

Lh. 1538

SERI/TP-332-599
UC CATEGORY: UC-59c, 61

CONF-800246--1

426
7-23-80
T.S

MASTER

BIOMASS GASIFICATION:
YESTERDAY, TODAY, AND
TOMORROW

T. B. REED

MARCH 1980

PRESENTED TO THE "ENERGY GENERATION
& COGENERATION FROM WOOD" CONFERENCE
OF THE FOREST PRODUCTS RESEARCH SOCIETY,
ATLANTA, GA., FEBRUARY 18-20, 1980

PREPARED UNDER TASK NO. 3356.40

Solar Energy Research Institute

1536 Cole Boulevard
Golden, Colorado 80401

A Division of Midwest Research Institute

Prepared for the
U.S. Department of Energy
Contract No. EG-77-C-01-4042

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price:

Microfiche \$3.00
Printed Copy \$4.00

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

BIOMASS GASIFICATION: YESTERDAY, TODAY, AND TOMORROW

T. B. Reed
Senior Scientist
Solar Energy Research Institute
Golden, Colo.

Abstract

The solid fuels, biomass and coal, can be converted by gasification into clean gaseous fuels that are easier to distribute and required for many technical processes. The simplest method of conversion is air gasification, producing a low-energy gas well suited for direct-heat or engine applications but unsuitable for pipeline use. Oxygen gasification produces a medium-energy gas composed primarily of CO and H₂, which can be used in industrial pipelines for operation of turbines for power and heat cogeneration or for chemical synthesis of methanol or ammonia. Steam or hydrogen gasification are also possible but external heat and energy sources are required. Slow pyrolysis produces a medium-energy gas, charcoal, and oil. Gases resulting from fast pyrolysis contain a high concentration of olefins (primarily ethylene), which are quite useful for synthesis of fuels or chemicals. This paper presents some of the most pertinent material from the three-volume SERI report, A Survey of Biomass Gasification.

Introduction

The production of fuel gas by pyrolysis and gasification of coal and biomass dates back to about 1800 and has been in widespread use at various times in Europe and in the United States. Coal was used predominantly in large plants to supply city-gas for cooking and lighting, while wood and other biomass forms were used for smaller power generation units, transportation, and agricultural process heat.

As the luxury of low-cost fossil oil and gas disappears, we will return to gasification as a method of supplying clean fuels and as an intermediate step in making the methanol, ammonia, gasoline, methane, ethylene, and other chemicals and fuels used in our present oil-based civilization.

A three-volume Survey of Biomass Gasification has recently been completed at the Solar Energy Research Institute. This paper provides a perspective on biomass gasification based on this survey.

Gasification Routes

The chemical changes required for the conversion of solid feedstocks into gaseous fuels are shown in Fig. 1, a ternary C-H-O composition diagram for fuels and combustion. In this diagram, oxygen is in the lower right corner; combustion of any fuel can be represented by a vector aimed

at this corner. The products of combustion are represented by the vertical line between CO₂ and H₂O. Combustion is complete and flame temperature is maximum at this line. Incomplete combustion is represented by the region to the left of this line, where combustion products still contain some H and CO.

Above about 1000 C, the only stable fuel gas molecules are CO and H₂, therefore, that high-temperature gasification terminates at the line connecting CO and H. However, at lower temperatures methane is thermodynamically stable and ethylene has transient stability, so that the gaseous fuel stability region is extended at lower temperatures toward these molecules.

Compositions to the left of both lines are solid or liquid fuels, and the composition fields of representative samples of biomass, coal, peat, and char are indicated in the diagram. (The dark circle B is the representative biomass composition CH_{1.4}O_{0.6}.)

"Gasification" can be defined as any process that shifts these solid fuels to the gaseous fuel stability region of the diagram. The arrows of Fig. 1 show the possible chemical changes for biomass gasification; similar arrows would indicate the conversion routes for coals, peat, etc. Note that a much greater change in composition is required to convert coal to gas than to convert biomass to a gaseous composition. In addition, coal is typically only 10-40% volatile, whereas biomass is 70-100% volatile, depending on its composition and the means of heating.

