

LOW COST FUEL FROM DEGASIFICATION OF COALBEDS

1

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INTRODUCTION

Coalbed degasification can provide significant quantities of low cost fuel with none of the difficult problems associated with other processes for unusual fuel production. The most compelling reasons for coalbed degasification focus on conservation, compatibility, and predictability, but other positive factors such as the use of existing technology, low cost of production, proximity to markets, favorable environmental circumstances, immediate availability, and a resultant enhancement in the ease and safety of producing coal are no less important.

The scientific and technical basis for coalbed degasification as a source of pipeline quality gas has already been established. All that now remains is the refinement of the techniques of gas production from coalbeds and further evaluation of the gas content of the lower rank deep subbituminous coalbeds of the Western States and of the anthracite of eastern Pennsylvania. The current work on coalbed degasification is a natural consequence of a methane control research program initiated by the U.S. Bureau of Mines in 1964 to develop methods of making coal mines safe from explosions of methane-air mixtures.

GAS CONTENT OF COALBEDS

The gas content of coalbeds, mostly methane, can be directly determined by measurement of samples of freshly collected coal cores (). It is becoming clear now that the amount of methane in coal is roughly proportional to the rank of the coal and the depth of the coal. Although most of the studies to date have been conducted in bituminous coals, there is no reason to expect that much of what Mott postulated () about the methane produced during coalification will not be supported by further investigation. Certainly the deeper Pittsburgh, Pocahontas, Beckley, Mary Lee, and Hartshorne coalbeds all contain enough gas to warrant serious consideration.

The composition of coalbed gas is compatible with pipeline quality gas. Kim's report () gives analyses of 13 coalbed gases, only one of which had a heat of combustion less than 900 Btu/ft³.

The absence of H₂S and SO₂ in coalbed gas makes it especially desirable because no special gas scrubbing is required before mixing with other pipeline gas.

CONSERVATION

The gas in coalbeds, especially in minable coalbeds, will be lost ultimately, unless degasification is practiced. More than 200 million cubic feet a day of methane is lost in the exhaust from bituminous coal mines. Almost all of this gas could be collected for use.

A ton of bituminous coal will yield about 25 million Btu upon combustion. If the average content of 250 ft³ of gas per ton of bituminous coal were to be recovered, this would amount to a 1 pct increase in our fuel resources for such coals; but since only a fraction of coal in any coalbed is extracted and nearly all the gas can be recovered, the increase in usable resources attributable to the contained gas is more like 3 pct of the produced coal. In an age of declining productivity, a 3 pct increase is indeed significant.

PREDICTIBILITY

2

Coalbeds can be located readily. The major bituminous coalbeds are well delineated and the deeper coalbeds are only now being exploited in this country. The gas content of an entire coalbed can be estimated and the resource base evaluated with only a modest investment as compared with that required for conventional gasfield exploration.

The Bureau of Mines has developed methods for routinely determining the gas content of coalbeds and as our techniques become more refined and a larger data base is established, even less effort will be required to estimate accurately the gas that can be recovered from bituminous coalbeds in the United States.

USE OF EXISTING TECHNOLOGY

The technology developed by the oil and gas industry can be applied now to produce gas from permeable coalbeds such as the Pittsburgh coalbed in western Pennsylvania and West Virginia, the Mary Lee coalbed in Alabama, and the Beckley coalbed in West Virginia. Gas wells have been producing gas from the Pittsburgh coalbed for many years () on structural highs, much as from favorable gas sands. We know now that such geologic structures are not essential. The gas wells drilled into coalbeds are not very productive initially but with hydraulic stimulation, a well established oilfield technique, productivity can be increased from 5- to 20-fold ().

Early experimental work has already shown that it will be possible to produce from more than one coalbed from a single borehole. It is not uncommon for several coalbeds to be found within a few hundred feet of vertical stratigraphic section. Almost all coal-bearing strata contain multiple beds and although multiple seam mining is not common in the United States as it is Europe, it is now being practiced with more frequency in the states of Kentucky, central Pennsylvania, Ohio, and West Virginia.

Even old ideas for producing oil from strata by horizontal drilling is being successfully applied to producing gas from coalbeds. Two notable examples are experiments conducted in the Pittsburgh coalbed by the Bureau of Mines where two sets of horizontal holes drilled radially into the coalbed from shaft bottoms have already produced more than 1 billion cubic feet of pipeline quality gas ().

Another technique, widely used by the petroleum industry, for producing oil from offshore oilfields by drilling angle holes from sites on the mainland, has been successfully applied to extracting gas from coalbeds.

The recitation of these successful efforts does not mean that further development work is unnecessary. It means only that refinements in these methods must be sought and that such refinements require no massive investment in research and development.

THE UNDERGROUND GASIFICATION OF A SUBBITUMINOUS COAL

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INTRODUCTION

The recently recognized energy shortage has generated an upsurge in government research devoted to both improving current technology to better utilize known energy reserves and providing new technology which will allow the country to convert energy resources to reserves. Underground coal gasification (UCG) technology may play an important role in both of the above categories.

