardwoods by tropical species to supply an industrial pyrolysis line.

1. INTRODUCTION.

On connaît mal les conditions d'emploi énergétique des bois tropicaux dont la nature et les constituants diffèrent quelque peu de ceux des bois tempérés. Aussi, pour parvenir à une exploitation plus rationnelle de ces essences, on a procédé dans un premier stade de recherche, à des essais de carbonisation en laboratoire sur des bois ou mélanges de bois.

2. CONDUITE DE LA RECHERCHE.

21 Matières premières utilisées.

On s'est approvisionné en échantillons de bois tropicaux offrant des caractéristiques aussi variées que possible. L'échantillonnage était constitué :

- d'Eucalyptus saligna x tereticornis (essence de reboisement à croissance rapide); (E)
- de Gmelina arborea (essence de reboisement à croissance rapide); (G)
- d'un mélange de bois tropicaux riches en lignine; (T1)
- d'un mélange de bois tropicaux riches en extrait à l'alcool benzène; (T2)
- d'un mélange de bois tropicaux pauvres en lignine et en extrait à l'alcool benzène (c'est-à-dire riches en cellulose et hémicelluloses); (T3)
- d'un mélange de feuillus français : Bouleau, Peuplier, Hêtre, Chêne à titre de référence; (F.F.)

On a donc au total testé six échantillonnages de bois de composition et provenances diverses.

22 Appareillage et mode opératoire.

La pyrolyse des bois a été effectuée en cornues placées dans des fours électriques régulés automatiquement. Les résultats de carbonisations correspondent à la moyenne de plusieurs essais (3 à 7 selon le cas).

Les carbonisations ont été conduites à 500° pendant 4h, avec une montée en palier de 4h soit environ 2 degrés à la minute. Les produits dégagés ont été refroidis dans des réfrigérants à eau et les condensats recueillis dans des flacons barboteurs refroidis à la glace. Les produits gazeux non condensables ont été récupérés dans des ampoules ou des ballons de plastique selon les quantités. Les volumes ont été mesurés à l'aide d'un compteur à gaz.

23 Essais effectués et résultats obtenus.

Analyse des bois.

On a procédé tout d'abord à l'analyse physicochimique des bois.

On a déterminé la densité, le pouvoir calorifique supérieur, l'extrait alcool benzène, l'extrait à l'eau, la lignine, les pentosanes, la cellulose, les cendres, la silice. Les résultats sont donnés au tableau I.

Carbonisation des bois.

Les bois ont été fractionnés en plaquettes de quelques centimètres sur quelques millimètres puis pyrolysés comme indiqué précédemment. Les rendements en charbon, en pyrolygneux et en gaz sont donnés au tableau II.

Analyse des charbons.

Les pourcentages de matières volatiles, cendres, phosphore, soufre et carbone fixe sont donnés au tableau III.

Analyse des pyrolygneux.

Une analyse des pyrolygneux a été effectuée par chromatographie gazeuse pour chacun des six échantillons. Les résultats sont donnés au tableau IV.

Analyse des gaz.

Les gaz recueillis au cours des tests définitifs de pyrolyse ont été analysés. On a utilisé l'appareil d'Orsat pour le dosage du gaz carbonique, de l'oxygène, de l'oxyde de carbone et de l'hydrogène formés. Les hydrocarbures (méthane, éthane, éthylène et autres composés de C₂ à C₅) ont été dosés par chromatographie gazeuse. Les résultats sont donnés au tableau V.

3. ANALYSE DES RESULTATS.

31 Conduite de la carbonisation.

Le processus de carbonisation avec un palier à 500° n'a pas mis en évidence de difficultés particulières d'emploi des bois tropicaux par rapport aux feuillus français. Toutefois, dans le cas du mélange T2 riche en extraits et, dans une moindre mesure, dans le cas du Gmelina, des déchets plus ou moins importants sont apparus sur les tuyaux d'évacuation du pyrolygneux et des gaz. Dans la pratique industrielle, un encrassement des circuits serait donc possible au cours du traitement de certains bois tropicaux riches en produits extractibles.

32 Rendements à la carbonisation.

Pour les bois ou mélanges de bois tropicaux, le rendement moyen en charbon de bois varie de 30,6 à 36,6% alors que le mélange de feuillus français donne 30,1% de charbon.

Les quantités moyennes de pyrolygneux obtenues à partir des essences tropicales vont de 42,9 à 50,6%; Les feuillus tempérés ont donné 53,1% de pyrolygneux. Il semble donc que dans l'ensemble, les feuillus tempérés donnent moins de charbon et plus de produits condensables que les bois tropicaux.

En ce qui concerne les gaz formés, on ne note pas de grandes différences entre les bois. On a environ 15 litres de gaz totaux pour 100 g de bois sec, à l'exception du Gmelina qui en a fourni 17,7 litres.

On a remarqué que ce sont les bois riches en carbohydrates qui donnent le moins de charbon et le plus de pyrolygneux. A l'inverse, les bois ou mélanges de bois contenant beaucoup de lignine et d'extraits ont un meilleur rendement en charbon. Le pyrolygneux varie aussi comme les teneurs en pentosanes des bois.

Tableau n° I : Caractéristiques physicochimiques des bois

	E	F.F.	G	T1	T2	T3
	Euca-lyptus	Feuillus Français	Gmelina	Mélange riche en lignine	Mélange riche en Ext.A.B.	Mélange pauvre en lignine + Ext. A.B.
Caractéristiques physiques						
Densité	0,68	0,57	0,36	0,75	0,73	0,51
p.c.s.	4820	4740	4875	4800	5015	4590
Caractéristiques chimiques (% bois sec)						
Ext. A.B.	1,5	2,15	2,95	0,95	16,6	2,5
Ext. eau	0,9	1,2	0,4	2,85	0,5	2,8
Lignine	31,6	22,7	25,05	35,3	26,55	23,5
Cellulose	44,5	42,05	48,15	42,8	37,0	40,7
Pentosanes	16,5	24,9	16,15	13,5	13,7	22,0
Cendres totales	0,3	0,5	0,9	1,0	0,95	2,7
SiO ₂	0,018	0,007	0,05	0,26	0,009	0,01
Lignine + Ext. A.B.	33,1	24,85	28,0	36,25	43,15	26,0
Cellulose + Pentosanes	61,0	66,95	64,65	56,3	50,7	62,7

Tableau n° II : Résultats moyens de carbonisation

	E	F.F.	G	T1	T2	T3
Rendement en charbon (1)	32,4	30,1	30,6	33,4	36,6	32,9
Rendement en pyrolygneux (1)	49,7	53,1	50,1	45,5	42,9	50,6
gaz totaux (2)	14,7	15,1	17,7	15,4	14,9	15,6

(1) : en % du bois sec - (2) : litres % sur bois sec

Tableau n° III : Analyse physicochimique des charbons

	E	F.F.	G	T1	T2	T3
Densité charbon	0,27	0,22	0,16	0,33	0,29	0,26
p.c.s.	8170	8070	8185	8000	7840	7710
Matières volatiles (1)	12,95	14,0	12,9	13,1	16,0	11,8
Cendres (1)	1,05	1,45	2,85	2,9	2,35	6,6
Phosphore (1)	0,105	0,031	0,034	0,128	0,009	0,016
Soufre (1)	0,014	0,024	0,024	0,035	0,020	0,063
Carbone fixe (1)	86,0	84,55	84,25	84,0	81,65	81,6

(1) : En % du charbon sec

Tableau n° IV : Analyse du pyrolygneux (% du bois sec)

	E	F.F.	G	T1	T2	T3
	Euca-lyptus	Feuillus Français	Gmelina	Mélange riche en lignine	Mélange riche en Ext.A.B.	Mélange pauvre en lignine + Ext. A.B.
Pyrolygneux total	50,5	52,1	47,4	46,5	44,8	51,2
Produits déposés	1,9	0,5	7,2	0,9	12,0	2,4
Jus de pyrolygneux :						
Phase aqueuse	38,8	42,3	33,9	35,1	30,9	40,7
Phase organique	8,3	6,8	5,2	8,7	1,7	5,6
Non récupérés	1,5	2,5	1,1	1,8	0,2	2,5
Principaux constituants (dans phase aqueuse et organique) % bois sec						
Méthanol	1,84	1,40	1,94	1,45	1,02	1,43
Ethanol + acide formique	0,10	0,09	0,04	0,02	0,03	0,03
Acétone	0,11	0,15	0,11	0,13	0,13	0,11
Acétate de méthyle	0,32	0,76	0,56	0,24	0,12	0,64
Acide acétique	2,35	3,62	2,44	1,89	1,96	3,82
Méthyléthylcétone	0,13	0,17	0,15	0,15	0,15	0,15
acétate d'éthyle	0,61	0,46	0,29	0,75	0,21	0,37
Gaïacol	0,37	0,58	0,07	0,47	0,17	0,23
Phénol+0. crésol m. + p. crésols	0,19	0,13	0,05	0,28	0,07	0,13

Tableau n° V : Analyse des gaz - Composition pondérale (% bois sec)

	E	F.F.	G	T1	T2	T3
H ₂	0,02	0,03	0,03	0,01	0,02	0,03
O ₂	0,42	0,10	-	0,33	0,40	0,56
CO ₂	14,1	14,0	15,7	15,1	14,0	13,0
CO	5,55	5,7	7,35	6,05	5,4	5,7
CH ₄	0,98	1,21	1,36	0,76	1,01	1,65
C ₂ H ₄	0,09	0,07	0,10	0,08	0,08	0,11
C ₂ H ₆ +C ₃ H ₈	0,19	-	0,21	0,22	0,29	0,41
C ₂ H ₆	0,20	0,21	0,27	0,19	0,20	0,33
Total hydrocarbures	1,46	1,49	1,94	1,25	1,63	2,64

Ces remarques ont d'ailleurs été confirmées par un essai ultérieur de carbonisation d'une pâte cellulosique blanche, ne contenant pratiquement que de la cellulose et des pentosanes, qui a donné un rendement en charbon inférieur à celui des bois, soit 28 % et sur de la lignine qui a donné 59 % de charbon.

33 Qualité des charbons.

Les caractéristiques physicochimiques des charbons diffèrent assez nettement selon l'espèce : densité variant de 0,16 à 0,33, p.c.s. de 7710 à 8185, taux de matières volatiles de 11,8 à 16 %, cendres de 1,05 à 6,6 %. Les charbons de bois obtenus à partir de feuillus français se classent à l'intérieur de ces fourchettes et ne se distinguent pas de l'ensemble des bois tropicaux.

Le mélange tropical T3 constitué de bois pauvres en lignine et en extraits accuse un taux de cendres très élevé (6,6 %). Ceci pourrait entraîner un refus pour certaines utilisations industrielles.

On a confirmé, au cours de cette étude, qu'une forte corrélation existait d'une part entre la densité des bois et la densité des charbons résultants, d'autre part entre les teneurs en cendres des bois et celle des charbons. Inversement, on n'a pas observé de corrélations entre les p.c.s. des bois et ceux des charbons. En fait les p.c.s. des charbons dépendent de leur constitution chimique finale (produits volatils, taux de cendres et de carbone fixe).

34 Composition des pyrolyseux.

La composition qualitative des pyrolyseux est la même. Quel que soit le bois ou le mélange de bois pyrolysés, on retrouve les mêmes constituants.

Cependant, l'analyse quantitative révèle quelques différences (on rappelle que les rendements totaux en pyrolyseux n'étaient pas identiques pour toutes les essences). Ainsi, pour les bois tropicaux, on a recueilli 1,02 à 1,94 % de méthanol; 1,89 à 3,82 % d'acide acétique; 0,21 à 0,75 % de gâicol; 0,12 à 0,75 % de phénols + crésols, soit, selon les cas, deux à six fois plus de produits. Seule l'acétone ne semble pas dépendre de la nature du bois puisque l'on n'a observé que peu de variations (0,11 à 0,15 %).

Il faut noter qu'ici aussi les feuillus tempérés ne se distinguent pas particulièrement des bois tropicaux.