Gasification and Pyrolysis Energies

The pyrolysis stages that occur when biomass (or coal) is heated are shown in Fig. 2 along with the temperatures of reaction and the possible mass and heat flow routes. Some or all of these stages occur both at the micro level of each particle and at the macro level of the bulk of the fuel. In designing a gasifier the necessary heat and mass flows for each stage must be provided.

Table 1 shows a set of idealized reactions for the pyrolytic reactions of cellulose and the amounts of energy required per units of input. The energy level changes are shown graphically in Fig. 3. Of course, in most cases it is not possible to pyrolyze to a single product, but these figures can be used to estimate the heat requirement at each stage. Note that the production of gases is endo-

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Table 1. ENERGY CHANGES FOR CELLULOSE THERMAL CONVERSION REACTIONS

| Chemical Reaction | Energy Consumed ^a | | Products | Process |
|---|------------------------------|---------------------|---------------|----------------|
| | ΔH_c (kcal/mole) | ΔH_c (kJ/g) | | |
| 1. $C_6H_{10}O_5 + 6 C + 5 H_2 + 2.5 O_2$ | +229.9 ^b | +5.94 | Elements | Dissociation |
| 2. $C_6H_{10}O_5 + 6 C + 5 H_2O$ | -110.6 | -2.86 | Charcoal | Charring |
| 3. $C_6H_{10}O_5 + 0.8 C_6H_6O + 1.8 H_2O + 1.2 CO_2$ | -80.3 ^c | -2.07 | Pyrolysis oil | Pyrolysis |
| 4. $C_6H_{10}O_5 + 1.2 O_2 + 6 CO + 5 H_2$ | +71.5 | +1.85 | Synthesis gas | Gasification |
| 5. $C_6H_{10}O_5 + 6 H_2 + 6 "CH_2" + 5 H_2O$ | -188.0 ^d | -4.86 | Hydrocarbons | Hydrogenation |
| 6. $C_6H_{10}O_5 + 6 O_2 + 6 CO_2 + 5 H_2O$ | -677.0 | -17.48 | Heat | Combustion |
| 7. $C_6H_{10}O_5 + 2 C_2H_4 + H_2O + 2 CO_2$ | +9.1 | 0.24 | Olefins | Fast pyrolysis |

^a1 kJ/g = 0.239 kcal/g = 430 Btu/lb = 0.860 MBtu/ton.

^bThe negative of the conventional heat of formation calculated for cellulose from the heat of combustion of starch.

^cCalculated from the data for the idealized pyrolysis oil C_6H_6O ($\Delta H_c = -745.9$ kcal/mole, $\Delta H_c = -149.5$ kcal/g).

^dCalculated for an idealized hydrocarbon with $\Delta H_c = -149.6$ kcal/mole. Note H_2 consumed.

thermic, while production of char and oil is exothermic. Slow pyrolysis, which produces a high proportion of char, can be exothermic while fast pyrolysis, producing ethylene, CO, and H_2 , is endothermic. In any case, pyrolysis, including heating to 500 C, requires a heat input typically less than 10% of the heat of combustion of the dry biomass. Wet biomass requires much more processing energy since the water must be driven off before pyrolysis.

Gasification Processes

Slow pyrolysis, indicated in Fig. 1 by the arrow P, is the simplest of the gasification routes, but the biomass energy is distributed among the gas, the oils and tars, and the char. When biomass or coal are heated to about 500 or 800 C, respectively, they disproportionate to these products. The amount of energy involved in this process is typically only a few percent of the heat of combustion of the fuel. Where there are markets for gas, oil, and char, slow pyrolysis is probably the preferred method of biomass conversion. On the other hand, although the energy requirement is low, transferring heat through an opaque mass of solids of low conductivity is difficult. It can be accomplished by recirculation of the pyrolysis gases, or by a minimal combustion of some of the gases; by recirculation of hot solids in a fluidized bed; or by radiant heating of finely divided, suspended solids. The reaction is complete for biomass in the range of 500-600 C; thus, materials problems are minimal, but separation of the volatile tars and oils from the gas is very difficult.

