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Analysis of Magma-Thermal Conversion of Biomass to Gaseous Fuel

Terrence M. Gerlach

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ANALYSIS OF MAGMA-THERMAL CONVERSION OF BIOMASS TO GASEOUS FUEL

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ABSTRACT

A wide range of magma types and pluton geometries believed to occur within the upper 10 km of the crust provide suitable sources of thermal energy for conversion of water-biomass mixtures to higher quality gaseous fuel. Gaseous fuel can be generated within a magma body, within the hot subsolidus margins of a magma body, or within surface reaction vessels heated by thermal energy derived from a magma body.

The composition, amount, and energy content of the fuel gases generated from water-biomass mixtures are not sensitive to the type, age, depth, or temperature of a magma body thermal source. The amount and energy content of the generated fuel is almost entirely a function of the proportion of biomass in the starting mixture. CH_4 is the main gas that can be generated in important quantities by magma thermal energy under most circumstances. CO is never an important fuel product, and H_2 generation is very limited.

The rates at which gaseous fuels can be generated are strongly dependent on magma type. Fuel generation rates for basaltic magmas are at least 2-3 times those for andesitic magmas and 5-6 times those for rhyolitic magmas. The highest fuel generation rates, for any particular magma body, will be achieved at the lowest possible reaction vessel operating temperature that does not cause graphite deposition from the water-biomass starting mixture.

The energy content of the biomass-derived fuels is considerably greater than that consumed in the generation and refinement process.

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INTRODUCTION

The Magma Energy Project was initiated to evaluate the scientific feasibility of obtaining energy from magma bodies and the high temperature margins of magma bodies within the upper 10 km of the Earth's crust (Barr and Zuppero, 1973; Colp et al., 1975; Colp, 1980). Alternative applications of magma energy in addition to the obvious exploitation of magma thermal energy for electric power generation are also under investigation. The alternatives include an interest in utilization of magma resources for production and refinement of fuels (Northrup et al., 1978). New methods for fuel generation and refinement are particularly attractive because the major conventional energy options for the future (coal and nuclear) are better suited for generation of electricity than for producing high quality liquid and gaseous fuels, which are most desirable for meeting certain demands. Fuels are highly versatile energy forms that can be stored, transported efficiently, and used to produce a wide range of important chemicals. Indeed, the most serious aspect of the energy problem in the near term may be the depletion of fuel resources.

Northrup et al. (1978) outline two methods for generating gaseous fuels in high-temperature magmatic environments: (1) H₂ generation by the interaction of water with ferrous iron oxide in magma or very hot rock, and (2) H₂, CH₄, and CO generation by conversion of water-biomass mixtures at high temperatures in magmatic environments. The first method has the advantage of being more than a fuel refinement process, but it also has several potential disadvantages. H₂-generation by this method would be restricted to those magmas with significant FeO contents, such as basalts and andesites. In the western U.S.A., for example, this would tend to rule out many potential shallow magma bodies within the upper 10 km of the continental crust (Smith and Shaw, 1975 and 1979). Water-rock reaction rates at hot rock or glassy surfaces along fractures

formed in the chill-zone around the injection site decrease after a surface reaction product layer forms (Northrup et al., 1978). The thermodynamics and kinetics of the process become less favorable as FeO is progressively oxidized to Fe₂O₃ and as the water cools the reactant glass or rock. Once the H₂ has been generated, the need to collect it represents a formidable engineering task that will be complicated by mass transfer related to water-magma (glass) interactions that will undoubtedly cause the return fluid to be a corrosive brine. It is also probable that some water would be lost to the melt by solution.

The second method proposed by Northrup et al. (1978) is essentially a fuel conversion or refinement process. Raw biomass is itself a fuel, but it can be hydrogenated and converted to more desirable higher quality gaseous fuels at high temperatures in the presence of water. Common cellulose (C₆H₁₀O₅) has been used to model the proposed water-biomass method. Common cellulose consists of 300 to 3000 glucose (C₆H₁₂O₆) units and comprises over 50% of the biosphere where it is a common cell wall and structural component. It is probably the most widespread organic material known (Morrison and Boyd, 1963). At elevated temperatures water and cellulose (biomass) react to produce CH₄ and CO₂:

As temperature increases, H₂ and CO become increasingly important due to a shift of the equilibrium:

The temperature at which H₂ and CO predominate over CH₄ is very sensitive to pressure; it increases sharply as pressure increases. At any temperature and pressure, the maximum amount of CH₄, H₂, and CO that can be generated by these reactions is limited by graphite formation.

The water-biomass method removes several difficulties posed by the water-magma interaction method. Reactions (1) and (2) do not depend on the chemical character of the magma; they only require a source of thermal energy. The water-biomass concept, therefore, allows greater flexibility with regard to magma type and, consequently, to site location than does the water-magma interaction concept. The problems associated with the injection of fluids into and recovery of fluids from magma would be avoided by containing the reactions within a closed-system heat exchanger such as proposed for extraction of heat from magma (Hardee and Larson, 1977; Hardee, 1981; Hardee and Dunn, 1981). The fuel-producing reactions would occur in a super-critical fluid and are expected to be rapid. The thermodynamics of water-biomass mixtures remain favorable to CH_4 generation below temperatures of 300°C , although the kinetics of the pertinent reactions at such low temperatures would probably become less favorable.

Northrup *et al.* (1978) introduced the chemical thermodynamic basis for the concept of gaseous fuel refinement from water-biomass mixtures in magmatic environments at elevated temperatures and pressures. This study examines several details of the concepts application in specific magmatic environments believed to be geologically realistic for the upper 10 km of the crust. The central purposes of this investigation are to understand how various types of upper crustal magma bodies would influence (1) the composition of the refined gaseous fuel, (2) its energy content, and (3) the rate at which it can be generated. It is especially desirable to know which magma bodies would allow generation of H_2 , which has often been proposed as the fuel of the future. Alternative environments for fuel generation, such as the hot subsolidus hydrothermal regions on the margins of cooling magma bodies, are briefly considered. The present study also examines the interplay of those factors that would be important in designing a scheme to optimize fuel generation from biomass in any of the potential magmatic environments.

