

480  
2/21/80

SERI/TP-332-495  
UC CATEGORY: UC-61,59c

DR. 712

PROBLEMS AND OPPORTUNITIES FOR  
SOLAR ENERGY IN BIOMASS, PYROLYSIS,  
AND GASIFICATION

T. REED

NOVEMBER 1979

**MASTER**

SOLAR FUELS WORKSHOP  
AIRPORT MARINA HOTEL  
ALBUQUERQUE, NEW MEXICO  
28 AND 29 NOVEMBER 1979

SPONSORED BY SOLAR THERMAL TEST  
FACILITIES USERS ASSOCIATION

PREPARED UNDER TASK NO. 3356.20

**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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

## 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~~<sup>5.00</sup>  
Printed Copy ~~\$4.00~~<sup>5.00</sup>

#### 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.

PROBLEMS AND OPPORTUNITIES FOR SOLAR ENERGY  
IN BIOMASS PYROLYSIS AND GASIFICATION

T. Reed

SERI

INTRODUCTION

The need for a continuing supply of liquid and gaseous fuels, as the oil and gas wells run dry, dictates that we must seek out the best and most efficient ways of converting renewable and fossil solid fuels to cleaner-burning liquid and gaseous fuels. One resource that should be explored is the use of direct solar energy to supply process heat for converting biomass rather than using some of the energy in the solid fuel. This would conserve the chemical energy in the solid fuel and extend the supply of solid fuel feedstocks.

We are presently completing a six-hundred page Survey of Biomass Gasification (SERI/TR-33-239, 3 volumes, 1979) as part of our gasification program at SERI, and this paper examines some of the problems of using direct solar heat in place of energy derived from the solid feedstock.

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 shown in the lower right corner; combustion of any fuel can then be represented by a vector aimed at this corner. The products of combustion are represented by the vertical line between  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Combustion is complete and flame temperature maximum at this line. The combustion vector will terminate on this line for complete combustion. Incomplete combustion will terminate to the left, with compositions still containing some  $\text{H}_2$  and  $\text{CO}$ .

Above about 1000 C, the only stable gas molecules under normal conditions are  $\text{CO}$  and  $\text{H}_2$ , so that high-temperature gasification will tend to terminate in the line connecting  $\text{CO}$  and  $\text{H}_2$ . However, at lower temperatures,  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  have at least kinetic stability, so that the gaseous fuel stability region is extended at lower temperatures toward these molecules.

Compositions to the left of these lines are solid or liquid fuels, and the compositions of representative samples of biomass, coal, peat, and char are shown to indicate the composition field of these fuels.

"Gasification" can be defined as any process that converts 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 there is a much greater change in composition required to convert coal to gas than to convert biomass to a gaseous composition. Note, also, that coal is typically

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.