Pyrolytic gasification techniques convert the liquid and solid products of pyrolysis to supply process heat and increase gas yields, often using steam to change the composition toward a gaseous fuel.

Fast pyrolysis (arrow F) minimizes the initial production of char and liquid from biomass and, with rapid quenching, produces large amounts of olefins, particularly ethylene. Olefins have a particularly high value as a feedstock for plastics, polymer gasolines, or alcohols for liquid fuels.

Oxygen/air gasification (arrow O) is the simplest means of obtaining gaseous fuels from solids. Heat is supplied by partial combustion of char to CO, and this gas then provides rapid heat transfer to the remaining feedstock. Because of the high reaction temperatures (typically 1000 C), the resulting gases are rich in CO and H_2 and therefore can be useful for chemical synthesis. If air is used as the source of the oxygen, the nitrogen dilution produces a low-energy gas suitable for immediate combustion but not for synthesis or pipeline use. Gasification with oxygen produces a medium-energy gas suitable for pipeline distribution, turbine operation, or synthesis of methanol, ammonia, or high-energy gas.

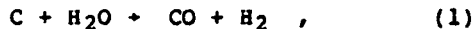
Methods of contact between oxidant and fuel fall into four categories. In an updraft gasifier (Fig. 4), which incorporates the simplest method, oxygen/air/steam contacts a bed of char on a grate, producing CO/CO₂ at high temperatures. This hot gas rises through the hot char, converting the char to CO and H_2 . At the next level the hot gases pyrolyze the incoming biomass, and, finally, at the top of the bed the gases dry the biomass. This counterflow heat exchange produces low-temperature exit gas, but unfortunately this gas is loaded with tars, oils, and water, which can cause problems in combustion unless the gas is burnt directly. About 10 manufacturers in the United States are now making updraft gasifiers.

In a downdraft gasifier (Fig. 5), the incoming gases pyrolyze the biomass and form char at the tuyeres (nozzles). The oily product gas then passes down through the bed of hot char which pyrolyses most of the tars, thus producing a cleaner gas for operation of engines. Over a million of these gasifiers were used during World War II for operation of cars, trucks, tractors, and small power plants. Ten manufacturers in the United States are developing downdraft gasifiers.

Fluidized-bed gasifiers are being developed for biomass (and coal) by several companies. They have potentially higher throughputs and faster pyrolysis rates but may have lower contact times and may provide less complete char removal.

Suspended-flow gasifiers could have the highest pyrolysis rates and thruputs for small-particle feedstocks such as sawdust. One manufacturer is developing this type.

Steam gasification (arrow S) is widely used with coal. A high proportion of char (typically 70-90%) is produced during the pyrolysis step. The cracking of water, where



is highly endothermic; therefore, steam is generally used in conjunction with oxygen to produce a mildly exothermic reaction. In biomass pyrolysis, much less char is produced (typically 0-30%), so that the use of steam is often not warranted; in fact, the pyrolysis gases may supply all the steam necessary. Several groups are developing high-pressure steam biomass gasification.

Hydrogen gasification (arrow H) is attractive if a cheap source of hydrogen is available. High pressures and possibly catalysts are required. Hydrogen is more likely to be used for liquefaction, a process being developed for biomass at a pilot plant in Albany, Oregon.

The Science of Gasification

Gasification was used widely in Europe and the United States during World War II. With the advent of low-cost oil and gas this technology fell into disuse. As a result, the scientific and engineering understanding of gasification is poor. An exception is the research done in Sweden after World War II. The SERI publication "Generator Gas: The Swedish Experience from 1939-1945" makes available this excellent scientific work in English translation (SERI/SP-33-140). The data are limited to downdraft air gasifiers, but an excellent summary of the relevant thermodynamic and kinetic principles is included. Another classic work in the field is "Modern Gas Producers" by N. E. Rambush, published in 1923 (available in microfiche from SERI). This book deals primarily with updraft coal gasifiers but also discusses the scientific principles involved.