THERMAL HISTORIES FOR 4 UPPER CRUSTAL MAGMA BODY MODELS

The temperatures of magmatic environments are complicated functions of the ambient geothermal gradient, host rock and pluton permeabilities, rates of hydrothermal fluid circulation, and the depth, size, shape, age, and composition of the emplaced magma body. Meaningful predictions of gaseous fuel generation from water-biomass mixtures in magmatic environments depend upon a knowledge of temperatures and pressures within magma bodies throughout their cooling histories. Unfortunately, no in situ measurements are currently available except for lava lakes.

In recent years there have been several numerical simulation studies of the thermal histories of magma-hydrothermal systems (Norton and Knight, 1977; Norton, 1977; Cathles, 1977; Norton, 1979; Norton and Taylor, 1979; Norton and Cathles, 1979). These models predict the heat and mass transfer consequences of the intrusion of idealized igneous plutons into crustal host rocks, including the effects of pluton size and shape, initial magma temperature (which relates closely to magma composition), host rock permeabilities, and the pressure-temperature dependent properties of water, the main fluid component responsible for heat transfer. The models conserve mass, momentum, and energy. Fluid pressure is computed from Darcy's Law, which is assumed to apply for flow through fractures at the flow rates considered in these models. Heat generated from chemical reactions between migrating fluids and pluton or host rocks can be taken into account. Variable grid spacings can be used to accommodate high surface heat flows. Boundary conditions can be written to allow or prohibit free flow out of the top surface and side boundaries of the computational domain; no flow is allowed out the base. Insulating or constant temperature boundary conditions can be specified.

The numerical simulations indicate that an igneous intrusion inevitably results in fluid circulation if the host rocks are permeable

and water-saturated. Thermal anomalies from igneous intrusions are sufficiently large to generate hydrothermal systems in which convective transport exceeds conductive transport when rock permeabilities are larger than 10^{-18} m^2 (Norton and Knight, 1977). Although in situ rock permeabilities are poorly known, the available data and estimations of rock permeabilities suggest that values greater than 10^{-18} m^2 characterize a substantial portion of the upper crust (Norton and Knapp, 1977). Hydrothermal convective cooling should, therefore, be a common heat transfer mechanism in the cooling of igneous intrusions and exert a strong influence on the length of time magmas can survive in the upper crust.

Models of the kind discussed above provide the only quantitative estimations currently available for the temperatures and fluid pressures in crustal magmatic environments during the cooling histories of igneous plutons. In this study, the results from four such pluton cooling models were used to define the magma "lifetimes" and corresponding temperatures and pressures considered in the gaseous fuel generation calculations. This approach allows the calculated fuel compositions to be related to depths in specific magma body types at various stages of their cooling history.

Four models have been chosen to characterize the range of temperatures and pressures expected above and within igneous intrusions at various stages of their cooling histories. The models will be referred to here as M1, M2, M3, and M4. It is assumed in each case that the rate of emplacement was rapid compared to the rate of heat transfer away from the intrusion into the host rocks. This condition requires magma flow velocities on the order of only a few cm/yr, which seems reasonable (Norton, 1977). Crustal preheating before pluton emplacement and magma replenishment afterwards are not considered in these models. The initial conditions, boundary conditions, and several other details of the models are summarized in Fig. 1 and Table 1.

Figure 1. Model half-spaces, initial conditions, and boundary conditions for (a) M1 (Cathles, 1977), (b) M2 and M3 (Norton and Knight, 1977), and c M4 (Norton, 1977). Additional details are summarized in Table 1 and text.

(a) M1

$$K_{\text{PLUTON}} = 10^{-16} \text{ M}^2 \text{ (SAME AS HOST ROCK)}$$

(b) M2 AND M3

$$K_{\text{PLUTON}} = 10^{-18} \text{ M}^2$$

(c) M4

$$K_{\text{PLUTON}} = \begin{cases} 0 \text{ M}^2 & \text{FOR } 700^\circ\text{C} \geq T \geq 1300^\circ \\ 10^{-17} \text{ M}^2 & \text{FOR } T < 700^\circ\text{C} \end{cases}$$

TABLE 1. Summary of some Characteristics of Pluton Models used in Fuel Calculations

<u>Parameter of Characteristic</u>	<u>M1^a</u>	<u>M2 and M3^b</u>	<u>M4^c</u>
Ambient geothermal gradient	20°C/km	30°C/km	20°C/km
Initial surface temperature	20°C	20°C	20°C
Nature of magma emplacement	Sudden, single event	Sudden, single event	Sudden, single event
Intrusion connected with deep magma reservoir?	No	No	Yes, (first 50,000 yrs only)
Thermal conductivity (water-saturated rocks)	.6 cal/m-sec-°C	.6 cal/m-sec-°C	.6 cal/m-sec-°C
Fluid phase	Pure H ₂ O	Pure H ₂ O	Pure H ₂ O
ΔH of fluid-rock interactions accounted for in model?	Yes	Yes	No
T,P dependence of fluid thermodynamic and transport properties accounted for in model?	Yes	Yes	Yes
Boiling and condensation allowed in mode?	Yes	No	No

a. From Cathles (1977)

b. From Norton and Knight (1977)

c. From Norton (1977)

Model M1 was calculated by Cathles (1977). It is a model for the small pods of magma that are emplaced within the volcanic piles that overlie batholiths and larger plutons from which they probably are derived. These bodies often have rhyolitic compositions and are emplaced at temperatures of at least 650-750°C and depths up to 5 km. M1 is probably most applicable to epizonal plutons like the porphyry plutons of southwestern U.S. and as the primary thermal source for some hot water systems.

Model M2 is the same as model P3 of Norton and Knight (1977). M2 is a model for the plutons that comprise calc-alkaline batholiths such as the Sierra Nevadas. These batholiths are large features of the upper 15 km of the earth's crust, and they form a plutonic foundation beneath volcanic arcs of continental margins. They are composed of hundreds of tonalitic to granitic plutons like M2. Petrologic evidence shows these plutons were emplaced at temperatures of 900-1000°C at depths of 3-15 km. M2-type plutons tend to be sharply bounded by steep contacts against each other and/or metamorphosed sedimentary and volcanic host rocks that separate their upper portions.