On a cherché à établir l'influence de la composition chimique des bois sur la formation de certains composés de pyrolyse. On a noté que des quantités plus importantes de méthanol sont produites par les bois riches en cellulose.

D'autre part, l'acide acétique et l'acétate de méthyl augmentent quand les bois contiennent beaucoup de pentosanes.

De plus, les dépôts condensables semblent suivre les teneurs en extraits alcool-benzène des bois.

Enfin, les bois riches en lignine donneraient moins d'acide acétique et les bois riches en extraits (alcool-benzène et eau) moins de méthanol.

On n'a pas observé de tendance très nette en ce qui concerne la formation de gâicol, de phénols ou de crésols. Toutefois, d'un point de vue théorique, ces constituants devraient être issus de la lignine car on retrouve des structures chimiques analogues. C'est effectivement pour le mélange T1, riche en lignine, que l'on observe un rendement maximum en gâicol, phénols, crésols.

35 Composition des gaz.

Quel que soit le bois ou le mélange de bois, les gaz de pyrolyse sont composés essentiellement de gaz carbonique, d'oxyde de carbone et de méthane. On trouve en plus petites quantités, de l'oxygène et de l'hydrogène, de l'éthane et de l'éthylène. La composition des gaz varie selon l'essence carbonisée. Le gaz carbonique est le constituant principal (de 45,7 à 53,8 % en volume ou de 13 à 15,7 % par rapport au bois initial); vient ensuite l'oxyde de carbone (de 31,2 à 35,7 % en volume ou de 5,4 à 7,35 % par rapport au bois initial). Les quantités de méthane varient de 7,4 à 16 % en volume (ou 0,76 à 1,65 % par rapport au bois) et les taux d'hydrocarbures totaux de 9,5 à 20,1 % en volume (ou 1,25 à 2,64 % par rapport au bois) soit du simple au double. On remarque que les résultats trouvés pour les feuillus français, se situent dans la fourchette moyenne des résultats globaux.

Le p.c.s. des gaz varie en fonction des teneurs en hydrocarbures totaux de 2170 à 3380 calories par litre, avec un chiffre de 2450 pour les bois français. Si l'on calcule le nombre de calories pouvant être fournies par 100 g de bois sec, des différences apparaissent également, les résultats s'écartant entre 33,4 à 52,7 kilo calories. Le mélange T3 et le Gmelina se détachent nettement et donnent les chiffres les plus favorables.

La recherche de corrélation entre la composition chimique du bois et celle des gaz s'est soldée par un résultat négatif. Il est donc très difficile de formuler des hypothèses sur l'origine des composés gazeux.

4. CONCLUSION.

Les essais réalisés montrent que l'on peut envisager sans trop de risques le remplacement de bois feuillus français par des bois ou mélanges de bois tropicaux pour l'approvisionnement d'une chaîne de carbonisation avec production de charbon, de pyrolyseux et de gaz. Toutefois, certaines différences pourront apparaître dans les rendements en produits de carbonisation, tant en ce qui concerne le charbon que les composants liquides ou gazeux. Il peut en résulter de légères modifications du réglage des appareils. La valeur énergétique des produits gazeux en particulier peut varier d'un mélange de bois à l'autre. Enfin, des risques accrus d'encrassement peuvent apparaître dans le cas de quelques bois tropicaux riches en extraits aux solvants organiques.

Il n'en reste pas moins démontré que l'utilisation énergétique ou chimique des bois tropicaux est envisageable.

D'un point de vue théorique, l'étude fournit une première série d'informations sur l'origine des corps obtenus à la pyrolyse. On pourrait accroître la production d'acide acétique et d'acétates par l'emploi de produits riches en pentosanes comme la paille ou augmenter le rendement en charbon en utilisant des bois riches en lignine.

Bibliographie.

- Colloque sur la valorisation énergétique des sous-produits agricoles 13-14 mars 1979 (APRIA, 35 rue Gal Roy, 75008 PARIS)
- Bois et Forêts des Tropiques : n° 159 (Janv.-Fév. 1975, p. 55) et n° 177 (Janv.-Fév. 1978, p. 51)
- Carbonisation des bois et carburants forestiers, par Ch. Marillier, Dunod 1941
- Le Coke, par Joison Foch et Boyer, Dunod 1970

GASEOUS FUEL FROM BIOMASS BY FLASH PYROLYSIS

S. CAUBET, P. CORTE, C. FAHIM, J.P. TRAVERSE

Laboratoire de Recherche sur l'Energie. Université Paul Sabatier,
31062 TOULOUSE Cédex - FRANCE

Summary

Thermal decomposition of biomass in an inert atmosphere is studied through basic components: cellulose, lignin, wood. Flash pyrolysis (heating rate 250 °C/s) allows the production of a medium heating value synthetic gas with gas phase thermal efficiency of up to 95%.

Light hydrocarbons (CH₄, C₂H₄, C₂H₂, C₂H₆) provide about 50% of the energy recovered in the gas. Ethylene represents 5% (Vol.) of the pyrolysis gas.

Résumé

On étudie la décomposition thermique de la biomasse en atmosphère neutre à travers ses composants de base: cellulose, lignine, bois.

La pyrolyse flash avec des vitesses d'échauffement d'environ 250 °C/s, permet de produire un gaz de synthèse à pouvoir calorifique moyen avec un rendement énergétique de conversion atteignant 95%.

Les hydrocarbures légers (CH₄, C₂H₄, C₂H₂, C₂H₆) représentent jusqu'à 50% du contenu énergétique du gaz. L'éthylène représente 5% en volume du gaz de pyrolyse.

1. INTRODUCTION

Large scale use of the biomass as a source of non-fossil renewable carbon is the only long-term solution to fossil fuel depletion. Flash pyrolysis allows potentially useful conversion of lignocellulosic materials to gaseous mixtures, which can be used either as gaseous fuel or as raw materials for chemical synthesis. The purpose of this work is to complete available data on this chemical process.

2. EXPERIMENTALMaterials

The experiments were carried out separately with the two basic components of the biomass: cellulose and lignin, and with beech wood, chosen as a typical example.

All samples were dried for 24h at 95 °C.

Wood and cellulose were shredded to 1-2mm particule size. Lignin was in the form of a fine powder (100 µm). Composition of the materials is given in Table I.

TABLE I

	Weight composition (%)		Elementary composition							
	WATER	ASHES	dry ash-free basis							
			C	H	O	C	H	O	H/C	O/C
CELLULOSE	2.0	0.3	44.4	6.2	49.4	6	10	5	1.67	0.83
LIGNIN	0.0	0.0	63.8	6.4	29.8	6	7.2	2.1	1.20	0.35
BEECH WOOD	2.5	0.5	48.3	6.0	45.1	6	8.9	4.2	1.49	0.70

Apparatus and method.

Figure I shows the laboratory reactor used for the experiments. After heating the reactor to the desired temperature, weighted samples of 1.30g were introduced into the hot zone with a feed rate of about 0.3g/mm for cellulose, 0.4g/mm for beech wood and 0.9g/mm for lignin. An original feeder was designed.

An inert gas flowed through the reactor.

The particles fell on the top of a porous alumina bed where they are pyrolysed. The pyrolysis gases were extracted at the bottom of the reactor. The total volume of gas produced in one run was measured. Gaseous

products were then analysed with a gas chromatograph.

The average heating rate of the particulates was measured. For an 850 °C reactor temperature, the heating rate reached 250 °C/s.

The residence time of the gases in the hot zone was roughly calculated.

After the pyrolysis stage, air was blown through the reactor instead of inert gas ; the char then burns.

Analysis of the combustion gases gives the amount of carbon in the char.

3. RESULTS

Experiments show that the most useful temperature range for gasification is 600-1000 °C. The gas product is primarily composed of carbon monoxide, carbon dioxide and hydrogen. Substantial amounts of hydrocarbons especially methane and ethylene are present in the gas. The gas volume always increases with temperature. For example, at 850 °C, 1g of cellulose yields 0.91 of pyrolytic gas which contains 12.2% (Vol) of methane and 5% (Vol) of ethylene. Table II presents the detailed results of the experiments.

The carbon, hydrogen and oxygen balances are given. The mass balance is also given assuming that char is almost pure carbon. Mass losses are due to non-recovered products : deposits of carbon black and tar outside the reactor hot zone ; water and other condensibles.

Figures II and III represent variations of gas yield (Y) and gas phase thermal efficiency (e) versus reactor temperature. The gas yield is defined as :

$$y = \frac{\text{gaseous product weight}}{\text{weight of organic matter introduced}}$$

and the gas phase thermal efficiency as :

$$e = \frac{\text{available energy in pyrolysis gas}}{\text{available energy in biomass sample}}$$

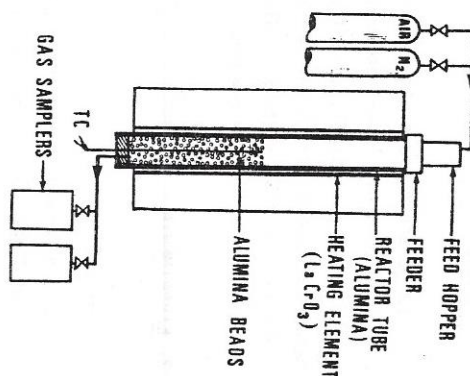


Fig. 1 : Laboratory apparatus used for biomass pyrolysis.

TABLE II

Gas analysis , % by volume

	T°C	t	Gas analysis, % by volume							hv	V	y	e	Hg/H	Og/O	Cg/C	Cs/C
			H ₂	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₂ H ₂								
CELLULOSE	600	7.5	13.85	42.50	32.35	6.40	3.70	1.10	3065	0.274	35.25	20.75	12.4	42.5	30.8	23.5	
	700	5.2	22.15	42.55	18.45	11.75	3.75	1.15	0.20	3865	0.564	59.8	53.9	47.5	64.75	57.8	19.3
	800	4.1	24.60	42.80	13.60	13.30	4.75	0.70	0.25	4260	0.806	79.9	83.3	75.6	81.7	80.8	13.6
	850	3.9	26.90	44.20	11.10	12.20	5.00	0.40	0.20	4180	0.883	84.0	91.1	82.4	84.7	85.9	8.0
	900	3.7	28.60	43.40	11.25	12.00	4.35	0.35	3675	0.939	87.6	93.8	87.1	89.4	88.3	8.1	
	1000	3.4	34.00	46.00	8.00	10.40	1.60	0.04	3675	1.063	91.1	96.6	91.9	95.3	88.9	7.9	
LIGNIN	700	3.7	17.00	41.20	13.55	25.10	1.95	1.30	4665	0.317	32.2	21.9	20.1	51.8	23.0	---	
	800	3.0	23.40	39.25	11.35	21.60	2.90	0.83	0.15	4555	0.425	39.8	28.7	44.6	63.1	27.3	---
	900	2.8	29.90	37.80	9.00	19.60	3.20	0.25	0.27	4485	0.507	43.3	33.8	54.3	66.8	30.1	---
	1000	2.2	36.80	37.80	8.25	15.60	1.23	0.02	0.29	3990	0.623	49.7	36.9	61.7	81.1	32.4	---
BEECH WOOD	700	5.0	18.75	43.24	17.11	16.26	3.54	0.94	0.15	4140	0.445	47.5	41.9	40.7	54.5	43.7	24.8
	800	3.8	21.10	43.10	15.60	14.80	4.34	0.72	0.31	4175	0.680	70.5	64.5	62.5	79.9	65.5	19.3
	850	3.7	21.50	42.80	13.30	16.70	4.80	0.46	0.43	4400	0.713	71.6	71.3	70.3	78.3	68.6	15.0
	900	3.5	24.85	41.80	13.20	15.35	4.37	0.23	0.20	4210	0.767	74.6	73.4	74.3	82.8	70.1	12.4
	1000	3.0	37.00	42.80	7.60	11.70	0.70	---	---	3655	0.954	77.2	79.2	87.7	87.5	69.2	12.0

t : Residence time of gases (s)
 hv: Heating value of pyrolysis gas (kcal/Nm³)
 V : Total volume of pyrolysis gas (NL)
 y : Gasification yield
 e : Gas phase thermal efficiency

Hg/H : Hydrogen balance
 Cs/C : % Initial carbon in the char
 Og/O : Oxygen balance
 Cg/C : Carbon balance (gasification)

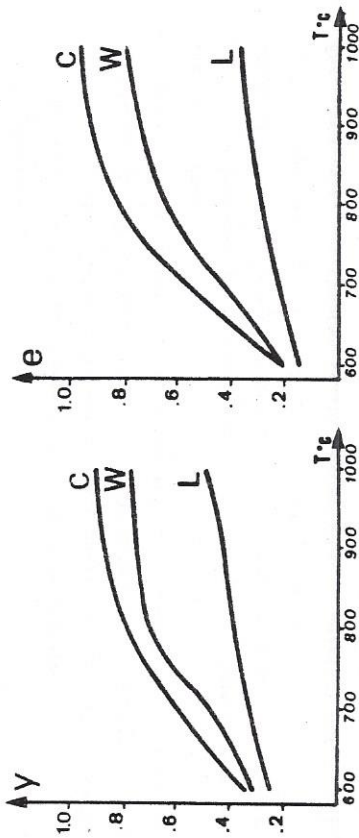


Fig. II: Gas yield (y) vs temperature Fig. III: Gas phase thermal efficiency (e) vs temperature

4. DISCUSSION

The results of the present work show that biomass materials can be converted to gaseous product with high gas yield and gas thermal efficiency.