Volume II of the SERI Survey of Biomass Gasification makes available additional scientific knowledge relevant to gasification. Included are chapters summarizing current knowledge of pyrolysis reactions, high-temperature thermodynamics and chemical equilibria of biomass reactions, kinetics of gasification reactions, biomass properties relevant to gasification, and the amount of biomass potentially available.

Present Status of Biomass Gasification

Volume III of the SERI Survey of Biomass Gasification assesses the present status

of biomass gasification and offers recommendations for future activities. Producers of gasification equipment and R&D efforts in progress are listed. The authors examine the economics of air gasification, the means used for gas conditioning, and the production of fuels and chemicals from synthesis gas. The institutional role in gasification and specific projects for the future are discussed. This volume will be published in early 1980.

Future of Biomass Gasification

Coal and biomass gasification go hand in hand and each has its place in liquid and gas fuels. Biomass gasification is simpler technically and requires less environmental control; small plants are likely to gasify biomass and large plants will use coal. This technical fit nicely matches the widespread, dilute sources of biomass and the higher energy concentrations of coal deposits.

Air gasifiers for biomass can provide process heat for industries generating biomass waste, such as food and paper processing plants. Air gasification will be the first gasification method to be commercialized because it is most suitable for retrofitting existing boilers and the costs are quite favorable for new installations.

Oxygen gasifiers may play a prominent role in gasification of municipal waste and biomass. A program is in progress at SERI to develop a high-pressure oxygen gasifier for biomass that will produce clean gas with no further scrubbing. It is expected that this gas will find direct use for operation of turbines, for pipeline distribution, and especially for chemical synthesis of methanol and ammonia.

Slow pyrolyzers are particularly simple and economic for production of gas, oil, and char, provided that all of these are needed. Pyrolytic gasifiers that recycle the energy from the oil and char to make gas are more complicated, but a number of groups are developing them.

Fast pyrolysis is particularly attractive because it minimizes oil and char production and maximizes the production of olefins (ethylene, etc.), which are particularly valuable for production of plastics, gasoline, or alcohol. Two programs at SERI are engaged in optimizing experimental conditions for ethylene production.

Summary

Biomass gasification will have wide-scale application because it produces a gas that can be used for process heat in existing gas and oil boilers. Soon it can also be used for production of medium-Btu gas for pipelines, turbine power generation, and chemical and synthetic fuel synthesis.