Model M3, the same as model P8 of Norton and Knight (1977), applies to an intrusion similar to M2 in composition and emplacement temperature but of batholithic proportions. Norton and Knight (1977) note that the 54 km flat top of the pluton is geologically unreasonable, but M3 does provide an example of an extreme condition that, together with M2, can be used to analyze the thermal history of magmatic bodies of batholithic proportions with broad convex tops.

Model M4 was calculated by Norton (1977) for a basaltic intrusion emplaced at 1300°C into an extensional tectonic environment at a depth of 6-10 km. The zones of extension allow rapid crustal emplacement of high temperature basaltic magmas derived from the upper mantle. Model M4 is meant to be applicable to near vertical basalt intrusions within

extension zones penetrating continental crustal blocks. The model is broadly applicable to environments characterized by basaltic volcanism and crustal extension such as the African rift zones, the Afar triangle, the Tertiary Brito-Arctic province, and the Basin-Range of western U.S.A. Shallow basaltic magma chambers are thought to exist within continental crust, but the data needed to evaluate their frequency and extent of occurrence are currently lacking (Smith and Shaw, 1975). Large expanses of basalt flows do occur in or adjacent to zones of Basin-Range faulting in the western U.S. and show a direct relation to dikes occupying normal faults and functioning as feeder conduits for the basalt floods. The Basin-Range region contains numerous examples of thermal anomalies that may be in part due to the presence of crustal basalt bodies: Long Valley and Imperial Valley of California and numerous localities scattered throughout Nevada, the Intermountain Seismic Belt of Utah, the Yellowstone region, and the Rio Grande Rift.

M4 also applies to some extent to basaltic magma bodies beneath mid-ocean ridges. Basaltic magma bodies are possible at shallow depths under moderately to rapidly spreading ridges because water apparently cannot penetrate close to their hot isothermal upper surfaces (Lister, 1977). Ophiolite suites contain gabbro masses with cumulative structures that could have formed by slow cooling of moderate to large magma bodies in oceanic ridge environments. Convection-conduction cooling models for ocean ridge hydrothermalmagma systems predict temperatures above 1050°C at depths greater than 6-8 km, depending on sea floor crust permeability (Fehn and Cathles, 1979). Models for mid-ocean ridge magma chambers, based largely on geochemical data, indicate they have widths of 4 to 6 km and occupy depths of 4 to 10 km (Hekinian *et al.*, 1976; Bryan and Moore, 1977). These models imply that heat exchangers for fuel generation in the upper portions of such bodies would operate at 800-1000 bars, somewhat below the analogous pressures (1700-2000 bars) for

continental basaltic bodies such as M4. It will be shown below that the amount and composition of fuels generated do not vary greatly in the pressure range 1000 to 2000 bars; therefore, fuel generation in the top portion of M4 provides a useful estimation of expected results for mid-ocean ridge magma chambers.

Figures 2, 3, 4, and 5 summarize the age-depth-temperature relationships for models M1, M2, M3, and M4, respectively. The curves represent temperatures with depth along a line bisecting the pluton. The normal 30°/km geothermal gradient and temperature-depth curves for geothermal wells from the Imperial Valley, Wairakei, and Broadlands (Ellis and Mahon, 1977) have been included for reference. The cooling history time scales are different for each pluton. These differences are in part due to differences in the type of magma, but they are mostly due to contrasting pluton sizes. Small epizonal plutons such as M1 cool in a relatively short time period on the order of 10,000 yrs. The larger plutons considered here may take several hundreds of thousands of years to cool completely. The time periods, temperatures, and depths favorable to the existence of magmatic or near magmatic conditions for each model are summarized in Table 2. Magma "life times" range from as short as 1500 yrs for M1 to as long as 600,000 yrs for M3. It should be mentioned again, however, that these models do not allow for processes of crustal pre-heating by earlier intrusives nor for the replenishment of magma bodies by multiple intrusion. Both of these processes can be expected to occur frequently in regions of high magmatic activity (Smith and Shaw, 1979). The magma "life times" in Table 2 are therefore minimum values. Nevertheless, the models summarized here do underscore the large range of space-time magma targets available for exploitation within the upper crust.

Figure 2. Depth vs temperature for model M1 (Cathles, 1977) at 1000, 5000, and 10000 yrs after emplacement. The $30^{\circ}\text{C}/\text{km}$ normal geothermal gradient and examples of temperatures in geothermal wells from Imperial Valley (I), Wairakei (W), and Broadlands (B) (Ellis and Mahon, 1977) are included for reference.

Figure 3. Depth vs temperature for model M2 (Norton and Knight, 1977) at 20000, 50000, and 100000 yrs after emplacement. The $30^{\circ}\text{C}/\text{km}$ normal geothermal gradient and examples of temperatures in geothermal wells from Imperial Valley (I), Wairakei (W), and Broadlands (B) (Ellis and Mahon, 1977) are included for reference.

Figure 4. Depth vs temperature for model M3 (Norton and Knight, 1977) at 20000, 160000, and 500000 yrs after emplacement. The 30°C/km normal geothermal gradient and examples of temperatures in geothermal wells from Imperial Valley (I), Wairakei (W), and Broadlands (B) (Ellis and Mahon, 1977) are included for reference.

Figure 5. Depth vs temperature for model M4 (Norton, 1977) at 20000, 80000, and 150000 yrs after emplacement. The 30°C/km normal geothermal gradient and examples of temperatures in geothermal wells from Imperial Valley (I), Wairakei (W), and Broadlands (B) (Ellis and Mahon, 1977) are included for reference.