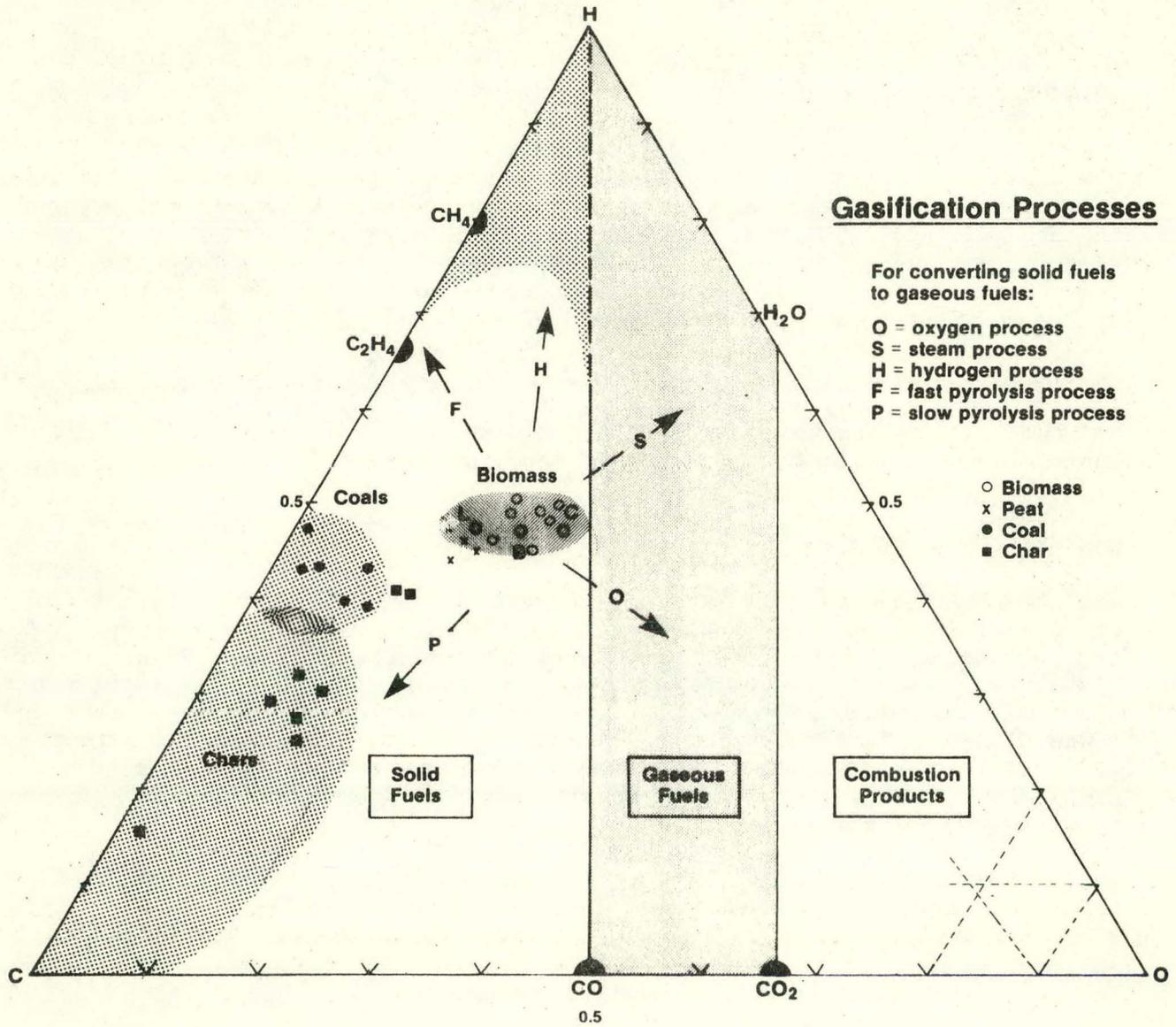


Figure 1. Chemical Changes During Biomass Gasification

only 10-30% volatile, whereas biomass is 70-100% volatile, depending on composition and 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 temperature of reaction and the possible mass and heat flow routes. Some or all of these stages will occur both at the micro level for each particle and at the macro level for the mass of the fuel in all pyrolysis and gasification processes, so that in designing a process it is necessary to provide the necessary heat and mass flow for each stage.

Table 1 shows a set of idealized reactions for the pyrolytic reactions of cellulose and the amount of energy required per unit weight of input, and Fig. 3 shows these heat inputs graphically. Of course, in most cases it is not possible to go to a single product, but these figures can be used to estimate the heat requirement at each stage.

One of the largest heat inputs is for drying (not shown); it is approximately 3-4 MBtu/ton of water removed. Pyrolysis that produces a high proportional char can be exothermic and, in any case, pyrolysis, including heating to 500 C, will require a heat input less than 10% of the heat of combustion of the biomass, i.e., about 1.6 MBtu/dry ton.