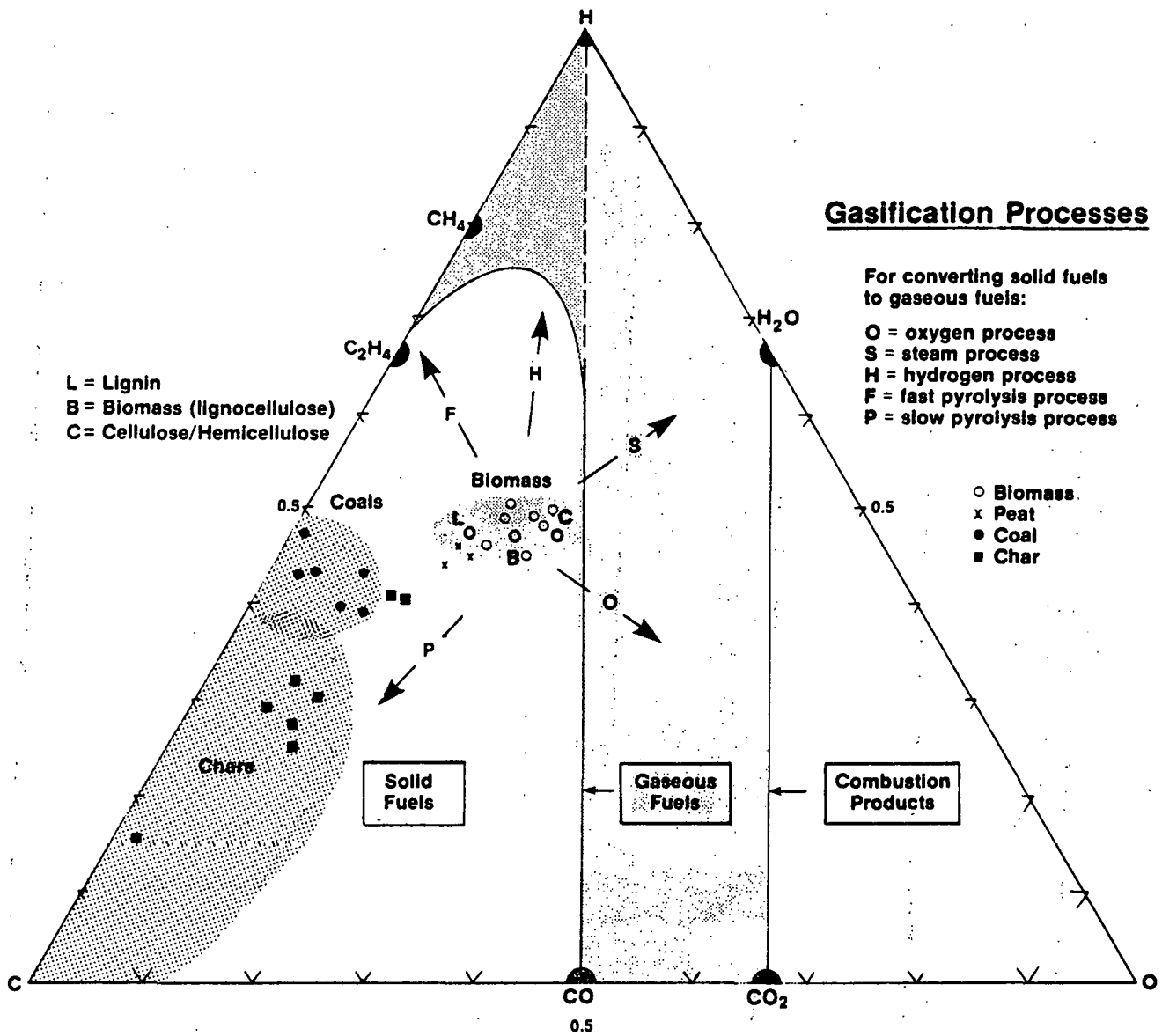


Figure 1. CHEMICAL CHANGES DURING BIOMASS GASIFICATION

| <u>Process:</u> | <u>Drying</u> | <u>Primary Pyrolysis</u> | <u>Secondary Pyrolysis</u> | <u>Char Gasification</u> | <u>Char Combustion</u> |
|-------------------------|---------------|--------------------------|----------------------------|--------------------------|------------------------|
| <u>Temperature (°C)</u> | <120 | 200-600 | 300-800 | 800-1100 | 800-1500 |