TABLE 2. Conditions for Fuel Generation by Models M1, M2, M3, and M4

<u>Model</u>	<u>Magma T-Range (°C)</u>	<u>Depth (km)</u>	<u>P-Range^a (kbar)</u>	<u>Magma "Lifetime" (yrs)</u>	<u>Heat Xcgr T-Range (°C)</u>
M1	> 650	2.75-5.	.75-1.5	1500	300-500
M2	> 750	4.5-9.	1.2-2.5	60000	300-600
M3	> 750	4.5-9.	1.2-2.5	600000	300-600
M4	> 1050	6.-10.	1.7-2.8	100000	300-900

a. Pressures were estimated from a lithostatic gradient of 275 bars/km based on a mean upper crustal density of 2.8 g/cm³.

FUEL COMPOSITIONS

The reactions causing conversion of the water-biomass mixtures to gaseous fuel species were assumed to occur rapidly compared to the fluid residence time within the heat exchanger. The calculated equilibrium compositions for water-cellulose mixtures were made with a CDC 6600 computer system and software adapted from steepest descent methods (Van Zeggren and Storey, 1970). The standard state thermochemical data for gaseous species were taken from the 1971 JANAF tables and the 1974, 1975, and 1978 supplements of the JANAF tables. The nonideal gas properties were approximated by the ideal mixing model. Measured fugacity coefficients were used for H_2O (Burnham *et al.*, 1969) and H_2 (Shaw and Wones, 1964; Presnall, 1969). The Redlich-Kwing equation was used to calculate the fugacity coefficients for the species CO , CO_2 , and CH_4 (Edmister, 1968).

The gaseous fuel compositions were calculated for starting mixtures containing a fixed wt.% cellulose along the $C_6H_{10}O_5$ - H_2O binary. Graphite saturation was used to limit the proportion of cellulose considered in the starting mixtures.* The range of heat exchanger temperatures and pressures used in the calculations was based on conditions for the models summarized in Table 2. The heat exchanger was allowed to run at temperatures up to within 150° of typical solidus temperatures for the magmas involved. Higher temperatures could of course be used but would result in smaller production rates as will be discussed below. The results for the four models are summarized in Tables 3, 4, and 5. All results in the discussion below (text and tables) are expressed in wt.%.

Favorable conditions for fuel generation could be exploited in magma bodies like M1 (Tables 2 and 3) for at least 1500 yrs after pluton

*Graphite is a potential fuel, but this investigation is restricted to gaseous fuels. Furthermore, graphite deposition in the heat exchanger would be undesirable.

TABLE 3. Fuel Compositions (wt.%) for Model M1

wt.% $C_6H_{10}O_5$:	CH_4			H_2			CO			H_2O			CO_2		
	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30
<u>2.75 km (.75 kbar)</u>															
300°C	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
400°C	2.91	5.89	G	.03	.03	G	.00	.01	G	88.76	77.66	G	8.30	16.42	G
500°C	2.75	5.73	8.72	.11	.10	.09	.02	.05	.07	88.41	77.34	66.28	8.71	16.78	24.84
<u>5 km (1.5 kbar)</u>															
300°C	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
400°C	2.94	G	G	.02	G	G	.00	G	G	88.83	G	G	8.22	G	G
500°C	2.85	5.83	G	.06	.05	G	.02	.03	G	88.63	77.55	G	8.44	16.53	G

G: graphite saturated

TABLE 4. Fuel Compositions (wt.%) for Model M2 and M3

wt.% $C_6H_{10}O_5$	CH_4			H_2			CO			H_2O			CO_2		
	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30
<u>4.5 km (1.2 kbar)</u>															
300°C	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
400°C	2.93	G	G	.02	G	G	.00	G	G	88.81	G	G	8.24	G	G
500°C	2.82	5.80	8.78	.07	.07	.06	.02	.04	.06	88.57	77.50	66.42	8.51	16.60	24.68
600°C	2.58	5.56	8.55	.19	.18	.17	.07	.15	.24	88.05	77.02	66.00	9.10	17.09	25.05
<u>9 km (2.5 kbar)</u>															
300°C	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
400°C	2.95	G	G	.01	G	G	.00	G	G	88.85	G	G	8.18	G	G
500°C	2.90	5.87	G	.04	.03	G	.01	.03	G	88.74	77.65	G	8.32	16.42	G
600°C	2.76	5.74	8.72	.10	.09	.09	.05	.11	.17	88.46	77.40	66.34	8.63	16.66	24.68

G: graphite saturated

TABLE 5. Fuel Compositions (wt.%) for Model M4

wt.% $C_6H_{10}O_5$	CH_4			H_2			CO			H_2O			CO_2		
	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30
<u>6 km (1.7 kbar)</u>															
300°C	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
400°C	2.94	G	G	.01	G	G	.00	G	G	88.83	G	G	8.21	G	G
500°C	2.86	5.84	G	.05	.05	G	.02	.03	G	88.66	77.58	G	8.40	16.50	G
600°C	2.68	5.66	8.64	.14	.13	.12	.06	.13	.20	88.27	77.22	66.19	8.85	16.86	24.85
700°C	2.33	5.30	8.28	.31	.30	.27	.20	.39	.61	87.59	76.59	65.65	9.58	17.43	25.18
800°C	1.83	4.72	7.69	.54	.54	.51	.49	.97	1.50	86.65	75.67	64.88	10.49	18.09	25.43
900°C	1.22	3.91	6.80	.81	.87	.84	1.01	2.05	3.13	85.62	74.55	63.93	11.35	18.61	25.30
<u>10 km (2.8 kbar)</u>															
300°C	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
400°C	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
500°C	2.91	G	G	.03	G	G	.01	G	G	88.75	G	G	8.30	G	G
600°C	2.78	5.76	G	.10	.08	G	.05	.10	G	88.50	77.44	G	8.57	16.62	G
700°C	2.55	5.52	8.50	.20	.19	.18	.15	.30	.47	88.03	77.02	66.04	9.07	16.97	24.82
800°C	2.17	5.10	8.07	.38	.37	.34	.37	.74	1.15	87.33	76.38	65.52	9.75	17.41	24.92
900°C	1.67	4.50	7.42	.60	.61	.58	.78	1.56	2.39	86.47	75.54	64.85	10.48	17.79	24.77

G: graphite saturated

emplacement. For a given water-cellulose mixture, the amounts and compositions of the M1 fuels are nearly constant for the range of heat exchanger temperatures considered over the range of pressures corresponding to depths between 2.75 and 5 km. Methane is the only fuel species of importance for M1. The total fuel concentrations increase approximately 3% for each 10% increment in the cellulose component of the starting mixture: 3% fuel for 10% $C_6H_{10}O_5$, 6% fuel for 20% $C_6H_{10}O_5$, and 9% fuel for 30% $C_6H_{10}O_5$. Graphite deposition prohibits use of 30% $C_6H_{10}O_5$ at temperatures below 500°C. Graphite deposition is unavoidable at any cellulose concentration of 10% or more at temperatures below approximately 300°C.