Operating conditions : residence time of gases (4s), atmospheric pressure in an isothermal reactor and continuous feeding can be easily obtained in an industrial process.

Our results are consistent with other processes described in the literature, considering the difference of raw materials and procedures (Ref. 1 to 4).

Pyrolysis gas can be burned directly as gaseous fuel without problem, because of its relatively high calorific value : (about 40% of that of natural gas).

Light hydrocarbons of high calorific value represent more than 20% of the gas volume i.e. 50% or more of the energy available in the gas : see curve on Fig. IV. The most interesting chemicals products are unsaturated hydrocarbons. Ethylene production reaches 5% of gas volume. Better ethylene yields could be obtained with shorter residence time and faster quenching of the gases.

The reaction enthalpy can be estimated ; assuming an average calorific value of 8000 kcal/Kg for unknown products. We find :

$$H = 630 \text{ kcal/Kg for cellulose}$$

$$H = 475 \text{ kcal/Kg for beech wood.}$$

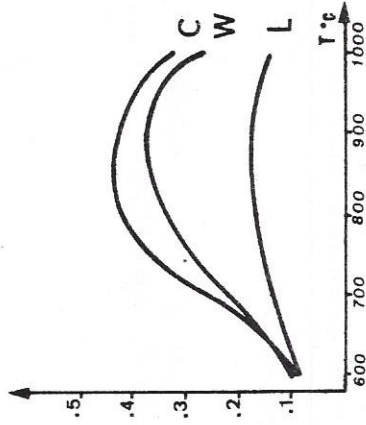


Fig. IV: Thermal hydrocarbons yield : available energy in hydrocarbon gas available energy in pyrolysis gas

These values represent less than 15% of the initial calorific value of the biomass.

From an industrial point of view, fluidized bed will be the most appropriate reactor. Fluidized bed studies will shortly be undertaken to optimize the conversion.

References :

- 1 - S. PRAHACS, H.G. BARCLAY, S.P. BHATTIA.
"Pulp and paper magazine of canada". 72, 6. (1971), 69-83.
- 2 - J. LEDE, P. BERTHELOT, J. VILLERMAUX, A. ROLIN, H. FRANCOIS, X. DEGLISE
"Revue Phys. Appl." 15 (1980), 545-552.
- 3 - R.S. BURTON, R.C. BAILIE.
"Combustion". Feb. (1974), 13-19.
- 4 - E. RENSFELT and A1.
"Symp. pap. Energy from Biomass and Wastes". Aug. 14-18 (1978) - Washington D.C., 465-594.

FAST PYROLYSIS/GASIFICATION OF LIGNOCELLULOSIC
MATERIALS AT SHORT RESIDENCE TIME

X. DEGLISE, C. RICHARD, A. ROLIN and H. FRANÇOIS

Laboratoire de Photochimie Appliquée
(Groupe de Recherches de Chimie du Bois)
Université de Nancy I - 54000 NANCY FRANCE

Work is funded by the Délégation Générale à la
Recherche Scientifique et Technique (DGRST)
and Commissariat à l'Énergie Solaire (COMES)

Summary

The results discussed in this paper point to the advantages of Fast Pyrolysis over air and oxygen gasification as a source of medium energy gas. Both rapid heating and short residence time of gases are employed in a single step pyrolysis-gasification of sawdust samples in a free-falling system. Gas yields are increasing with temperature and moisture content (for temperatures upper than 700°C). Tables of products, H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆ and C₂H₂ are shown with volume balance and overall formulae of char for different temperatures and moisture contents. Experimental results provide indirect information on the heat of reaction which shows that fast pyrolysis is slightly endothermic for temperatures upper than 600-700°C, and exothermic under 700°C.

1. INTRODUCTION

Two main types of gasifiers have to be distinguished (1) :

- The production of a low energy (air gasification : 5000 KJ/m³) or a medium energy (oxygen gasification : 12500 KJ/m³) gas requires near-equilibrium product distribution, large particles, slow heating rates and long residence times.

- The increasing in energy content of the gas (medium energy gas : 19000 KJ/m³) with non equilibrium product distribution requires small particles, fast heating rates and short residence times.

Fast pyrolysis, corresponds to the second type of gasifier and is able to produce hydrocarbons such as C₂H₄ and C₂H₂ giving a higher heating value to the gas and valuable products for chemical industry.

2. EXPERIMENTAL (2) (3)

Pyrolysis of sawdust samples (100 to 300 mg, particle size : 25 to 400 µm) was performed in a free falling system : vertical quartz tube in an electrical furnace (from 500 to 1000°C). Heating rate of 1000°C/s and residence times of less than a second were estimated. After an experiment the gaseous products were expanded into calibrated volumes and analyzed by gas chromatography (flame ionization detector for hydrocarbons, and thermal conductivity detector for H₂, CO and CO₂). Water formation during the pyrolysis of dry wood was determined by the difference between the total pressure measured on the gauge and the pressure of the analyzed gas. (The monitored gases : H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₂H₂ and H₂O represent more than 99 % of the products, only traces of other hydrocarbons were detected). From carbon, hydrogen and oxygen balances the overall formula of char is obtained at different temperatures.

Materials : softwood (Douglas fir) and hardwood (Beech) were studied at different moisture contents (from 0 to 100 %).

3. RESULTS AND DISCUSSION

The yields of the major pyrolytic products versus temperature are presented in Table 1 for the fast pyrolysis of dry material.

The char yield decreases with increasing temperature and levels out around 800°C. The yield of the gas increases with temperature, and the water yield remains almost constant. The overall formulae of char are given in Table 2. The overall composition of char appears not to be very different for Douglas fir and beech from 500 to 1000°C. These results are in

the wood studied has apparently no influence on the composition of gases and residues and yields of products.

The yields of CO and CO₂ show significant decreases when increasing pyrolysis temperature. The hydrogen yield shows a dramatic increase in our temperature range. The CH₄ and C₂H₆ yields increase, present a maximum around 700 and 750°C respectively and gradually decrease for higher temperatures. The C₂H₂ yield increases with temperature. The heating values of the pyrolytic gas increase to a maximum of 20000 KJ/m³ around 750°C and then show a slight decrease until 18000 KJ/m³ at 1000°C.

For fast pyrolysis of Douglas fir and beech, the moisture content of wood has practically no influence for temperature below 700°C. The yields of gases versus temperature and moisture content of wood (Figure 1, Douglas fir) are increasing with temperature over 700°C and moisture content.

Figure 1 - Yields of gases versus temperature and moisture content of wood (Douglas fir).

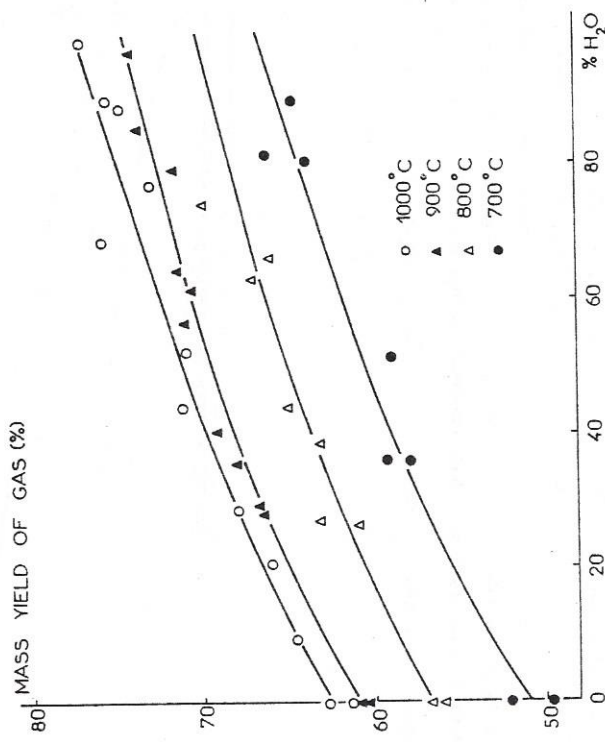


Figure 1 - Yields of gases versus temperature and moisture content of wood (Douglas fir).

For 1 kg of wood, pyrolysed at 1000°C with a 100 % moisture content, we obtain 1 m³ of gas and a heating value of 16000 KJ/m³. The influence of moisture content on the evolved gas composition is shown in figure 2.

At constant temperature the hydrogen yield shows a dramatic increase

good agreement with literature data (3).

TABLE 1 - Mass yields (%) of the major pyrolytic products of dry input feed versus temperature.

a) Dry softwood		600	700	800	900	1000
T°C	500	26.8	52.25	59.6	60.3	61.3
Gases*	13.85	61	33.5	25.6	27	26
Char	79.4	12.2	14.25	14.8	12.7	12.7
Water	6.75					
b) Dry hardwood		600	700	800	900	1000
T°C	500	29.7	48.8	58	60.4	67.6
Gases*	16.7	57.5	37.8	29.6	26.4	21
Char	75.8	12.8	13.4	12.4	13.2	11.4
Water	7.5					

(*) H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₂H₂

TABLE 2 - Overall formulae of char versus temperature.

	Douglas fir		Beech	
500°C	CH _{1.33}	O _{0.51}	CH _{1.33}	O _{0.48}
600°C	CH _{1.15}	O _{0.39}	CH _{1.14}	O _{0.35}
700°C	CH _{0.76}	O _{0.22}	CH _{0.90}	O _{0.24}
800°C	CH _{0.52}	O _{0.12}	CH _{0.73}	O _{0.19}
900°C	CH _{0.48}	O _{0.18}	CH _{0.58}	O _{0.14}
1000°C	CH _{0.28}	O _{0.16}	CH _{0.43}	O _{0.07}

The variations of the yields of gases are shown in Table 3. The nature of

TABLE 3 - Yields of the major gases (% volume a : dry beech, b : dry Douglas fir).