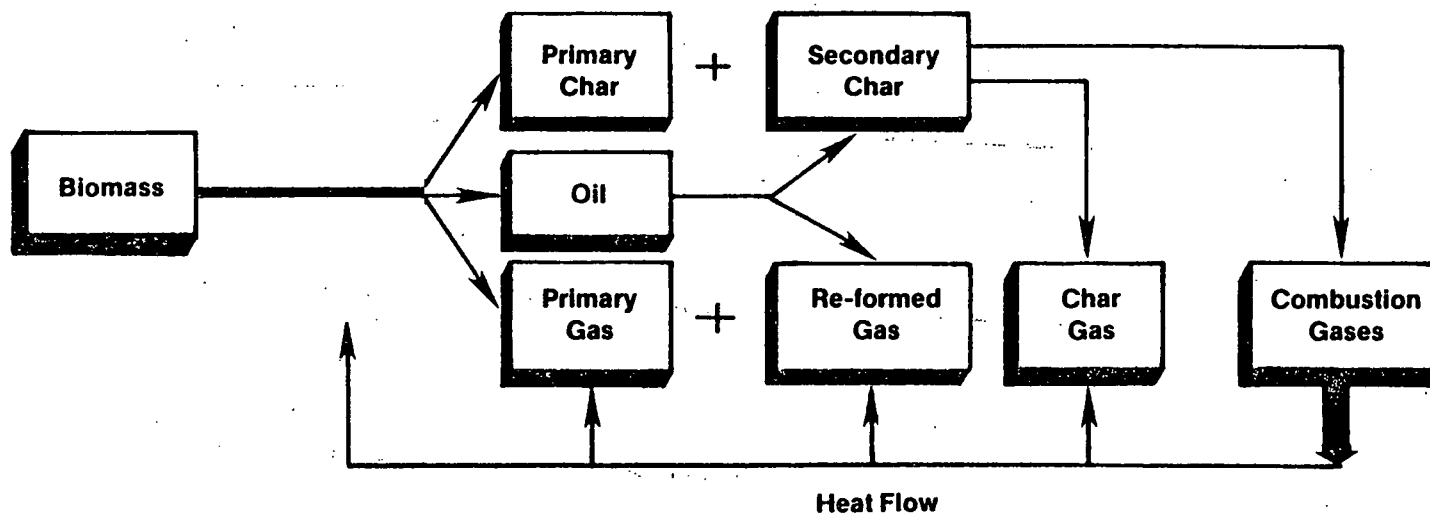


Figure 2. HEAT AND MASS FLOWS IN PYROLYSIS AND GASIFICATION PROCESSES

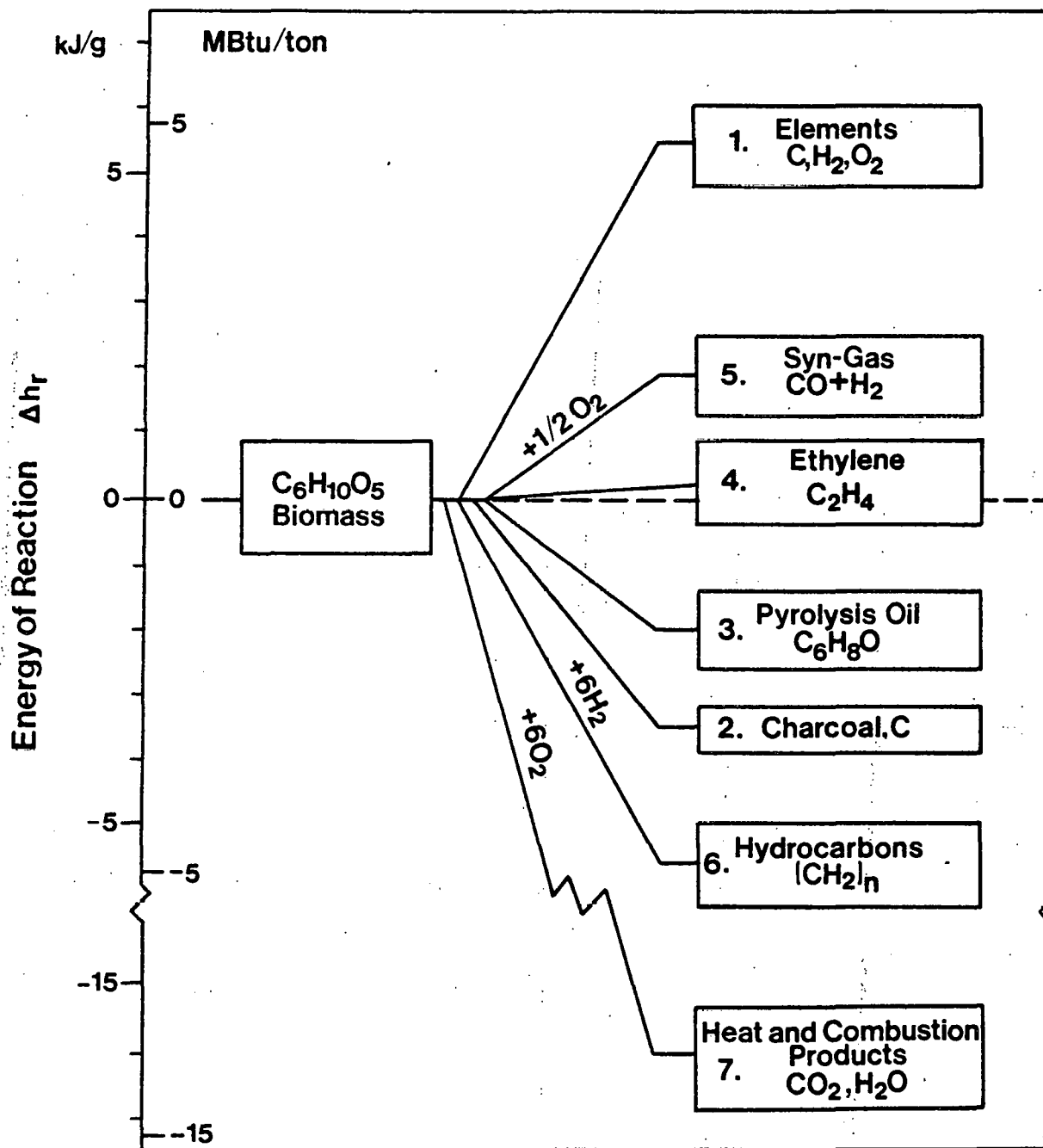