Sufficient technology is at hand to successfully produce a low-Btu gas from relatively shallow (<1000 ft.) deposits of bituminous, subbituminous and lignitic coal (1, 2, 3). Most recently the Bureau of Mines' Laramie Energy Research Center has conducted an underground gasification experiment at Hanna, Wyoming, in a 30 ft. thick seam of subbituminous coal at a depth of 400 ft. The results from Hanna have been more favorable than previous results in the U. S. and other countries (4) in two important categories: a gas of higher Btu content (125 Btu/scf) has been produced and during a 6½-month period of optimum operation there was little or no gas leakage from the underground system (3). However, applicability to deeper deposits (>1000 ft.) is not yet proven.

In order to evaluate UCG's feasibility, methods of measuring the physical and chemical occurrences in an inaccessible reaction zone must be developed. While experiments are underway to implant sophisticated instrumentation in the gasification pathway in the second UCG experiment at Hanna, such instrumentation would probably not be economically feasible in a commercial process. Consequently, it is of paramount importance to develop both inexpensive remote sensing and material and energy balance techniques to continuously evaluate the in situ process in order to maximize gasification efficiency and resource utilization. A material balance method derived by Elder et. al. (1) has been applied to data obtained from the first UCG experiment at Hanna. Results of these material balance calculations are presented as well as the problems involved in measuring factors necessary for performing a material balance.

GEOLOGICAL CONDITIONS

In attempting to build an underground reactor in a coal seam, important factors to be considered are the rate and pressure of water influx and the directional permeability of the coal. In addition, strata above and below the coal seam must have significantly lower permeabilities than the coal in order to prevent leakage from the reaction zone. The rate of water influx is related to both the permeability of the seam and to the hydrostatic pressure. In the experiment at Hanna, the seam of choice, the Hanna #1, is 180 to 200 feet below the water table. A 80-90 psig hydrostatic pressure is thereby imposed upon the reaction zone. Another important factor in the movement of water and gases within the seam is the directional nature and extent (both vertical and horizontal) of the natural

fractures within the coal seam (5, 6). A thorough understanding of these natural fractures should aid in development of true in situ process control.

The Hanna #1 seam used during this experiment is a 30-foot thick subbituminous coal seam lying at a depth of 350 to 400 feet. It dips to the northeast at 6 to 9°, is isolated by outcrop on three sides, and displaced by faulting on the fourth (2). Strata above and below the coal consist of less permeable shales with 15 feet above and 4 feet below the coal.

GASIFICATION TECHNIQUE USED AT HANNA

While many techniques have been used in UCG (7), the chosen method in the Hanna experiment was the percolation or filtration method. Success of this method depends on the development of sufficient permeability between vertical boreholes to maintain a sufficient flow of gasification agent and product gas. The critical step in development of the underground reactor is establishing the initial linkage between vertical boreholes, i.e., increasing air acceptance by some means. Therefore, the water and the natural fracture direction in the coal play obvious roles in affecting the UCG experiment. The initial permeability of the coal seam to injected air is quite low (1-10 millidarcys). However, injection of air at pressures in excess of hydrostatic pressure expels water from the natural fracture system thereby increasing permeability. The degree of permeability increase is not predictable unless the natural fracture directions and the transmissivity of the coal are known. An experiment is planned to evaluate these parameters (8).

The most reliable method of linking boreholes prior to gasification is that of reverse combustion(3). A fire is ignited in the borehole to be vented and air is fed to this combustion zone by injection into an adjacent borehole. Thus the combustion front propagates countercurrent to the gas flow. This is in contrast to forward combustion wherein the combustion front proceeds in the same direction as the gas flow. The practical advantages of a reverse combustion mode over a forward combustion mode are:

1. The possibility of tars, produced from carbonization, plugging the natural fractures in the coal is obviated because the tars are not driven into the coal ahead of the combustion zone.
2. Directional control of combustion front movement is attained because the combustion front will proceed toward the source of air.

During establishment of linkage between wellbores using reverse combustion, two distinct phases have been found by monitoring air injection rate and pressure. Initially air is injected at relatively high pressure (250-300 psig) and low flow rates for a period of several days. During this time a narrow combustion front proceeds toward the source of air. When breakthrough between wellbores occurs, an abrupt drop in pressure occurs after which the flow of gas is relatively unrestricted. The gas produced during the linkage process is usually of high Btu content (approx. 175-200 Btu/scf) with high methane and low carbon monoxide content characteristic of a carbonization gas. However, once breakthrough is achieved allowing high volume-low pressure gas flow, gasification rather than carbonization becomes the predominant mode. Gasification is characterized by high carbon monoxide and low methane content in the product gas.