T°C	500	600	700	800	900	1000
CO	a	55.5	59	54	51	50
	b	59	62	56	53.5	51.5
CO ₂	a	26.5	13	9	8	7
	b	22	11.5	5	5	4.5
H ₂	a	2	8	14	18	21
	b	2.5	8	15	19	24
CH ₄	a	11.5	14	15	15	14
	b	12.2	13	16	14.5	13.5
C ₂ H ₆	a	3.5	4.7	6.5	6.5	6.0
	b	3.5	4.2	6.5	6.5	5.6
C ₂ H ₂	a	0.7	1.1	1	0.5	0.5
	b	0.7	1	1	0.5	0.2
C ₂ H ₄	a	0.3	0.2	0.5	1.0	1.5
	b	0.1	0.3	0.5	1.0	1.7

MOLES OF GAS PER MOLE OF DOUGLAS FIR (24g)

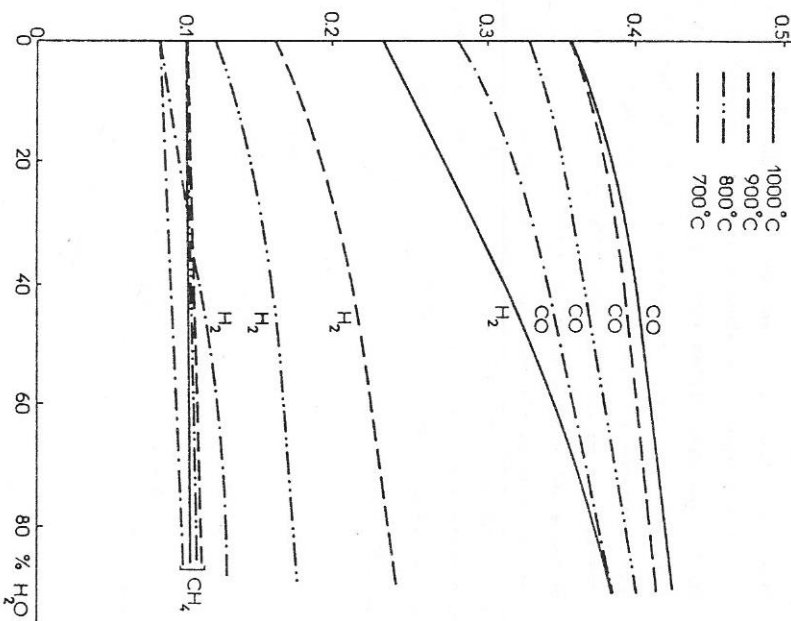


Figure 2 - Influence of moisture content on the evolved gas composition.

with the moisture content. For short residence time the influence of water does not result entirely from steam-gasification as the increase of H_2 does not correspond to the increase of CO.

The heating values of the products (gas + char) are very close to the heat content of the dry input feed material. At 600°C the char represent 76 % of the total heating value of the input feed, whereas at 900°C it represent only 40 %.

Calculated data from experimental results show that fast pyrolysis reaction is slightly endothermic only above 700°C. Heats of reaction are shown in Table 4.

As the heats of combustion of dry wood are : Douglas fir : 19980 KJ/kg, beech : 19540 KJ/kg ; the heat of reaction for gasification to a

medium energy gas (17000 KJ/m³) is less than 10 % of the wood heat content.

TABLE 4 - Heat of reaction for fast pyrolysis (KJ/kg of dry wood).

1) Softwood		2) Hardwood	
T°C	0 % H ₂ O	T°C	0 % H ₂ O
500	-500	500	-40
600	-410	600	16
700	-625	700	375
800	-540	800	430
900	200	900	1080
1000	540	1000	1460
580	1040	1030	1970
1400		1970	

4. CONCLUSION

These bench scale fast-pyrolysis experiments over the temperature range 500°C to 1000°C and for moisture contents from 0 to 100 %, provide data on the yields of the pyrolytic products, the composition of the gaseous phase, the heating value of the products, and the heat of reaction. These experiments shows that moisture content enhance the gasification but with higher heats of reaction. These data are useful as guidelines in the operation of future continuous flash-pyrolytic pilot plants we plan to develop (¹).

References

- (¹) T. MILNE - A survey of Biomass Gasification, Vol II, chapter 5 SERI July 1979.
- (²) J. LEDE, P. BERTHELOT, J. VILLERMAUX, A. ROLIN, H. FRANÇOIS and X. DEGLISE - Revue Phys. Appl. 15, 545 (1980).
- (³) X. DEGLISE, C. RICHARD, A. ROLIN and H. FRANÇOIS - Revue Gén. Thermique, on press. November 1980.
- (⁴) X. DEGLISE, J. MORLIERE and Ph. SCHLICKLIN - Energy from Biomass Conference - Brighton G.B. November 1980.

MASS AND ENERGY BALANCES FOR A TWO FLUIDISED-BED
PILOT PLANT WHICH OPERATES ON WOOD FAST PYROLYSIS

X. DEGLISE : Prof. Université de Nancy 1
C.O. 140 - 54037 NANCY CEDEX, FRANCE
P. MORLIERE : R and D Director TNEE (Tunzini-Nessi Entreprises d'Equipe-
ments) - 1, Place H. de Balzac - 95100 ARGENTEUIL, FRANCE
Ph. SCHLICKLIN : Dr. Ing. Centre de Recherches de Pont-à-Mousson
B.P. 28 - 54700 PONT A MOUSSON, FRANCE

Abstract

Laboratory results provide for the drawing and calculation of the flow-sheet of a possible industrial facility, which can produce a medium BTU gas (17-19 MJ/Nm³) not diluted with nitrogen and without need for oxygen plant. It operates on small size particles of wood residues.

With the two main input parameters (pyrolysis temperature and moisture content of the feed), the mass and energy balances were computed and the operating conditions are available for self sufficient energy operation. The efficiency of the system in term of energy was previously fixed.

The results of calculations for the case of pyrolysis of beech at 750°C and 10 % moisture content are given.

The pilot facility (1 t/day) will be demonstrated at the Research Center of Pont-à-Mousson, a subsidiary of Saint-Gobain - Pont-à-Mousson Company, in Pont-à-Mousson (France).

A partir de travaux menés au Laboratoire de Photochimie Appliquée de l'Université de Nancy 1 (Professeur X. Deglise), nous avons cherché à concevoir un système industriel permettant la transformation des déchets lignocellulosiques, et plus spécialement de bois, en un gaz combustible suffisamment riche pour pouvoir être transporté et distribué. Les expériences de laboratoire ont montré en effet que l'on pouvait par pyrolyse rapide dans la gamme de température de 700 à 1000°C obtenir 50 à 80 % du contenu énergétique du bois sous la forme d'un gaz possédant un PCI compris entre 17 et 19 MJ/Nm³ (4100 à 4600 Kcal/Nm³) tout-à-fait comparable au gaz de four à coke ou au gaz dit "de ville".

L'installation décrite ici - qui a fait l'objet d'une demande de brevet français - constitue un des meilleurs schémas utilisant au mieux l'énergie thermique générée pour assurer la bonne marche du système en couvrant les besoins thermiques de la pyrolyse proprement dite et de la préparation de l'alimentation (séchage des matières au degré de siccité requis).

Le schéma de l'installation, dont un pilote est prévu au Centre de Recherches de Pont-à-Mousson, est donné par la figure 1, qui montre en outre les résultats du calcul des bilans matière et énergie effectués pour des conditions réalistes de fonctionnement qui seront justifiées plus loin.

Le bois entrant à 50 % d'eau (1 kg de bois anhydre + 0,5 kg d'eau) est séché jusqu'à une valeur comprise entre 10 et 20 % d'eau. Le séchage est effectué dans une tour à entraînement (licence Air Industrie du Groupe SGPM) qui utilise, d'une part, de l'air préchauffé par les gaz sortant du séchoir lui-même et, d'autre part, par les gaz de combustion du résidu carboné solide ou "char" provenant de la pyrolyse.

Le bois séché et légèrement préchauffé est envoyé dans le réacteur de pyrolyse où il est mélangé, dans un lit fluidisé par une recirculation des gaz de pyrolyse, à des particules réfractaires portées à la température adéquate par la combustion du "char" qui est effectuée dans un réacteur séparé travaillant lui aussi en lit fluidisé.

Les gaz produits servent à un premier préchauffage de l'air de combus-

tion du "char", cette récupération assurant la production d'un gaz sec par la condensation de la vapeur d'eau existant dans ces gaz.

L'air de combustion du "char" reçoit encore deux préchauffages avant son admission dans le réacteur de combustion :

- par les gaz de combustion sortant de la jaquette du réacteur de pyrolyse qu'ils contribuent à maintenir à la température désirée,
- par les gaz de combustion lors de leur passage dans le cyclone à la sortie du réacteur de combustion destiné à les débarrasser des cendres du "char".

Les gaz de combustion sortant du réacteur de combustion du "char" sont utilisés en 4 endroits :

- pour le 3ème préchauffage de l'air de combustion dans le cyclone de décondensage,
- pour maintenir le réacteur de pyrolyse à la température de réaction,
- pour le 2ème préchauffage de l'air de combustion,
- enfin pour le séchage du bois d'alimentation.

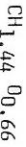
Nous avons établi les bilans matière et énergie pour l'installation décrite ci-dessus pour différents cas caractérisés par un couple de valeurs : température de pyrolyse - humidité du bois. Cette première approche comporte des approximations car un certain nombre de paramètres ne pourront être déterminés que par l'expérience sur le pilote projeté. Néanmoins ces calculs permettent de cerner la zone de travail possible, c'est-à-dire les conditions d'équilibre du système supposé en régime établi. Un modèle plus complet de l'installation est en cours d'élaboration.

Nous donnons ci-après un exemple de ce calcul effectué pour la pyrolyse effectuée à 750°C de bois de hêtre amené à 10 % d'humidité.

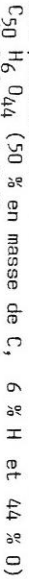
Le tableau de la page suivante donne toutes les valeurs nécessaires aux bilans calculées à partir des données expérimentales. Ce tableau présente les valeurs pour les températures de pyrolyse comprises entre 700 et 900°C par pas de 50°C.

L'ensemble montre la cohérence des résultats expérimentaux sur lesquels il s'appuie. On notera en particulier que la somme des énergies contenues dans le gaz et le "char" conduit à une valeur très proche de celle obtenue pour le bois tant expérimentalement qu'en utilisant la formule de Dulong et Boile. Nous avons calculé par cette formule les pouvoirs calorifiques du bois et du char.

Pour le bois dont la formule réduite (ramenée à 1 atome-gramme de carbone) est :



et la formule pondérale :



La formule de Dulong et Boile :



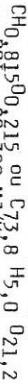
donne

$$\text{PCS} = 19,775 \text{ MJ/Kg}$$

d'où l'on tire :

$$\text{PCI} = 18,457 \text{ MJ/Kg}$$

Pour le char de hêtre pyrolysé à 750°C on a la formule :



qui donne un PCI = 28,389 MJ/Kg

Les calculs de bilans sont menés de la manière suivante :

- 1) On calcule d'abord les débits et température du mélange d'air préchauffé et de fumées de combustion permettant de sécher le bois à la valeur désirée. Pour ne pas commencer la décomposition du bois dans le séchoir, il faut que le gaz chaud ne dépasse pas 250°C. Dans le cas d'un séchage de 50 à 10 % le gaz est admis à 210°C.