Figure 3. ENERGY CHANGES IN CELLULOSE THERMAL CONVERSION REACTIONS

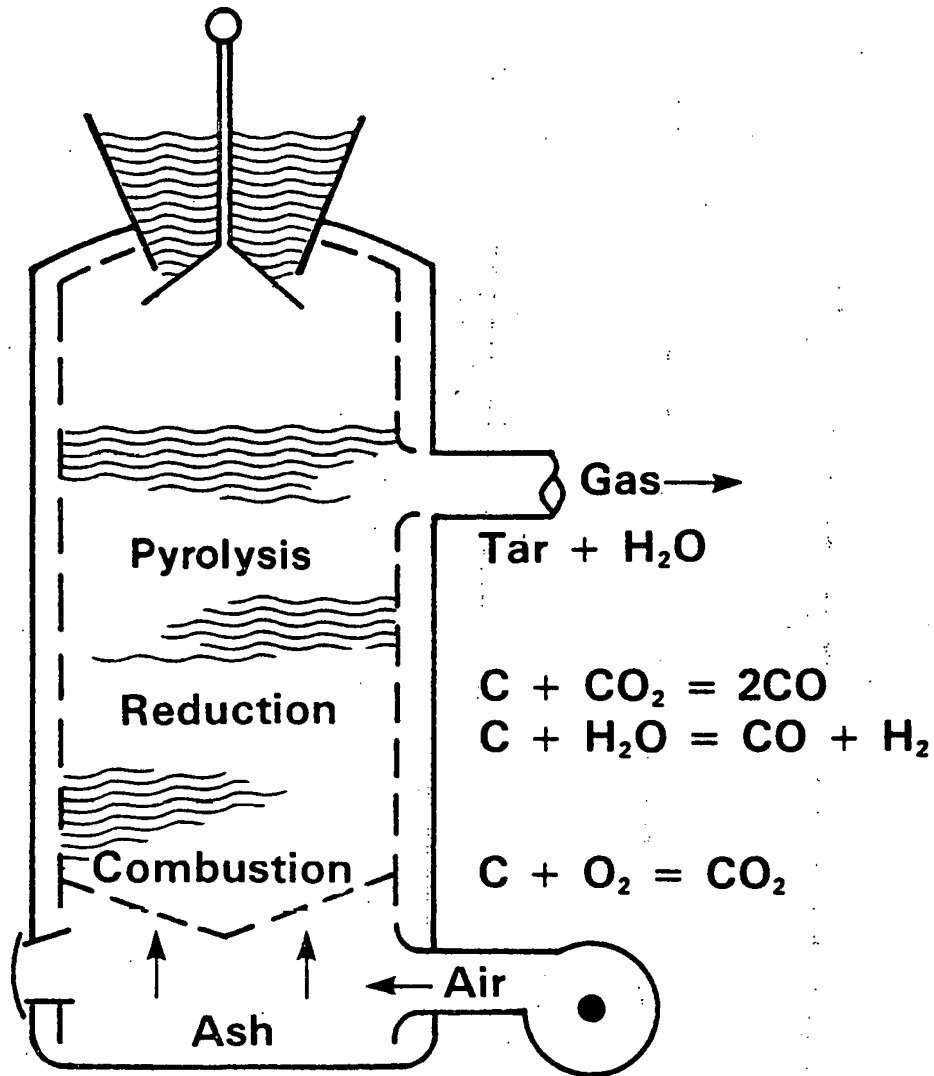