The results for fuel generation by models M2 and M3 (Table 4) are very similar to those for M1 in spite of the fact that M2 and M3 fuels would be generated at twice greater depths (4.5 to 9.0 km) and at temperatures that could be up to 600°C. Methane is again the only important fuel. Total fuel concentrations continue to show a 3% increase for each 10% increment in the cellulose component of the starting mixture even though the pressures are up to twice those for M1. Conditions leading to graphite deposition follow the same pattern as for M1. There is one factor for models M2 and M3, however, that is significantly different from M1: the period of time favorable to fuel generation after pluton emplacement lasts for 60,000-600,000 yrs for M2 and M3 (Table 2), rather than 1500 yrs as for M1.

Except for a few differences related to higher temperatures and pressures, the results for M4 (Table 5) are also similar to those for M1, M2, and M3. At temperatures above 700°C, however, H_2 and CO can become important fuel species in addition to CH_4 , which begins to decrease with increasing temperatures. H_2 begins to replace CH_4 as the principal fuel gas at 800-900°C; this is not immediately evident from the wt.% data in Table 5 but it follows from the high energy content per gram of H_2 compared to that of CH_4 . Total fuel concentrations again show a 3%

rise with each 10% increase in the cellulose component of the starting mixture even for pressures up to 2.8 kbar. The graphite deposition pattern for the upper portions of the basaltic body is similar to those of M1, M2, and M3, but it becomes a more serious obstacle at the higher pressures in the deeper parts of M4 for heat exchanger temperatures below 500°C.

Alternative Methods

Several calculations were performed to evaluate the fuel-generating potential of heat exchangers operating at 300-600°C in pluton margins at very hot subsolidus-hydrothermal conditions. The results based on M2 are given in Table 6. Fuel compositions and total fuel concentrations are very similar to those for M2 (magma) except for somewhat higher H₂ and CO and slightly lower CH₄. This difference reflects the lower pressures in the heat exchanger, which is now pressurized to the pressures of the fracture-filling hydrothermal fluid instead of the higher more nearly lithostatic pressures in the magma body. The most notable effect of the pressure change is to shrink the stability field of graphite; starting mixtures with 10% C₆H₁₀O₅ are now usable at 300°C. The range of depths available for the subsolidus exploitation at heat exchanger temperatures up to 600°C moves downwards as cooling advances. Typical examples of fuel generation at usable depths corresponding to 20,000, 50,000, and 100,000 yrs after pluton emplacement are given in Table 6. The fluid pressures corresponding to these depths were computed from Cathles's (1977) observation that they follow the normal hydrostatic gradient (100 bars/km) in convective systems if permeability variations are minor to moderate in scale. Resistance to upward fluid flow compensates for the much decreased fluid densities near the hot pluton and increases pressures to levels similar to those for the normal hydrostatic gradient.

TABLE 6.. Fuel Compositions (wt.%) for Model M2 (subsolidus-hydrothermal)

wt.% C ₆ H ₁₀ O ₅ 20,000 yrs 5 km (.5 kbar)	CH ₄			H ₂			CO			H ₂ O			CO ₂		
	10	20	30	10	20	30	10	20	30	10	20	30	10	20	30
300°C	2.96	G	G	.01	G	G	.00	G	G	88.86	G	G	8.18	G	G
400°C	2.88	5.86	G	.04	.04	G	.00	.01	G	88.70	77.61	G	8.37	16.48	G
500°C	2.66	5.65	8.64	.15	.14	.13	.03	.05	.08	88.22	77.16	66.12	8.94	17.02	25.03
600°C	2.23	5.20	8.21	.36	.35	.33	.11	.22	.34	87.30	76.27	65.32	9.99	17.95	25.80
50,000 yrs 6 km (.6 kbar)															
300°C	2.96	G	G	.01	G	G	.00	G	G	88.87	G	G	8.17	G	G
400°C	2.90	5.87	G	.04	.03	G	.00	.01	G	88.73	77.63	G	8.33	16.45	G
500°C	2.70	5.69	8.68	.13	.12	.11	.02	.05	.08	88.31	77.25	66.19	8.83	16.89	24.94
600°C	2.31	5.29	8.29	.32	.31	.29	.10	.20	.32	87.48	76.45	65.49	9.78	17.74	25.62
100,000 yrs 6.5 km (.65 k bar)															
300°C	2.96	G	G	.01	G	G	.00	G	G	88.87	G	G	8.17	G	G
400°C	2.90	5.88	G	.03	.03	G	.00	.01	G	88.74	77.65	G	8.32	16.44	G
500°C	2.72	5.70	8.69	.12	.12	.11	.02	.05	.07	88.35	77.28	66.23	8.79	16.85	24.90
600°C	2.35	5.32	8.33	.31	.30	.27	.10	.20	.31	87.55	76.53	65.56	9.69	17.66	25.54

G: graphite saturated

The final option considered was that of using a fluid to transfer magma heat to a surface reaction vessel containing a water-cellulose mixture. The reactor was assumed to operate at 150 bars for temperatures of 300° to 600°C. Because of the appreciably lower pressures, H₂ yields become important above 500°C, but CH₄ remains the major fuel gas for this configuration (Table 7). Total fuel yields are similar to those discussed above for any given concentration of C₆H₁₀O₅ in the water-cellulose mixture. Graphite deposition is no problem even at temperatures as low as 300°C with up to 40% C₆H₁₀O₅ in the initial mixture.