### **GASIFICATION PROCESSES**

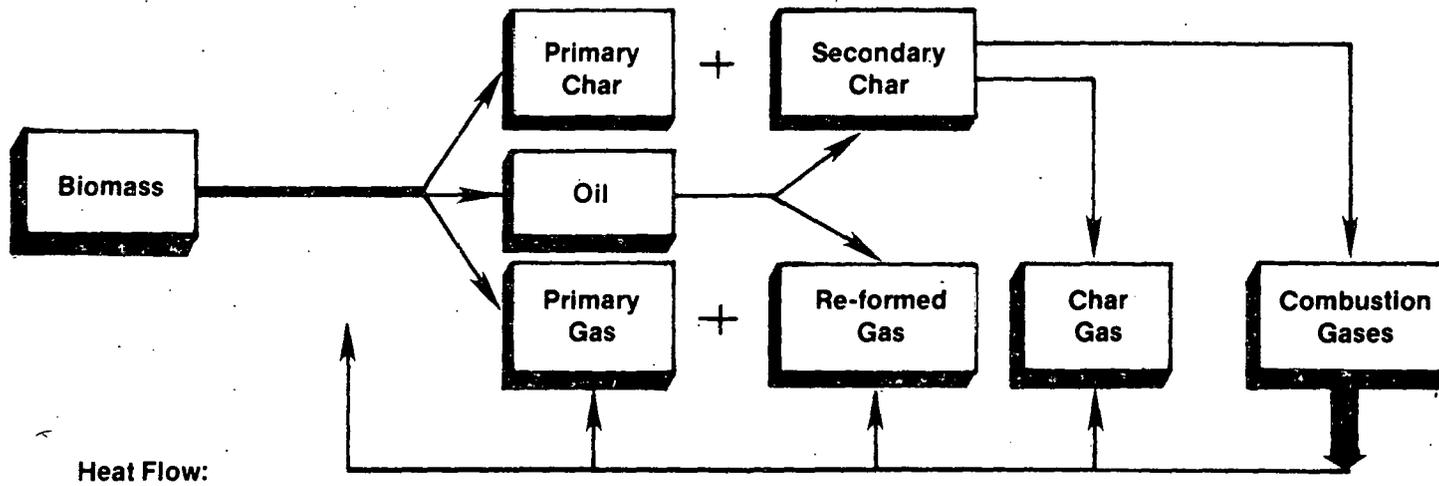
Pyrolysis, indicated by the arrow P, is the simplest of these routes. When biomass or coal are heated to about 500 or 800 C, respectively, they disproportionate to form gases, liquids, and char. The energy involved in this process is typically only a few percent of the heat of combustion of the fuel. Where there are markets for the three products, gas, oil, and char, pyrolysis is probably the preferred method of biomass conversion. On the other hand, although the energy requirement is low, the problem of transferring heat to and 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 will be complete for biomass feeds in the range 500-600 C; for coal at 900 C.

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

Fast Pyrolysis (arrow P) can minimize the initial production of char and liquid from biomass. In addition, it is found that with rapid quenching large amounts of olefins, particularly ethylene, are produced, and olefins have a particularly high value as a feedstock to make plastics, polymer gasolines, or alcohols for liquid fuels.

Oxygen/Air gasification (arrow O) is the simplest means of obtaining gaseous fuels from solids. The heat necessary for the process is supplied by an ini-

Process:	Drying	Primary Pyrolysis	Secondary Pyrolysis	Char Gasification	Char Combination
Temperature (°C)	<120	200-600	300-800	800-1100	800-1500



**Figure 2. Heat and Mass Flows in Pyrolysis and Gasification Processes**

Table 1. ENERGY CHANGE FOR CELLULOSE THERMAL CONVERSION REACTIONS

	Chemical Reaction	Energy Consumed <sup>a</sup>		Products	Process
		$\Delta H_r$ (kcal/m)	$\Delta h_r$ (kJ/g)		
1.	$C_6H_{10}O_5 \rightarrow 6 C + 5 H_2 + 5/2 O_2$	+229.9 <sup>b</sup>	+5.94	Elements	Dissociation
2.	$" \rightarrow 6 C + 5 H_2O$	-110.6	-2.86	Charcoal	Charring
3.	$" \rightarrow 0.8 C_6H_8O + 1.8 H_2O + 1.2 CO_2$	-80.3 <sup>c</sup>	-2.07	Pyrolysis oil	Pyrolysis
4.	$" + 1.2 O_2 \rightarrow 6 CO + 5 H_2$	+71.5	+1.85	Synthesis gas	Gasification
5.	$" + 6 H_2 \rightarrow 6 "CH_2" + 5 H_2O$	-188.0 <sup>d</sup>	-4.86	Hydrocarbons	Hydrogenation
6.	$" + 6 O_2 \rightarrow 6 CO_2 + 5 H_2O$	-677.0	-17.48	Heat	Combustion
7.	$" \rightarrow 2 C_2H_4 + H_2O + 2 CO_2$	+9.1	0.24	Olefins	Fast Pyrolysis

<sup>a</sup> 1 kJ/g = 0.239 kcal/g = 430 Btu/lb = 0.860 MBtu/ton.