HETRE à 10 % d'eau

Soit 1 kg bois sec + 0,1 kg d'eau
1 mole bois + 0,135 mole d'eau
(= 1 at-g de C)

	Température de pyrolyse (en °C)				
	700	750	800	850	900
GAZ					
- Inble de gaz par mole de bois					
CO	0,275	0,300	0,325	0,337	0,349
CO ₂	0,047	0,051	0,055	0,0555	0,052
H ₂	0,077	0,1015	0,126	0,144	0,162
CH ₄	0,079	0,088	0,097	0,0985	0,100
C ₂ H ₆	0,035	0,0375	0,042	0,040	0,038
C ₂ H ₄	0,004	0,0055	0,003	0,0025	0,002
C ₂ H ₂	0,003	0,0045	0,006	0,0085	0,011
H ₂ O produite	0,123	0,112	0,100	0,105	0,105
- Gaz sec					
hote	0,518	0,586	0,654	0,684	0,714
Masse g	12,308	13,527	14,746	15,07	15,394
Volume	0,483	0,547	0,610	0,638	0,666
- Eau de gazéification					
en mole	0,518	0,586	0,654	0,684	0,714
en masse	0,513	0,564	0,614	0,628	0,641
sur le carbone	0,481	0,530	0,579	0,591	0,603
- Energie dans le gaz MJ					
pour 1 mole de bois (24 g)	0,213	0,240	0,268	0,276	0,285
pour 1 kg de bois sec	8,874	10,017	11,156	11,520	11,884
PCI MJ/Mm ³	18,376	18,309	18,289	18,042	17,841
CHAR					
- Hote	0,519	0,470	0,421	0,409	0,397
- Formule	CH _{0,90} O _{0,24}	CH _{0,815} O _{0,215}	CH _{0,73} O _{0,19}	CH _{0,655} O _{0,165}	CH _{0,59} O _{0,14}
- Masse molaire	16,74	16,255	15,77	15,255	14,82
- Masse					
par mole de bois (g)	8,688	7,640	6,639	6,255	5,883
par kg de bois sec (kg)	0,362	0,318	0,277	0,261	0,245
- PCI calculé MJ/kg	27,854	28,389	29,021	29,779	30,545
ENERGIE RECUPEREE (MJ/kg bois)					
- sur gaz	8,874	10,017	11,156	11,520	11,884
(%)	(46,8)	(52,6)	(58,1)	(59,8)	(61,3)
- sur char	10,084	9,029	8,037	7,761	7,489
- Energie totale du bois (PCI)	18,958	19,046	19,193	19,281	19,373

2) On calcule ensuite toutes les valeurs intéressant le réacteur de pyrolyse :

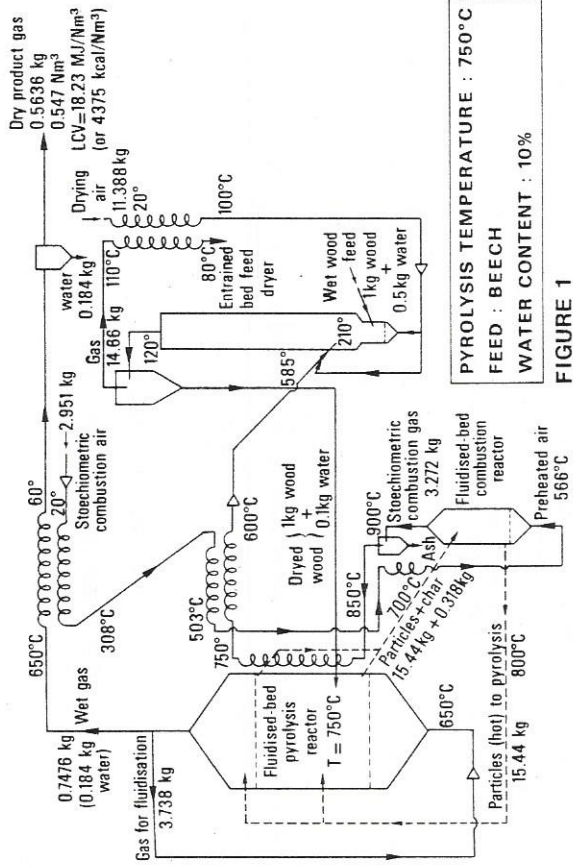
- humidité du gaz produit en tenant compte de l'eau de l'alimentation,
 - chaleur de réaction pour la pyrolyse du bois (par interpolation des valeurs expérimentales)
 - chaleur totale de réaction en tenant compte des contenus calorifiques des réactifs et des produits ainsi que du réchauffage des gaz de fluidisation
 - débit de caloporteur pour couvrir les besoins calorifiques du réacteur de pyrolyse en admettant une chute de température de 100°C pour le caloporteur.
- 3) Puis on calcule les différentes étapes du préchauffage de l'air stoechiométrique de combustion du char.
- 4) Enfin on calcule le bilan de la combustion du char en déterminant d'abord la température théorique de combustion de celui-ci. Puis on vérifie que l'énergie contenue dans le char permet, une fois les besoins calorifiques nécessaires au réchauffage du caloporteur satisfaits, et compte tenu du préchauffage de l'air de combustion, de porter les gaz à une température au moins égale à la température théorique de combustion calculée plus haut. Dans le cas de l'exemple : mètre à 10 % d'eau, température de pyrolyse 750°C, on arrive aux chiffres suivants :

température théorique de combustion : 2 200°C
température possible pour les fumées : 2 255°C

En effectuant ces calculs pour différentes conditions de température de pyrolyse et d'humidité du bois, on peut tracer une courbe frontière dans la représentation : % d'humidité - température de pyrolyse, au-delà de laquelle le système n'est plus autosuffisant en énergie avec les seuls résidus solides de l'opération.

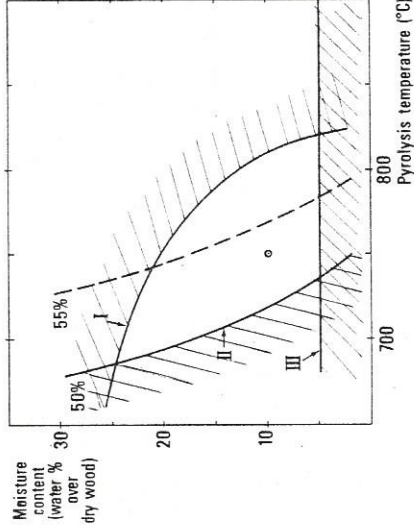
Cette représentation est donnée à la figure 2 bi-après où figurent également la limite pratique de dessiccation du bois (5 %) et une courbe correspondant à une fraction déterminée de l'énergie contenue dans le bois et récupérée dans le gaz. Sur la figure 2 nous avons adopté les valeurs de 50 % en trait plein et 55 % en trait pointillé.

On définit ainsi un domaine de travail où le système trouvera un point d'équilibre, la température de pyrolyse s'ajustant à la teneur en humidité de l'alimentation. Mais il faudra tenir compte des effets rétroactifs des différentes parties du système et c'est ce que nous permettront de vérifier le pilote et le modèle mathématique prévus.



PYROLYSIS TEMPERATURE : 750°C
FEED : BEECH
WATER CONTENT : 10%

FIGURE 1



DETERMINATION
OF OPERATING CONDITIONS

Curves :

I : thermal energy self sufficient upper limit

II : output gas over input feed : % in term of energy (% of energy recovery)

III : practical lower limit of wood moisture content

FIGURE 2

TWO NEW TYPES OF BIOMASS GASIFIERS
DEVELOPED AT C.N.E.E.M.A.

J.F. NOÏLE

Centre National d'Etudes et d'Expérimentations du Mécanisme Agricole
(C.N.E.E.M.A.) FRANCE

Summary

In FRANCE, wood gasification technology was and is still used on an industrial scale since a long time (De Lacotte devices). Its further development was thwarted for economical difficulties. This technology is suited for granular materials. In order to take advantage from other non granular products (straw, sawdust, rice hulls, peanut husks, etc ...) an agglomerating process was necessary but too expensive to be implemented. So, such products are to be used as such. The problem was to be solved from two standpoints :

1. Modernization of packed bed gasifiers for rough products,
2. Development of a suspension bed gasifier for fine products.

These devices are now available on the french market.

The present packed bed gasifier is two times smaller than the older types. Consequently investment costs are reduced. This gasifier is designed so that ashes are carbon free and gases tar free, thus its output is increased and its polluting effect eliminated.

For the suspension bed gasifier (horizontal shaft cyclone) those same problems are solved. The high turbulence generated by gases causing the product to be in suspension, gives rise to very fast mass and heat exchanges, thus gasification reactions are also very fast.

I. INTRODUCTION

In FRANCE, gasifiers and the associated problems are known from a long time and equipment manufactured on an industrial scale have proven their worth (X). The both prevailing De LACOTTE and DUVAULT down draft gasifiers are still sold and allow several gasification systems in the world to be presently running. These systems are fixed bed gasifiers in which wood is not entrained by gas but is fixed. Down draft gasifiers are also sold presently by the IMBERT company in the Federal Republic of GERMANY. Both De LACOTTE and Down draft gasifiers are expensive devices, and cannot process non granular products (straw, sawdust, rice hulls, ..), Problems C.N.E.E.M.A. has been working on for some years.

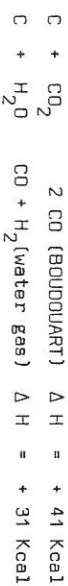
II. GASIFICATION TECHNOLOGIES

The De LACOTTE gasifier (Cf. figure)

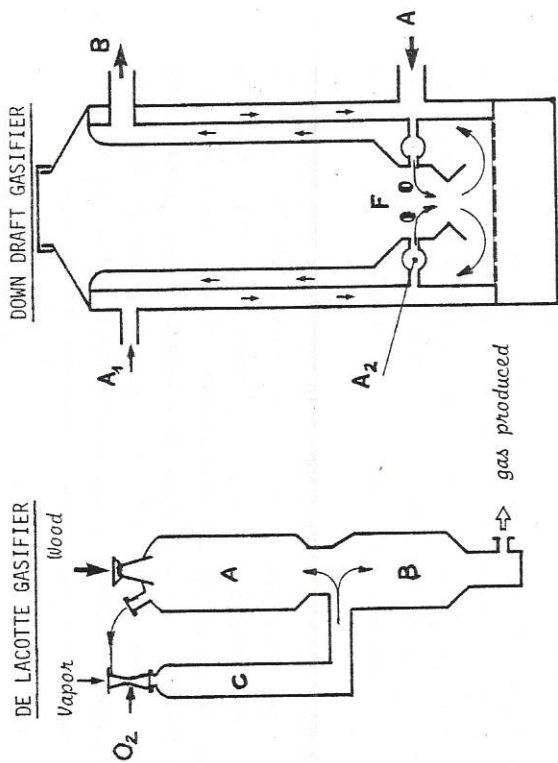
This gasifier which consists of two vessels (A and B) and an important combustor (C) is top fed.

Pyrolysis of wood is made in the upper vessel. Products driven off from pyrolytic process pass to the combustor C in which they burn with oxygen (when synthesis gas is required) or air (when only lean gas is required).

Hot gases (1 000 - 1 100°C) released from combustion flows through the constricted zone between the two vessels, practically following the axis of the gasifier. Consequently gases are well distributed within the wood pile. One quarter of gas released flows up to vessel A and ensures wood pyrolysis, the three quarters left flowing through vessel B. Charcoal produced in vessel A flows down through vessel B where it is gasified according to the following reactions by water vapour and carbon dioxide contained in hot gases.



* Gasifiers used on cars during World War II which were not all properly designed are not returned to here.



A = Main air inlet
 A₁ = Additional air inlet
 A₂ = Heating chambers
 B = Gas outlet
 F = fuel box

It can be drawn from the above-mentioned information that the "prime mover" of gasification comes from heat produced by combustion of part of the wood product; combustion gas heat content is used in endothermic reactions of charcoal gasification (BOUDOUARD and water gas). When gasification begins if the temperature is 0°C (or temperature at which charcoal is gasified by combustion gases) combustion gases give up their sensible heat between 0°C and 600°C, temperature under which gasification process is practically ineffective. This sensible heat quantity reduces the charcoal gasification rate but two solutions which are not incompatible can be implemented for improving this rate.

- 1) Increase temperature of combustion gases.
- 2) Increase the volume of combustion gases passing through charcoal.

The first solution cannot be applied owing to the peculiar characteristics of Wood fuel. At temperatures higher than those above mentioned (1 000 - 1 100°C) i.e. about 1 300°C, ashes become very fluid entailing slag production which hinders running of the unit.

Down draft gasifier (Cf. figure) *

This gasifier is less sophisticated and consist of only one vessel. Gases can only be withdrawn from the base of the unit. They are forced to pass through a constriction in which air supplies create a combustion area. In this area pyrolysis of wood is made as well as cracking or combustion of tars produced. Then charcoal is gasified by hot combustion gases in the conical area formed after the constriction.

The main advantage of this gasifier is its simple design. But for high powers (higher than 500 KW), the diameter of the vessel is important so that air supplied do not reach to produce a flame zone up to the constriction centre. In this way, cracking or combustion of tars is not made and tars can be found in gases produced.