Figure 4. SCHEMATIC DIAGRAM OF UPDRAFT GASIFIER

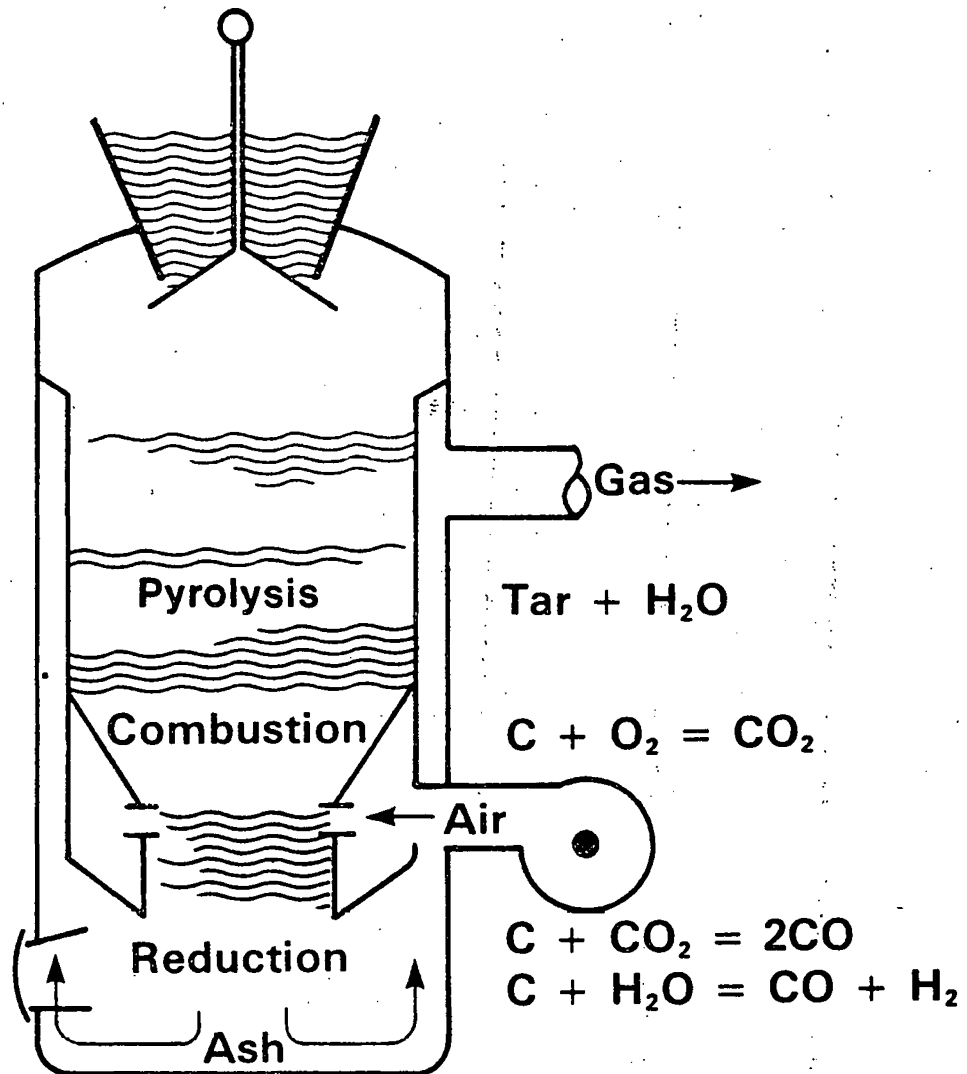


Figure 5. SCHEMATIC DIAGRAM OF DOWNDRAFT GASIFIER