<sup>b</sup> The negative of the conventional heat of formation calculated for cellulose from the heat of combustion of starch.

<sup>c</sup> Calculated from the data (3) for the idealized pyrolysis oil  $C_6H_8O$  ( $\Delta H_c = -745.9$  kcal/m,  $\Delta H_f = -149.6$  kcal/g).

<sup>d</sup> Calculated for an idealized hydrocarbon with  $\Delta H_c = -149.6$  kcal/m. Note  $H_2$  consumed.

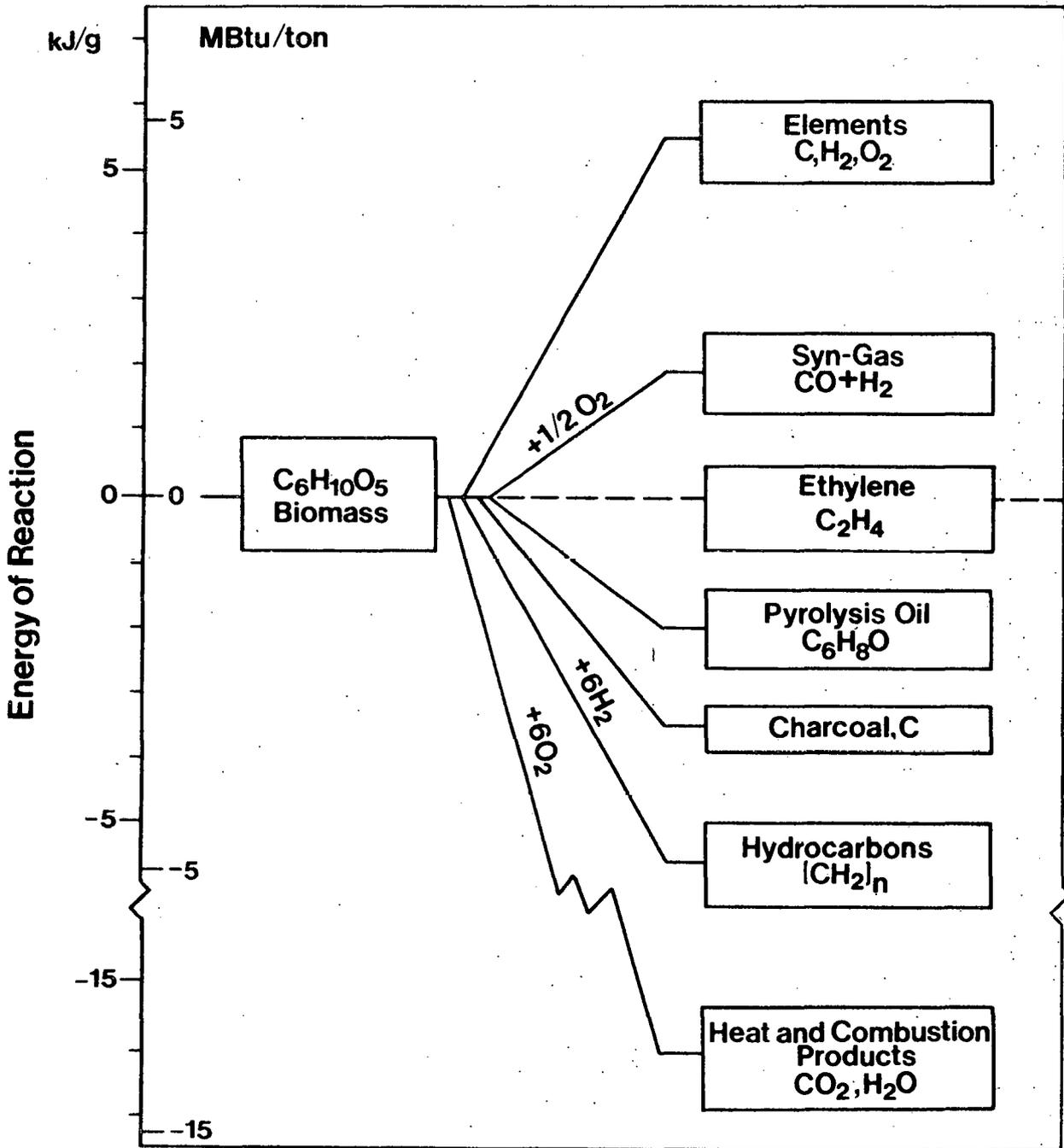


Figure 3. Energy Change in Cellulose Thermal Conversion Reactions

tial combustion of char to CO and CO<sub>2</sub>, and these gases then provide 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<sub>2</sub> and therefore useful for chemical synthesis, provided oxygen is used. Unfortunately, if air is used as the source of the oxygen, the nitrogen dilution produces a low energy gas that is suitable for immediate combustion but not for synthesis or pipeline use.