Air is blown at a very high speed in order that a combustion zone could be generated up to the bed centre. Temperature at the air intake level is then very high ("torch effect") reaching about 1 300°C. Matters and gas flowing is hindered under these conditions by ash changing into slag just like the De LACOTTE gasifier when a total gasification is aimed at.

This gasifier is not well suited to an oxygen-blown gasification with a view to produce synthesis gas. On the one hand, temperature reached with an oxygen combustion is very high and to bring down it to 1 300°C, which is the degree reached with air, oxygen has to be diluted with a great deal of water vapour. On the other hand, gasifier sizes required for chemical synthesis units are huge. For example, in the case of a "modest" plant for methanol synthesis producing 500 T/day (plants presently running produce from 1 000 up to

* It's a gasifier diagram of a down draft gasifier for use with trucks during World War II and not a DUVANT gasifier. However the running principle is similar

1 500 T/day), 2.5 Kg of dried wood are required to produce one kilo of methanol. Consequently 500 x 2.5 = 1 250 T i.e. 52 T/h should be gasified.

It's impossible to foresee more than 10 gasifiers which implies that they would have an output of 5 T/h, but presently a down draft gasifier (bigger than those which produce 700 Kg/h of methanol) releasing gases without tars has not yet been developed.

III. C.N.E.E.M.A. RESEARCH WORKS

If the gasification principle is not new, improvements can be made concerning size of gasifiers (and consequently investment) their output (without carbon in ashes and without tars in gases) and their easy operation (problems raised by flowing of solid products - bridging effect- or gases).

Moreover, other products lighter than wood can be processed for example, straw, sawdust, rice hulls, ground nut or coffee husks, etc ... Such residues cannot be processed in a fixed bed gasifier. When they are in deep beds, gases travel along preferential flue shaped passages on account of their low density and resistance to gas flow. As this phenomenon increases, the gasifier cannot go on running. If granulated these residues for use with fixed bed gasifier are too expensive. Two gasifier types taking account of the crop fuel initial granulometry (because modification of granulometry would be too costly) are required as follows :

- Fixed bed gasifiers for wood, coconut husks, maize cobs and more generally for all heavy products with a high granulometry.
- Fluidized bed gasifiers for light and fine products.

Such gasifiers are not yet available on the market.

1) Fixed bed gasifier

a) The De LACOTTE principle consists in burning pyrolysis products in a separate chamber. Gases produced are free from tars. This process is used again.

b) A special heat resisting steel fan has been designed to activate the hot gas circulation in the bed in order to maintain the top column temperature at 600°C. Consequently the new fuel is immediately dip into this atmosphere at 600°C where it is subjected to a thermal shock. Thermal transfers are more rapid with the previous technology (top column temperature at 100°C). Drying and pyrolysis of the product are carried out in a very little sized zone. The total size of the unit is divided by a factor equal to 2 for a same power.

Uncompletely burnt gases from combustion of volatile matters is recycled by a fan on the reacting charcoal. During the gasification process, a quantity of gases, two or three times higher than that of a gasifier without recycling, passes through charcoal. The temperature at which charcoal is gasified by such gases, with a same quantity of calories can be brought down from 1 300°C to 900°C maintaining a complete gasification. At 900°C ashes are not under a melting slag state. Ash fertilizer content (almost all phosphorus and potassium initially contained in the fuel) can be assimilated by crop roots if ashes are recycled.

A horizontal gasifier in which a load of wood is pushed on by a piston has been chosen. Very hot gases can uniformly pass through the entire section of the pile of wood standing at a certain natural angle of rest. There is no problem of material mechanical strength because gases can directly pass through charcoal. Hot gas distribution is easy on the wood pile which remains identical whatever the gasifier width. Very big units can be foreseen. As the De LACOTTE process allows an oxygen blown gasification, the unit is matched to synthesis gas production. With the horizontal design, savings can be made as far as structure, skip hoists, ladders and observation passageways are concerned ... Beside these specifications, this unit runs just like the De LACOTTE gasifier.

A prototype of 200 Kwe allows to prove that this process is fully justified. Running of such prototype has been tested with wood, coconut husks and maize cobs.

The following results were obtained :

- . 1Kg of wood - 10 % moisture content - 3 800 Kcal/kg
- . Gases produced :
 - mean composition CO = 16
 - CO₂ = 12
 - H₂ = 20
 - N₂ = 50
 - CH₄ = 2
- LHV = 1 170 Kcal/Mm³
- Volume = 2,5 Mm³
- . Output $\frac{1\ 170 \times 2,5}{3\ 800} = 0,77$

If such gas production is burnt in a dual-fuel engine the following energy equivalence is :

- 1 Kg of wood with a 10 % moisture content = 1 Kwh

A second prototype of 700KW is presently under investigation (march 1978). Tests will be carried out with urban wastes.

2) PILLARD fluidized bed gasifier

a) Light materials concerned such as chopped straw, sawdust, coffee husks, rice hulls, etc... have a wide range of granulometry. A cyclone type furnace with horizontal axis was used. Whichever the particle size may be, particles are uniformly laid on the wall by centrifugal force, remaining nearly the same time can be processed under the same conditions.

b) Two zones have to be foreseen in this unit, i. e. :

- A zone operating at a mean temperature (500°C) where the crop material is fed. In this zone, a rapid pyrolysis of the product is made.

- At the other end of the unit another zone operates at very high temperatures (1 000°C) owing to air supplies and ensures charcoal gasification as well as tar cracking. The gas withdrawn from the two zones at 600°C is recycled. It allows :

- . The product fluidization (since gasification air would

be insufficient).

. The cold gas supply around flames at the level of air inlet to maintain steel sheets at a low temperature, so that too important stresses are not applied to sheets and ashes do not adhere to them.

Tests were carried out with a prototype of 400KW (Ø 1,2 m l = 2,5 m) by Ets PILLARD at MARSEILLE (FRANCE) since January 1978. Satisfactory results were achieved with straw, rice hulls and coffee husks ; performances look like those above-mentioned for wood material.

Charcoal dust obtained by pyrolysis can be completely gasified. If such dust is pelleted charcoal can be produced from annual crops such as straw or from wastes which can be of interest for many African countries.

c) In fluidized bed gasifiers wood (or other crops) fuels are fluidized by gases, a reaction which entails high speed heat and mass exchanges between fuels. Chemical reactions are faster than with fixed bed gasifiers. These units are more compact.

3) Future of these technologies

It seems particularly attractive for the future to produce from biomass a liquid fuel which can be stored and transported such as methanol. Fertilizers (synthesis of ammoniac) and basic carbonaceous products for chemical industry (hydroliquefaction) can also be derived from biomass.

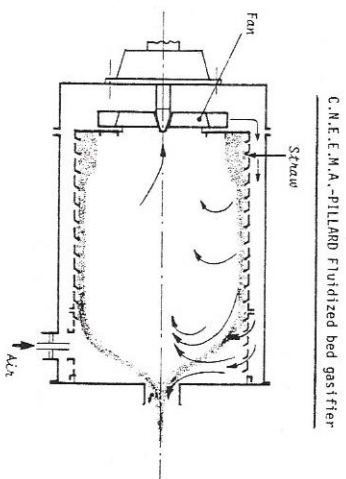
In the two first cases only, gasification of plant materials with a view to produce synthesis gas may require a new approach since further synthesis imply techniques which proved their worth.

Hydroliquefaction consists in changing directly at 250 bars, 300°C, biomass into oil comparable with fuel oil in the presence of a synthesis gas produced from biomass gasification.

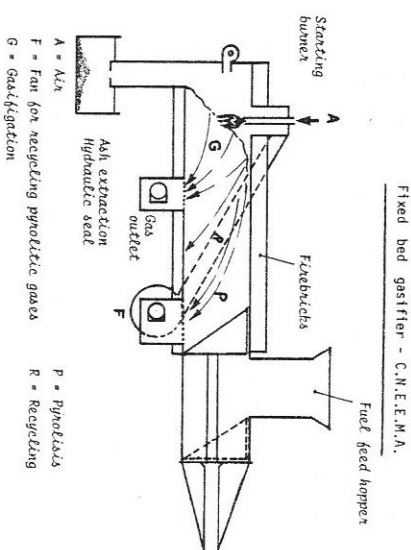
A study carried out by TECHNIP, for C.N.E.E.M.A., and concerned with methanol and ammoniac synthesis from plant material shows that raw material account for half the final cost of methanol (*) or ammoniac.

The importance of a good output of gasifiers which can take advantage of plant materials under the best conditions is underlined.

Such processes were not necessarily cheap with old technologies. It would be interesting presently to have gasifiers, matched to products to be processed, available since there remains the key of many future theories dealing with biomass utilization.



C.N.E.E.M.A.-PILLARD Fluidized bed gasifier



Fixed bed gasifier - C.N.E.E.M.A.

* 100 \$/t in MALI, i. e. the present world rate

KINETIC STUDIES OF PYROLYSIS AND GASIFICATION
OF WOOD UNDER PRESSURE WITH STEAM AND OXYGEN.

A. DIVRY, P. DUBOIS and J.C. RENARD

Laboratoires de Marcoussis, Centre de Recherche de la
Compagnie Générale d'Electricité, 91460-Marcoussis-France

Summary

These kinetic studies are part of the wood gasification programme of the "Compagnie Générale d'Electricité". The general purpose of this programme is the building of plants for methanol synthesis from wood. This programme is conducted by NOVEMBERG and is carried out by "Les Laboratoires de Marcoussis, Centre de Recherches de la Compagnie Générale d'Electricité", "Les Ateliers et Chantiers de Bretagne" and by "CGEP-Alsthom".

The aim of the present studies is to determine wood pyrolysis and gasification parameters which are needed for the design and the operation of a fixed bed gasifier working under pressure with steam, oxygen and partial or total electrical heating.

In this paper we describe an experimental apparatus which has been built to carry out these kinetic studies. This apparatus comprises main four parts : a test vessel fitted with an electrical heater, a steam generator and an oxygen feed, a treatment and measurement device for the output gas and a quench device for gas sampling from the test vessel.

The main parameters which will be measured are the optimal residence times of wood and charcoal in the pyrolysis and gasification zones, the gasification rate and yield and the electrical properties of charcoal pyrolysed at different temperatures.

Every part of the apparatus has been tested and experimental studies are now under progress.

1. INTRODUCTION

These kinetic studies are part of the wood gasification programme of the "Compagnie Générale d'Electricité". The general purpose of this programme is the building of plants for methanol synthesis from wood. This programme is conducted by NOVELERG and is carried out by "Les Laboratoires de Marcoussis, Centre de Recherches de la Compagnie Générale d'Electricité", "Les Ateliers et Chantiers de Bretagne" and by "CGEE-Alsthom".

The aim of the present studies is to determine wood pyrolysis and gasification parameters which are needed for the design and the operation of a fixed bed gasifier working under pressure with steam, oxygen and partial or total electrical heating. The results of these studies will be used to design and to analyse working conditions of a wood gasifier, operating in the 1-20bars range and which will be in operation at Marcoussis by the end of the first term of 1981.

2. EXPERIMENTS

2.1. Apparatus

Figure 1 gives the flow diagram of the apparatus which comprises four parts :

- a test vessel fitted with an inner electrical heater.
- a steam generator and an oxygen feed
- a treatment and measurement device for the output gas.
- a quench device for gas sampling from the test vessel.

A - Test vessel

The test vessel is a room temperature pressure shell fitted with an inner thermal insulation and an inner electrical heater (see figure 2). Wood or charcoal are placed in an inconel basket lined with alumina. Produced gas is collected at the top of the basket and for gasification studies, steam and oxygen are introduced underneath the basket. This vessel is equipped with a safety valve, a gas sampling tube (see-D) and with several thermocouples for gas and wood or charcoal temperature measurements.

B - Steam generator and oxygen feed

Water stored under nitrogen pressure in a stainless-steel vessel is supplied to the evaporator through an electrical flow-meter (see figure 1). The evaporator is held at a temperature higher than the saturation temperature so that the steam flow-rate is equal to the measured flow-rate of

the water.