ENERGY CONTENT

The energy content of the fuel gases and of the steam produced from H₂O-C₆H₁₀O₅ mixtures for the various models discussed above are summarized in Table 8. The energy content tabulated for steam is its enthalpy at the pressure and temperature of interest expressed as calories per gram of the starting mixture. The energy content tabulated for the fuel is the heat of combustion computed for its complete combustion at 1000°C, also expressed as calories per gram of the starting mixture. The 1000°C heats of combustion are 12,000, 30,000, and 2,400 cal/g for CH₄, H₂, and CO, respectively. The contribution of CO to the heats of combustion for the fuel were insignificant in all cases examined here.

The energy content of the gaseous fuel remains nearly constant over the range of temperatures and pressures dictated by the models considered above. It is approximately 360, 725, and 1080 cal/g of starting mixtures containing 10, 20, and 30% C₆H₁₀O₅, respectively (Table 8). The enthalpy of the water always increases with temperature, but it is relatively insensitive to the range of pressures involved here.

To compare the fuel and steam energy contents per unit of starting mixture, let

TABLE 7. Fuel Compositions (wt.%) for a Surface Boiler System (150 bars)

	CH_4			H_2			CO			H_2O			CO_2		
	10	20	40	10	20	40	10	20	40	10	20	40	10	20	40
wt.% $\text{C}_6\text{H}_{10}\text{O}_5$															
300°C	2.92	5.90	12.03	.02	.02	.02	.00	.00	.00	88.79	77.69	55.48	8.26	16.39	32.47
400°C	2.73	5.72	11.87	.12	.11	.09	.01	.01	.03	88.35	77.28	55.16	8.79	16.88	32.85
500°C	2.30	5.28	11.50	.34	.33	.27	.04	.09	.19	87.41	76.36	54.41	9.92	17.95	33.63
600°C	1.60	4.49	10.73	.67	.70	.60	.20	.41	.89	85.95	74.80	53.15	11.57	19.60	34.63

TABLE 8. Energy Content of H₂O-C₆H₁₀O₅ Mixtures (cal/gram of mixture)*

Model	P(bars)	T(°C)	10%C ₆ H ₁₀ O ₅		20%C ₆ H ₁₀ O ₅		30%C ₆ H ₁₀ O ₅	
			Fuel	Steam	Fuel	Steam	Fuel	Steam
M1	750	400	358	387	716	339	G	G
		500	363	514	719	450	1075	385
	1500	400	359	379	G	G	G	G
		500	360	476	715	416	G	G
			$\bar{x}=360$		717		1075	
			$\sigma=2.2$		2.1			
M2 & M3	1200	400	358	380	G	G	G	G
		500	360	481	718	421	1073	361
		600	368	585	725	512	1083	439
	2500	400	357	383	G	G	G	G
		500	360	470	714	411	G	G
		600	362	556	718	486	1077	417
			$\bar{x}=361$		$\bar{x}=719$		1078	
			$\sigma=3.9$		$\sigma=4.6$		5.0	
	1700	400	356	379	G	G	G	G
		500	359	471	717	412	G	G
		600	365	564	721	494	1078	423
		700	377	651	735	569	1089	488
		800	393	729	752	637	1112	546
		900	414	803	779	699	1143	599
	2800	500	358	470	G	G	G	G
		600	365	555	718	486	G	G
		700	370	630	723	552	1085	473
		800	383	707	741	618	1098	530
		900	399	786	760	687	1122	590
M2 (subsolidus) (20000 yrs)	500	300	358	281	G	G	G	G
		400	358	429	715	376	G	G
		500	365	574	721	502	1078	430
		600	373	678	734	592	1092	507
	600 (50000 yrs)	300	358	281	G	G	G	G
		400	360	392	713	343	G	G
		500	363	543	731	475	1077	407
		600	376	659	733	576	1089	493
	1700	400	356	379	G	G	G	G
		500	359	471	717	412	G	G
		600	365	564	721	494	1078	423
		700	377	651	735	569	1089	488
	2800	500	358	470	G	G	G	G
		600	365	555	718	486	G	G
		700	370	630	723	552	1085	473
		800	383	707	741	618	1098	530

Table 8 (Continued)

			10%C ₆ H ₁₀ O ₅		20%C ₆ H ₁₀ O ₅		30%C ₆ H ₁₀ O ₅	
Model	P(bars)	T(°C)	Fuel	Steam	Fuel	Steam	Fuel	Steam
	650 (100000 yrs)	300	358	281	G	G	G	G
		400	357	390	715	341	G	G
		500	363	532	721	465	1077	399
		600	377	650	733	568	1088	487
			$\bar{x}=364$ $\sigma=8.1$		724 8.7		1084 6.9	
Surface Boiler	150	300	356	284	714	247	1450	178
		400	364	625	720	546	1452	390
		500	379	691	735	603	1466	430
		600	398	736	759	640	1489	455
			$\bar{x}=374$ $\sigma=18.5$		732 20.0		1464 18.0	
							40% C ₆ H ₁₀ O ₅	
							Fuel	Steam

G: graphite saturated

*Energy content of "fuel" is the heat of combustion value at 1000°C for the CH₄, H₂, and CO generated from 1 gram of the H₂O-C₆H₁₀O₅ mixture. The energy content for "water" is the enthalpy content of the steam generated from 1 gram of the H₂O-C₆H₁₀O₅ mixture.

$$R_{f/s} = \frac{\Delta H_{fc}}{\Delta H_s} \quad (3)$$

where ΔH_{fc} is the heat of combustion for the fuels and ΔH_s is the enthalpy content of the steam, each expressed as cal/g of the starting mixture for some temperature and pressures of interest. The values of $R_{f/s}$ range from .5 to 1.3 for starting mixtures containing 10% $C_6H_{10}O_5$. At 20 to 30% $C_6H_{10}O_5$, $R_{f/s}$ is between 1 and 3. For surface boilers, where up to 40% $C_6H_{10}O_5$ is permitted, $R_{f/s}$ is between 3 and 8. The larger values for $R_{f/s}$ always occur at lower temperatures in any model for any concentration level of $C_6H_{10}O_5$; this is because of the lower enthalpy content of steam at lower temperatures.