The method of contact between oxidant and fuel falls into four categories. In an updraft gasifier (Fig. 4), the simplest form, oxygen/air/steam contacts a bed of char on a grate producing CO/CO<sub>2</sub> at high temperatures. This hot gas then passes up through the hot char, converting it to CO and H<sub>2</sub>, then at the next level the hot gases pyrolyse the incoming biomass and finally at the top of the bed they 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 fifteen manufacturers in the U.S. are now making updraft gasifiers.

In a downdraft gasifier (Fig. 5), the incoming gases pyrolyse and form char on first contact at the tuyeres (nozzles), and then the oily product gas passes down through a bed of hot char that 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 U.S. are now developing down-draft gasifiers.

Fluidized bed gasifiers are now being developed for biomass (and coal). Potentially, they have higher thruputs and faster pyrolysis rates, but may have lower contact times and provide less complete char removal. Several companies are now developing fluidized bed gasifiers.

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

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



is highly endothermic, so in general steam is 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) can potentially be attractive if there is a cheap source of hydrogen available. High pressures and possibly catalysts will be required. Hydrogen is more likely to be used for liquefaction and

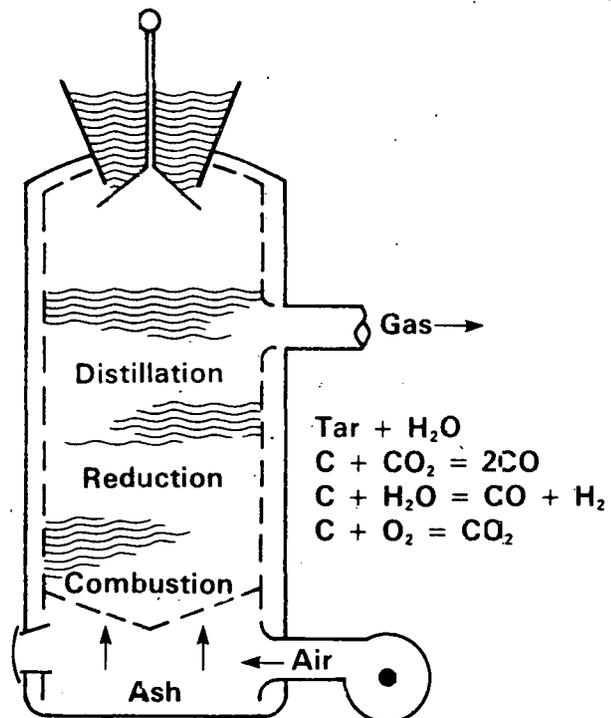


Figure 4. Schematic Diagram of Updraft Gasifier

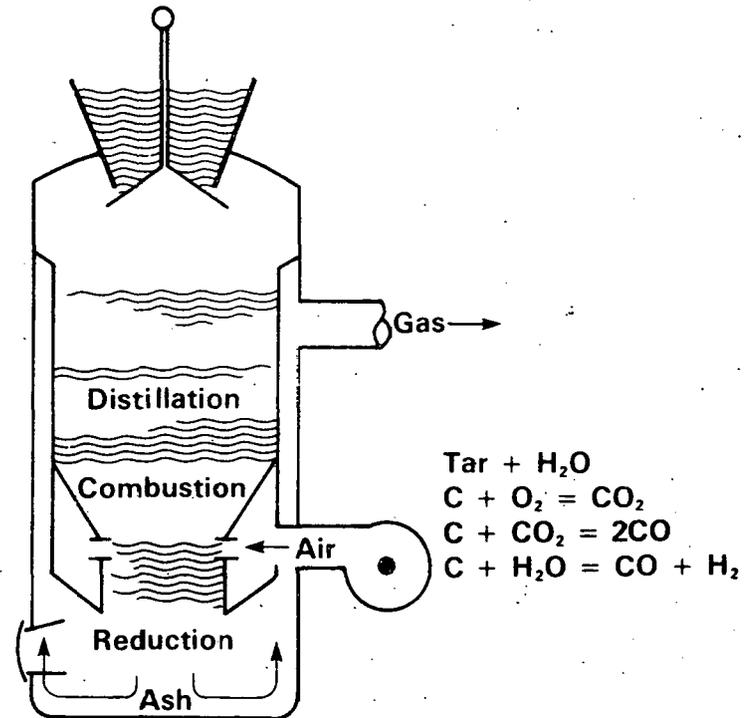


Figure 5. Schematic Diagram of Downdraft Gasifier

this is being developed for biomass at the pilot plant stage in the Albany, Oregon liquefaction process.

### SOLAR HEAT INPUTS FOR PYROLYSIS AND GASIFICATION

In all the processes described above, the heat for the process is derived from the biomass itself, either by direct combustion during the reaction or by separate combustion of the char or waste gases, followed by gas, liquid, or solid heat transfer to the biomass or coal. Combustion of these by-products typically generates temperatures of 1500 C or greater—much higher than required anywhere in the steps of Fig. 2. Although energy is now available at relatively low costs (typically 1-3 \$/MBtu), it is wasteful to use this very high grade chemical energy for process heat if other forms can be substituted. This logic has focused attention on the possible use of solar heat for some or all of the heat inputs of Fig. 2.

The most obvious task for solar heat in biomass or coal conversion is in drying, where temperatures of less than 200 C are adequate. In fact, biomass has always been dried using solar energy before fossil fuel became very cheap. No doubt, solar heat will return as the favored drying method, and direct solar assistance can make a real contribution, as can improved "passive" solar drying techniques such as stack drying of chips, girdling of trees, field crop drying, etc.