Oxygen under pressure is heated at a temperature close to the steam temperature and mixed with the steam at the test vessel inlet. Oxygen flow-rate is measured with an electrical flow-meter.

C - Treatment and measurement device for the output gas

At the outlet of the test vessel, gas is cooled down through a water heat-exchanger and flow through a decanter in order to condense non-volatile products. The clean gas flows through an upper pressure regulator and leaves the apparatus at the atmospheric pressure. Pressure and flow-rate of the clean gas are measured, upstream the pressure regulator, with electrical pressure-gauge and flow-meter. In addition, below the pressure regulator, there is a sampling gas device for chromatography composition analysis.

D - Quench device for gaz sampling from the test vessel

The gas sampling tube of the test vessel is connected to a quench device joined it self to a vacuum pump (see figure 1). This device comprises a sampling vessel, in which gas samples are taken at low pressure (a few tens of Torr) and a draining vessel to clean the piping before sampling. A sampling cycle is automatically achieved through electromagnetic-values driven by logical circuit.

2.2. Measured parameters

The following parameters are measured :

- A) - Residence times of wood and charcoal in the pyrolysis and gasification zones as a function of :
 - . the sizes of wood and charcoal logs
 - . the operating pressure
 - . steam and oxygen partial pressures
- Gasification rate and gasification yield as a function of the state of pyrolysis of the wood.

These parameters are determined through the measurements of the flow rate and of the composition of the gas produced at different temperatures between 200°C and 900°C.

- B) Electrical properties of charcoal produced from wood pyrolysed at different temperatures and pressures. The table 1 gives room temperature electrical resistivity of charcoal from different kinds of wood pyrolysed at atmospheric pressure.

Table 1 - Electrical properties of charcoal

Kind of wood	Pyrolysis temperature (°C)	Resistivity at 20°C (Ωcm)		$\frac{\rho_{\perp}}{\rho_{\parallel}}$
		Parallel to the fibre direction, ρ_{\parallel}	Perpendicular to the fibre direction, ρ_{\perp}	
Balata rouge	500	2,86	3,36	1,2
	700	$5,2 \cdot 10^{-2}$	1,82	19,2
AKO	500	$1,35 \cdot 10^5$	$5,95 \cdot 10^5$	4,4
	700	$1,16 \cdot 10^{-1}$	$1,15 \cdot 10^{-1}$	1
Bilinga (Gabon)	500	$1,45 \cdot 10^{-1}$	$4,1 \cdot 10^{-1}$	2,8
Jaboty (Guyanne)	500	$1,34 \cdot 10^{-1}$	$6,5 \cdot 10^{-1}$	4,8
Beech	500	$1,6 \cdot 10^5$	$1,35 \cdot 10^6$	8,4

3. CONCLUSION

The apparatus for kinetic studies of pyrolysis and gasification of wood has been built and every part of it has been tested. Experimental studies are now under progress.

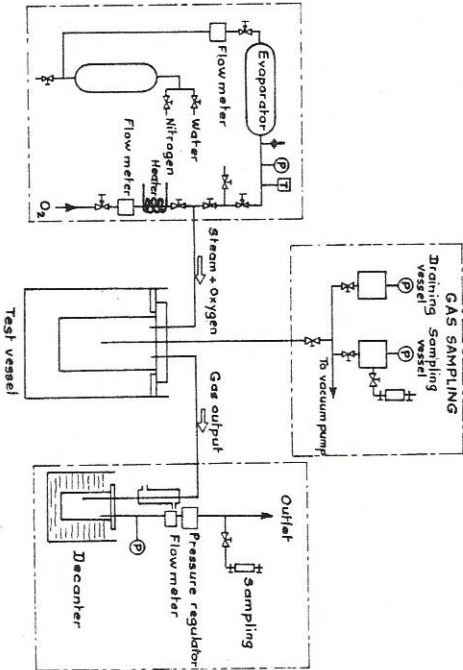


Figure 1: FLOW DIAGRAM OF THE APPARATUS FOR PYROLYSIS AND GASIFICATION KINETIC STUDIES

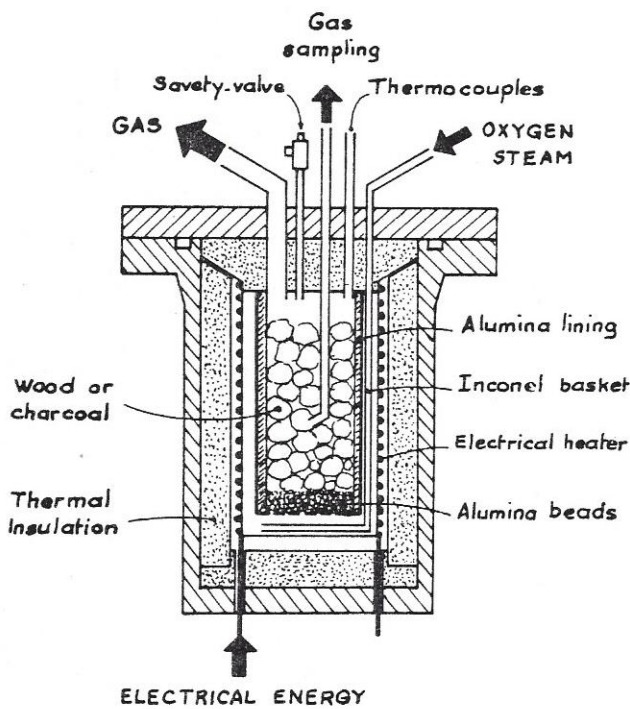
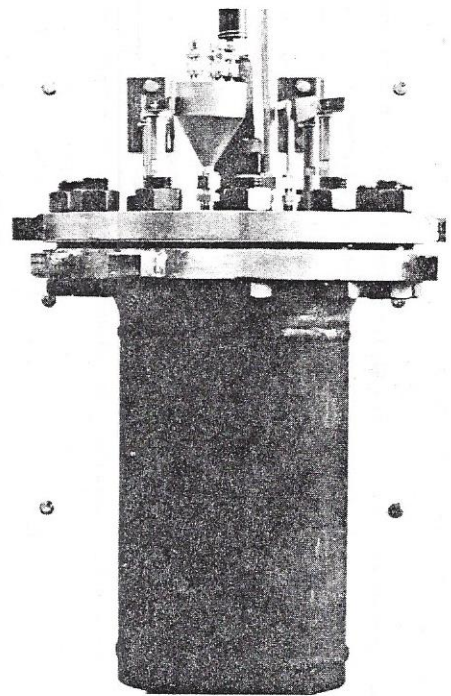


Figure 2: TEST VESSEL



For CREUSOT-LOIRE research on wood gasification is the object of a very large programme. Only a part of it will be funded by the European Communities. All the programme will be described in this paper. The part which is to be sponsored by the European Communities and makes the object of the final report will be described later.

The programme first presented to the European Communities includes four main stages :

Stage 1 : Getting kinetic and thermodynamic data on wood gasification :

This stage includes :

- construction of a laboratory test rig for wood gasification, equipped with oxygen, steam and carbon dioxide feed systems.
- the a priori computation of gaseous balance in terms of the reagent analyses and of the operating conditions;
- the experimental study of wood gasification in terms of temperature and pressure conditions, of the reactive medium analyses and of the size of biomass pieces to be gasified.

Stage 2 : Design and implementation of a fluidized bed gasifier :

The equipment mostly includes a fluid bed gas generator of 400 mm inside diameter.

In order to reach a swift steady load operation, a low thermal inertia unit is to be provided. The gasifier will thus include a steel casing insulated from the outside, equipped at its base with a perforated grate supporting the fluid bed.

The reactor is to be equipped with a sufficient number of temperature probes to allow the establishment of the unit thermal chart.

Pressure probes will allow to check the pressure under and above the fluid bed. By holding the pressure slightly below atmospheric pressure above the fluid bed emission of harmful gas (CO) into the station atmosphere can be avoided.

The fluid bed will be fed with pure oxygen and steam ; injection of CO₂ may be tested.

PROCESS AND EQUIPMENT FOR THE FLUID BED

OXYGEN GASIFICATION OF WOOD

G. CHRYSOSTOME

Engineer - Energy division

CREUSOT-LOIRE

B.P. 31

F - 71208 LE CREUSOT

Summary

The aim of the research is to develop a fluidized bed oxygen gasification of wood. A new process as well as the equipment allowing its implementation are to be developed. The combination of fluidized bed and oxygen allows to obtain a medium B.T.U gas free of any nitrogen. The use of fluidized bed allows to reduce wood preparation and feeding. Sawdust can also be gasified. Due to fluidized bed temperature homogeneity and to the fact that counter flow is avoided the medium B.T.U gas is free of any tar. The research project involves three main stages : 1 - getting kinetic and thermodynamic data with the help of a low thermal inertia research reactor ; 2 - developing and implementing a fluidized bed gasogene that may be fed with wood, bark and sawdust ; 3 - operating a pilot reactor under various operating conditions.

A part of the gas produced by the gasifier will be sent to gas analysers. The most important part will be fired from a special burner into an ancillary combustion chamber in order to avoid any discharge of polluting gas into the atmosphere.

The reactor will be completed with a cyclone and equipped with wood injection systems. The larger wood pieces are to be fed onto the fluid bed by an endless screw system. Sawdust will be sent through a pneumatic conveying system within the fluid bed itself.

All fluid and solid flows are to be metered with appropriate devices.

Stage 3 : Gasifier operation

The main parameters having consequences on the resulting gas analysis which are to be systematically tested are :

- Fluidization gas analysis : $\frac{O_2}{H_2}$ ratio
- fluid bed temperature
- fluidizing velocity
- Influence of the stoichiometric ratio
- dimensions of the pieces of wood

Besides their influence on the resulting gas analysis the effect of such parameters on the rate of elutriation and on the possible tar content is to be examined.

Periodical samplings taken in the bed while the unit is in operation will allow to determine the analysis of the fluid bed. The main purpose of the sampling is to detect any possible enrichment of the fluid bed by alkaline elements.

These elements are liable to entail the sintering of the fluidized bed while in operation on a continuous industrial basis.

Stage 4 : Preliminary project for an industrial unit :

The preliminary project of an industrial unit, the size of which is still to be determined, will allow to estimate the corresponding investment. The cost of the unit plus that of utilities (O_2 , H_2O , etc...) will permit to calculate the price of the resulting gas.

Several hypotheses as to the cost of raw materials, will be considered.

At the request of the F.C. we have shortened the programme to be sponsored :

This programme non includes :

- erection of the fluid bed gasifier.
- experimental study of the ways to introduce the wood into the gasifier.
- Influence of the dimensions of wood pieces on gasification.

At the end of the research the following results are expected to be available :

- ways to introduce the wood into the gasifier : It means out of the bed or into the bed.
- best size of wood pieces : It means pieces of wood or sawdust.

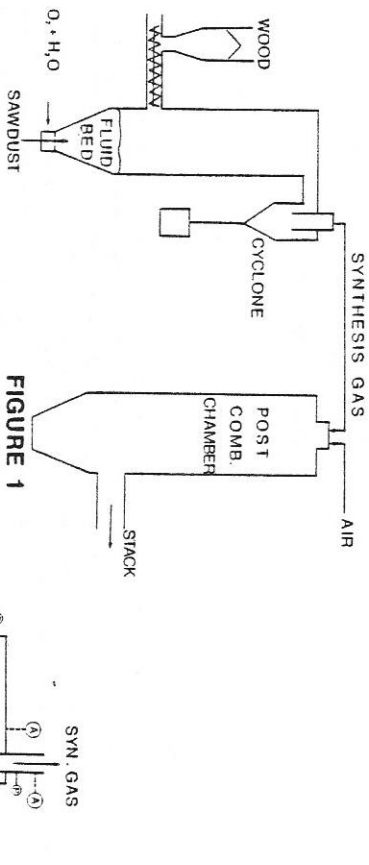


FIGURE 1

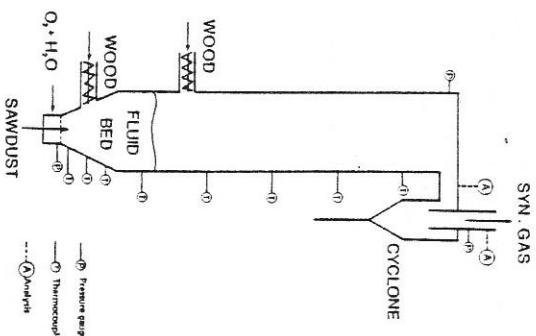


FIGURE 2

PRODUCTION OF A LOW-BTU FUEL GAS BY COCURRENT GASIFICATION OF SOLID WASTES

J.J. Hos, A.A.C.M. Beenackers,

F.G. van den Aarsen and W.P.M. van Svaaij

Twente University of Technology

P.O. Box 217,

Enschede, The Netherlands.