The energy consumed in gaseous fuel generation, ΔH_{fg} , has been estimated based on the assumption that ΔH_{mix} and $\left(\frac{\partial \Delta H_{fg}}{\partial p}\right)_T$ are negligible. Thermodynamic data are not available for $C_6H_{10}O_5$ as such but were estimated from the thermodynamic data of similar compounds (e.g., glucose, cotton, dry plant material (Loomis, 1971)). The calculated values for ΔH_{fg} as a function of temperatures and expressed as cal/g of $C_6H_{10}O_5$ in the starting mixture are given in Table 9. ΔH_{fp} is an estimation of the total heat absorbed in heating the cellulose component, converting it with H_2O to CH_4 and CO_2 by reaction (1) and heating these products to the temperature of interest. The magnitude of ΔH_{fg} relative to ΔH_{fc} , the heat of combustion value of the fuel produced, can be expressed by the ratio

$$R_{c/g} = \frac{\Delta H_{fc}}{\Delta H_{fg}} \quad (4)$$

For a given fuel generation temperature, the values of $R_{c/g}$ are nearly constant for all models and $C_6H_{10}O_5$ concentration levels. They range from 11 to 12 at 300-400°C to 6 to 7 at 900°C. ΔH_{fg} should also contain some measure of the energy required to grow, harvest, collect,

TABLE 9. Energy Consumed in Production of Fuel (ΔH_{fg}) from $H_2O-C_6H_{10}O_5$ mixtures (cal/g $C_6H_{10}O_5$)

$T(^{\circ}C)$	ΔH_{fg} (cal/g $C_6H_{10}O_5$)
300	270
400	310
500	360
600	410
700	470
800	520
900	580

and transport the biomass and to prepare the starting mixture. The large values for R_c/g would seem to leave a comfortable margin for these currently unknown quantities.

The ΔH_{fc} values for fuels generated from $C_6H_{10}O_5$ were also compared with the ΔH combustion for the same amount of raw $C_6H_{10}O_5$. The heat of combustion for $C_6H_{10}O_5$ was estimated from that of cotton (which is nearly 100% $C_6H_{10}O_5$) and other similar substances such as dry wood and bagasse; it is approximately 4000 cal/g (Loomis, 1971). The ΔH_{fc} of the fuel produced is about 3600-3800 cal/g of $C_6H_{10}O_5$ used in the generation process. The additional "refinement cost" of 200-400 cal is largely due to oxidation of some carbon in the cellulose to CO_2 by H_2O during the conversion process.

RATES OF GASEOUS FUEL GENERATION

The heat transfer rate (q_e) per unit surface of a heat exchanger in a magma body is given by

$$q_e = q_o (r_o/r_e) \quad (5)$$

where r_e is the heat exchanger radius, r_o is the radius of the heat exchanger plus the solidified crust surrounding it, and q_o is the heat transfer rate into the heat exchanger crust under steady-state conditions (Hardee, 1981). The ratio r_o/r_e can be calculated from

$$\frac{r_o}{r_e} \ln \frac{r_o}{r_e} = \frac{K(T_o - T_e)}{r_e q_o} \quad (6)$$

where K is the thermal conductivity of the heat exchanger crust, T_o is the solidus temperature of the magma, and T_e is the heat exchanger operating temperature (Hardee, 1981). Given q_e from (5), the total heat extracted by the heat exchanger (Q) is

$$Q = A q_e \quad (7)$$

where A is the surface area of the heat exchanger.

The fuel generation rates were calculated by first solving (6) for r_o/r_e , using T_o and q_o values appropriate for magmas corresponding to M1, M2, M3, and M4 models and assuming heat exchanger operating temperatures (T_e) from 400°C to within 150° of T_o . These results were used to compute q_e and Q from (5) and (7). The total steam extraction rate (Q_s) was computed from the relationship

$$Q_s = \left(\frac{\Delta H_s}{\Delta H_s + \Delta H_{fg}} \right) Q \quad (8)$$

The gaseous fuel generation rate (Q_f) was then obtained from

$$Q_f = R_{f/s} Q_s \quad (9)$$

The data for the parameters in the calculation of gaseous fuel generation rates were taken from Hardee (1981):

Thermal conductivity	K	2.98 W/m°C
Radius heat exchanger	r_e	25 cm
Length heat exchanger	L	1000 m
Area heat exchanger	A	1571 m ²
Magma solidus temperature	T_o	650°C (rhyolite, M1) 750°C (andesite-dacite, M2 & M3) 1050°C (basalt, M4)
Magma heat transfer rate	q_o	1 kW/m ² (rhyolite, M1) 3.5 kW/m ² (andesite-dacite, M2 & M3) 7.6 kW/m ² (basalt, M4)

Data for ΔH_s , $R_{f/s}$, and ΔH_{fg} were obtained from Tables 8 and 9.

Table 10 is a summary of the rates of heat extraction and fuel conversion for heat exchangers in the top portions of M1, M2, M3, and M4 magma systems. The table shows the heat transferred to the heat exchanger (Q) for various heat exchanger temperatures (T_e). The heat extracted as steam (Q_s) and the gaseous fuel generation rate (Q_f) are shown as

a function of heat exchanger operating temperature (T_e) and the proportion $C_6H_{10}O_5$ is the starting mixture. The rate of energy consumption for converting raw biomass to gaseous fuels is equal to the difference between Q and Q_s .