Pyrolysis occurs at temperatures of 200-500 C for biomass (and 500-800 for coal) and therefore is the next most accessible area for direct solar input. Since a bed of biomass is opaque, direct solar pyrolysis will require an indirect heating of a gas, liquid, or solid, which in turn will pyrolyse the biomass. Several molten salt or molten metal processes are now under development for biomass pyrolysis and would seem to be potentially able to use a direct solar heat input. A further advantage would be that the molten material could provide at least some storage of this intermediate temperature heat. Several fluidized-bed processes are now under development that externally heat a fluidized bed of inert material, such as sand, that is then used to pyrolyse the biomass. Finally, processes exist in which the pyrolysis gases of the biomass are used as the heat-transfer medium. Either of these approaches could accept a solar input.

The gasification of the char is the most difficult and highest-temperature step in biomass and coal gasification. Char is converted to gas with steam or CO<sub>2</sub>, according to reaction (1) or (2):



Both of these reactions are very endothermic and kinetically slow below about 800 C, so that if the energy is to be supplied from direct solar input, it will have to be supplied at very high temperature, probably requiring point-focus collection, the most expensive form of direct solar conversion. Again, the heat transfer is likely to require an intermediate solid, liquid, or gas, which then contacts the biomass or coal, thus further complicating the process.

**SUMMARY**

Passive solar input for drying crops and wood already make a significant input to the U.S. energy budget, and active solar drying, requiring temperatures below 200 C, can easily make an important substitution for fossil fuels in drying.

Pyrolysis of biomass typically requires less than 1.6 MBtu/dry ton at a temperature of 500 C, and this could potentially be supplied by direct solar heating. The heat input is likely to be by indirect heating of a solid, liquid, or gas heat-transfer agent.

Fast pyrolysis requires modest heat inputs with high heat-transfer rates at temperatures over 900 C and thus may be particularly suited to focusing collectors as energy sources.

Char gasification, using steam or CO<sub>2</sub>, requires large energy inputs at temperatures over 900 C and thus is the least likely field of application of solar energy.

Ultimately, the large-scale application of solar energy to biomass pyrolysis and gasification will depend on the relative cost of direct solar versus biomass inputs. Biomass energy inputs now typically cost 1-3 \$/MBtu; when direct solar heat costs begin to approach this level, we may begin to use direct solar process heat for biomass conversion.\*

---

\*Costs should include prorated investment for solar thermal collectors, provision for storage (since biomass energy will work 24 hours a day), or overdesign of the plant to work only during high insolation, etc.