Summary

At Twente University of Technology a research programme is being carried out on the conversion of biomass into a low-Btu fuel gas in cocurrent moving bed gasifiers. The purpose of this programme is to study the suitability of this reactor for the conversion of organic solid wastes into a clean fuel gas.

Important features of the cocurrent moving bed gasifier are:

- a fuel gas free of tar and acids can be produced;
- gasification together with firing of the fuel gas requires low excess air rates;
- the fuel gas can be supplied either to a boiler or to an internal combustion engine;
- the solid waste is exposed to temperatures in between 1000-1600 °C.

Experimental results have been obtained on gasification of wood wastes, maize cobs and municipal solid waste.

Wood wastes such as chips, shredded crates, shavings and sawdust were gasified in reactors with a capacity of 20 - 50 kg of wood waste per hour. The lower heating value of the gas produced was 3000 - 6000 kJ/Nm³, depending on the moisture content of the feedstock.

With respect to wood wastes, the stage of commercialization has been reached. Shelled maize cobs were gasified in reactors with a capacity of 10 kg per hour. The gas was fired successfully in a diesel engine.

Municipal solid waste was gasified to yield a fuel gas with an L.H.V. of 4000 kJ/Nm³. A problem area is the removal of cinderling or slagging residues from the gasifier. Further research will be carried out concerning the application of this gasification process to feedstocks containing components with melting points below 1000 °C.

Existing thermodynamic models were verified and a kinetic model was developed. A new research subject is the development of an omnivorous fluid bed gasifier producing a clean fuel gas.

1. INTRODUCTION

Due to scarcity of energy resources a good deal of attention is paid to the conversion of solid wastes into energy. The most wide spread method to attain this conventional incineration, remains unsatisfactory in many respects. Not only high excess air rates are usual, but also corrosion prevention and meeting the emissivity standards are often problematic. Gasification, defined here as the complete conversion of carbonaceous solids into a combustible gas, is a way out for dealing with these problems, since a fuel gas can be cleaned easily before burning and no high excess air rates are required.

Taking this into consideration and noticing the ever increasing quantities of solid wastes being produced, a research programme on gasification was set up at Twente University of Technology. The cocurrent moving bed reactor was selected, mainly because of its simple construction. In addition the fuel gas produced with this reactor type contains only small amounts of condensable organic matter and also in situ gascleaning was in principle possible.

Initially only wood waste and maize cobs were gasified in reactors having a capacity of 2 - 5 kg of solid waste per hour. About 2.5 Nm³ of dry gas per kg of solid waste with a lower heating value of 5000 kJ/Nm³ was obtained. Later on fundamental research was carried out to develop reaction engineering models for different parts of the gasifier (1). Separate projects were set up to evaluate the utilization of the cocurrent moving bed gasifier with respect to various types of solid waste.

The projects concern gasification of municipal solid waste, coal and the implementation of gasifiers for agricultural wastes in developing countries. In this contribution attention will be paid to the principles of gasification in cocurrent moving bed reactors and to the results achieved with it at Twente University of Technology. More over, new research programmes, recently started at THT will be described briefly.

2. THE COCURRENT MOVING BED GASIFIER

The main part of the reactor is a vertical shaft, in which air and solid waste enter at the top (Fig. 1).

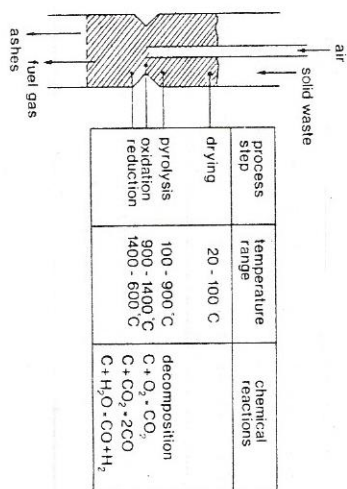


Fig. 1 Principles of concurrent gasification.

Gas and ashes leave the reactor at the bottom. The solid waste is ignited in the narrowest cross section of the reactor very near the place where the air is introduced. In this section partial combustion of the solid matter takes place. The incoming oxygen is rapidly consumed to form char and a steam and carbon dioxide containing gas mixture. This is called the oxidation zone of the gasifier and temperatures are as high as 1500 °C. The heat produced in this zone has two functions. Firstly it brings about drying and thermal decomposition of the solid matter in the pyrolysis zone. Secondly the char below the oxidation zone reacts endothermically with carbon dioxide and steam to form hydrogen and carbon monoxide. This zone is called the reduction zone. As a result the temperature of the gas leaving the gasifier has dropped to 700 °C. The flowrate of the solids through the gasifier is determined by the rate of char conversion and the rate of ash removal. Consequently the air flow rate is an important control variable. The reduction of the cross sectional area of the gasifier and the position of the air inlet tube both are very important factors for the production of a fuel gas which is free of organic condensables produced in the pyrolyses zone (tars). In a well designed gasifier both factors contribute to the formation of flow patterns that prevent pyrolyses products from flowing directly into the reduction zone along the relatively cold wall of the gasifier. Instead all pyrolyses products are forced to pass the area where the highest temperatures prevail and they are completely decomposed. Rules for designing and upscaling the required reactor geometry were developed by Groeneveld (2). The design of a concurrent moving bed gasifier was found

to be strongly dependent on the shape and size of the solid waste to be gasified, as well as its moisture content and inert content (3).

3. EXPERIMENTAL RESULTS

Experiments were carried out with gasifiers ranging in capacity from 2 - 50 kg of solid waste per hour. For detailed descriptions see (3). Woodlocks, chips, maize cobs, shavings and saw dust were gasified in experimental runs from 6 to 8 hours. Shredded M.S.W. was used as M.S.W. as received contains objects too large to be gasified in the present reactors. Data concerning typical experiments are summarized in table I. The efficiency mentioned in this table is defined as the percentage of the lower heat of combustion of the solid waste that is recovered as lower heat of combustion in the fuel gas.

Table I: experimental results.

Solid Waste	Wood, chips	Wood, shavings sawdust	Maize cobs	M.S.W. shredded
Dimensions average (cm)	3	0.5	10	5
Moisture (weight %)	8	9	7.5	5
Exp. time (hr)	6.5	8.0	6.0	2.0
Materials				
IN:				
Solid waste	21.4	17.3	13.0	12.5
Air	42.9	35.0	25.6	29.8
OUT:				
Dry Gas	58.9	46.8	37.7	36.6
Water	5.0	4.3	0.6	4.3
Ash	0.2	0.9	0.2	4.2
Dry Gas composition				
CO	25.4	21.7	18.6	16.7
H ₂	14.2	15.8	14.0	12.4
CO ₂	7.8	9.6	13.9	10.3
N ₂	49.4	50.4	51.5	58.0
CH ₄	1.8	1.7	1.4	1.0
Ar, O ₂	1.2	0.8	0.6	1.5
Energy				
Solid waste (MJ/kg)	17.15	16.87	13.40	12.60
Dry Gas (MJ/kg)	4.75	4.50	3.42	3.22
Efficiency (%)	77	73	74	75

The ashes together with charlines were recovered from the ashchamber and a cyclone, the total weight being 1-5 % of the solid wastes gasified. The amount of tars, char and ashes recovered in the scrubber following the cyclone was about 500 mg/Mm³ fuel gas. After a total of 100 hours of operation it was not yet necessary to clean the piping following the scrubber. Special subjects under investigation are the influence of moisture content

of the feedstock and air preheating on the properties of the fuel gas, removal of slugging or cinderling residues from the reactor and in situ removal of acid gaseous components. Until so far the following conclusions are drawn:

- Solid wastes can be gasified without additional measures if average dimensions are in between 10^{-3} - $5 \cdot 10^{-2}$ m., if the moisture content is below 30 wt. % and if ashes and inert do not form cinderling or slugging residues.
- Drying of the feedstock and preheating of the gasification air considerably increase the heating value of the fuel gas produced.
- Preliminary tests indicate that in situ removal of acid gaseous components should be possible (3).
- Producing a tar free gas is highly dependent on reactor geometry.

An interdependence exists between tar production, solids flow rate and solids diameter (1).

- The main problem area in gasifying M.S.W. is the removal of cinders from the reactor.

- Fuel gas produced from maize cobs can be fired in a diesel engine.
- The lower heating value of the fuel gas was 4000 KJ/Nm^3 and it was operated dual fuel (4).

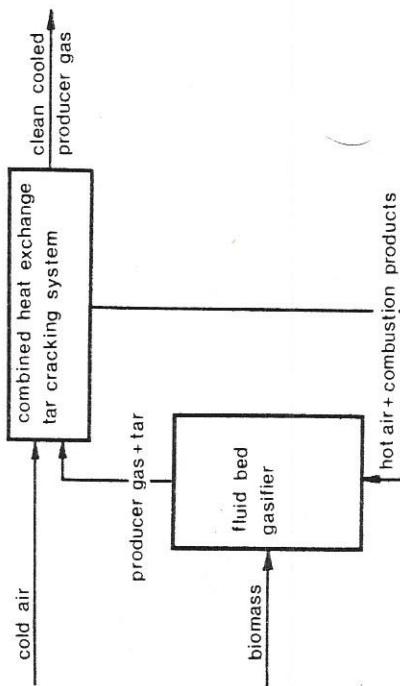
4. FUTURE DEVELOPMENTS

A second generation gasifiers will be developed aiming at better efficiency, less tar, larger feedstock flexibility and higher production capacity per unit reactor volume.

Concerning the cocurrent moving bed gasifier, further research concentrates on the effects of recycling of pyrolysis gases to the feed air, followed by external combustion to realize higher capacities at a similar low level of tar content of the producer gas.

Because some biomass feedstocks are difficult to gasify in moving bed reactors, new research has started in the field of fluidized bed gasification which is expected to be suitable for gasifying any biomass material. Additionally it is expected that with this reactor type very large capacities per unit volume of reactor can be realized

Special attention will be paid to the utilization of waste heat and tars within the process to obtain an omnivorous gasification system that



operates tar free and with a high overall thermal efficiency. The kinetics of gasification in fluidized beds, the mechanism of tar cracking and the modelling of the gasifier will receive special attention.

ACKNOWLEDGEMENTS

This research is sponsored by the Dutch Ministry of Public Health and Environmental Hygiene and by the commission of the European Communities, Directorate General for Research Science and Education. The authors wish to express their gratefulness towards the members of the committees for stimulating our research and towards all co-workers at Twente University.

REFERENCES CITED

1. Groeneveld, M.J. and Van Swaaij, W.P.M. The Design of Co-current Moving Bed Gasifiers fueled by Biomass. Symposium papers ACS "Thermal Conversion of Solid Wastes and Biomass", Washington D.C. (1979), pp. 463-479.
2. Groeneveld, M.J. The cocurrent moving bed gasifier, PhD-Thesis, Twente University of Technology, Netherlands (May 1980).
3. Hos, J.J.; Groeneveld, M.J.; and Van Swaaij, W.P.M. Gasification of organic solid wastes in cocurrent moving bed reactors. Symposium Papers IGT "Energy from biomass and wastes IV", Orlando, (Fla) U.S.A. (1980), pp. 333-351.
4. Stassen, H.E.M. Gasification by partial combustion project in Tanzania, Progress report, Twente University of Technology, Netherlands (July 1980)