All of the extraction rates presented in Table 10 are sensitive to the parameter q_0 , the magma heat transfer rate to the heat exchanger crust. The values used were taken from Table 2 of Hardee (1981) and chosen to be representative of rhyolitic (M1), andesitic-dacitic (M2 and M3), and basaltic (M4) magma. The values chosen introduce a conservative bias because they correspond to the case of laminar flow in the convecting magma. Hardee (1981) argues that the possibility of turbulent flow although marginal for rhyolitic and andesitic magma is strongly favored for basaltic magmas. Hence the extraction rates for models M4 and possibly M2 and M3 may be too small by a factor of 2 to 3.

Regardless of the uncertainties surrounding the precise value of the parameter q_0 , it is obvious that any set of reasonably chosen values will show that the rates of fuel generation are highest for basaltic magmas (M4), intermediate for andesite-latitude magmas (M2 and M3), and lowest for rhyolitic magmas (M1). These differences are due to differences in magma solidus temperatures (T_0) and in magma viscosities, which have a strong effect on the magma heat transfer term (q_0). It is also evident that the highest fuel generation rates will be achieved for a particular water-cellulose mixture in a given magmatic regime by operating the heat exchanger at the lowest possible temperature that avoids graphite deposition; this procedure maximizes the term $(T_0 - T_e)$ in (6).

CONCLUSIONS

There are numerous economic and technical details surrounding the concept of gaseous fuel generation by magma-thermal conversion of biomass that require specialized investigations. The present analysis serves to

Table 10. Heat extraction and fuel conversion rates (MW) for heat exchangers with a 25 cm radius and 1000 m length installed in the upper portions of magma systems M1, M2, M3, and M4.

<u>Te(°C)</u>	<u>Q</u>	10% C ₆ H ₁₀ O ₅		20% C ₆ H ₁₀ O ₅		30% C ₆ H ₁₀ O ₅	
		Q _S	Q _f	Q _S	Q _f	Q _S	Q _f
<u>M1</u>							
400	4.4	4.1	3.8	3.8	7.9		G
500	2.8	2.6	1.8	2.4	3.8	2.2	6.0
<u>M2, M3</u>							
400	10.3	9.5	9.0		G		G
500	9.1	8.5	6.4	7.8	13.3	7.0	20.9
600	5.0	4.7	2.9	4.3	6.1	3.9	9.6
700	4.1	3.8	2.2	3.5	4.4	3.2	6.9
<u>M4</u>							
400	21.0	19.4	18.4		G		G
500	19.8	18.4	14.0	16.9	29.3		G
600	18.8	17.6	11.4	16.2	23.6	14.6	37.2
700	17.3	16.1	9.3	14.8	19.1	13.4	29.9
800	15.8	14.8	8.0	13.6	16.1	12.3	25.1
900	14.4	13.4	6.9	12.3	13.7	11.1	21.2

G: graphite saturated

examine the overall scientific basis of the concept, to sharpen in a quantitative way various implications inherent in it, and to predict the sensitivities of the fuel generation process to parameter variations.

There are ample options for generating gaseous fuels from water-biomass conversion with magma-thermal energy. A wide range of magma types and pluton styles believed to occur within the upper 10 km of the crust provide suitable sources of thermal energy for water-biomass conversion throughout magma lifetimes of 1,500 to 600,000 yrs. Fuels can be generated within a magma body, within the hot subsolidus margins of a magma body, or within surface reaction vessels heated by thermal energy derived from a magma body. The surface reactor scheme is particularly attractive as regards dealing with the problems of biomass-derived sulfur and ash accumulation during fuel generation.

The composition, concentration, and energy content of the fuel gases generated from a particular water-biomass mixture does not change appreciably with the type, age, depth, or temperature of the magma body. For any upper crustal magma body, the concentration of generated fuel and its energy content is almost entirely a function of the proportion of biomass in the starting mixture. CH_4 is the main gas that can be generated in important quantities by magma-thermal energy under most circumstances. CO is never an important fuel product. The possibilities for significant H_2 generation are restricted either to heat exchangers operating at high temperatures ($> 800^\circ\text{C}$) in the tops of very shallow basaltic magma bodies (e.g., mid-ocean ridge basalts) or to surface reaction vessels operating at temperatures in excess of 600°C . Under either of these conditions, H_2 production would be achieved at the cost of a reduction in the rates of both fuel generation and heat extraction by associated steam production.

The rate at which gaseous fuels can be generated from water-biomass mixtures is strongly dependent on the type of magma involved. Fuel

generation rates for basaltic magmas are at least 2-3 times those for andesitic magmas and 5-6 times those for rhyolitic magmas for similar biomass concentration levels and generating temperatures. For any given magma, the highest fuel generation rates will be achieved at the lowest possible operating temperature that does not cause graphite deposition from the water-biomass mixture being employed.

The deposition of graphite is a complex function of the operating temperatures and pressures and the proportion of biomass in the starting mixture. The problem of graphite deposition would therefore have to be worked out for each particular environment of interest, but a few generalizations can be made for fuel generation in heat exchangers operating in upper crustal magma bodies: (1) at 300°C, less than 10% biomass can be used; (2) at 400°C, 10 to 20% biomass can be used, depending on depth; (3) at 500°C, 20 to 30% biomass can be used, depending on depth; (4) at temperatures in excess of 600°C, 30 to 40% biomass can be used. Inasmuch as fuel generation rates would be optimized at lower temperatures (400-500°C), 20% biomass is probably a realistic upper limit for biomass concentrations in the starting mixtures. This concentration level may also prove to be an upper limit for other reasons not considered in this study (economic factors, technical factors related to preparation of starting mixtures, etc.). The surface reactor circumvents the problem of graphite deposition down to 300°C even for biomass concentrations up to 40%.

The energy content of the biomass-derived fuels is considerably greater than that consumed in the generation and refinement process for all conditions examined, especially at lower operating temperatures. The energy costs of biomass production, harvest, collection, transport, and preparation for refinement must ultimately be included in this accounting, however, before the conversion of biomass to gaseous fuels by magma-thermal energy can be properly compared with alternative

methods to achieve the same end. Alternative methods could be designed to take advantage of several of the attractive features mentioned above for surface reactors. These might include, for example, utilizing heat from nuclear reactors, coal-fired power plants, and various sources of industrial processes.

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