Thus a gasification scheme using the percolation method consists of two regimes, one of linking at high pressure and the other of gasification at low pressure. The linking process, being of short duration and low gas flow rates,

utilizes only a small fraction of the coal that is eventually affected between a pair of boreholes. Due to the high pressure involved, leakage from the system can be severe (75% gas loss) during the linking phase. Leakage during gasification has not been observed at Hanna. The seam water apparently acts as an effective gas seal during this low pressure operation (3).

FACTORS INVOLVED IN A MATERIAL BALANCE

A prerequisite for calculating a material balance on a system is a detailed knowledge of the reactants and products. In the case of UCG, it is impossible to determine the precise stoichiometry of the coal to be gasified. A chemical and mineralogical examination of a core taken from the Hanna #1 coal seam reveals the lack of homogeneity with respect to depth. Table 1 lists the ash content, fixed carbon/volatile matter ratio, and C/H ratio of samples from a 30-foot core.

TABLE 1. - Core Analysis of Hanna #1 Coal Seam as a Function of Depth

Depth	% Ash ^{1/}	Fixed Carbon/ Volatile Matter	C/H Ratio ^{2/}
378.7	27.4	1.00	12.5
379.3	21.6	1.05	12.9
381.5	39.4	0.70	11.7
383.0	4.6	1.29	13.8
383.5	8.8	1.04	12.6
384.0	19.2	1.00	12.5
384.5	11.8	1.13	12.9
385.5	19.7	1.04	12.8
386.0	24.5	0.94	12.0
386.5	14.0	1.07	13.2
387.0	9.0	1.06	12.4
387.5	9.4	1.19	13.2
388.0	6.2	1.08	12.9
388.5	9.7	1.04	13.3
389.0	21.7	1.02	12.9
390.0	20.5	1.03	12.1
391.5	36.7	0.21	14.3
392.0	14.5	0.77	13.4
393.0	3.8	1.06	12.8
393.5	9.7	1.00	13.0
394.0	14.4	1.06	12.9
394.5	29.3	0.86	11.9
395.0	24.1	1.03	12.8
396.0	15.1	1.04	12.9
396.5	14.9	1.10	13.1
397.0	15.7	1.09	13.4
399.0	16.8	1.26	13.6
400.0	6.4	1.33	13.8
400.5	7.1	1.19	13.4
401.0	4.3	1.17	13.5
402.0	11.5	1.13	13.1
402.5	23.2	1.06	12.9

^{1/} Moisture free basis

^{2/} Moisture and ash free basis

MATERIAL BALANCE CALCULATIONS

Material balance equations may be written as follows:

$$\begin{aligned} \text{Hydrogen Balance (H): } & H \text{ (from char)} + H \text{ (from volatile matter)} + H \text{ (from formation water)} \\ & = H \text{ (total in products)} \end{aligned} \quad 1)$$

$$\text{Carbon Balance (C): } C \text{ (from char)} + C \text{ (from volatile matter)} = C \text{ (total in products)} \quad 2)$$

$$\begin{aligned} \text{Oxygen Balance } (\emptyset): & \emptyset \text{ (from char)} + \emptyset \text{ (from volatile matter)} + \emptyset \text{ (from formation water)} \\ & = \emptyset \text{ (total in products)} - \emptyset \text{ (from air)} \end{aligned} \quad 3)$$

Then let:

- x = pounds of char entering the reaction zone
- y = pounds of volatile matter entering the reaction zone
- z = pounds of water entering the reaction zone

Substituting the data from Table 2 into the material balance equations:

$$H = 0.0083x + 0.116y + 0.111z$$

$$C = 0.970x + 0.498y$$

$$\emptyset' = 0.0003x + 0.347y + 0.889z$$

$$\text{Where } \emptyset' = \emptyset \text{ (total in products)} - \emptyset \text{ (from air)}$$

Solving these equations for x, y and z with quantities expressed in pounds:

$$x = 1.10C + 0.93\emptyset' - 7.45H$$

$$y = -0.12C + -1.82\emptyset' + 14.55H$$

$$z = 0.05C + 1.84\emptyset' - 5.67H$$

From Table 2 the weight ratio of volatile matter to char is 0.92; the weight ratio of moisture and ash free (maf) coal to char is 1.92; and the weight ratio of maf coal to volatile matter is 2.08.

Therefore:

$$1.92x = \text{weight of maf coal completely gasified and}$$

$$2.08(Y - 0.92x) = \text{weight maf coal carbonized only}$$

This material balance has been applied to a 6½-month operational period in five day increments. During this period both nitrogen and argon balances showed that there was little or no leakage from the underground system and thus a leak free system is assumed in the material balance. Additional assumptions are steady state conditions during the period considered, carbonization at 900°C, no condensation of products prior to gas sampling at the surface, no reactions of oxygen with any materials other than coal, and the laboratory carbonization assays indicate the stoichiometry of the char and volatiles under seam reaction conditions. The results of this material balance are listed in Table 3 along with average air injection rates, average gas production rates and average product gas heating values for the periods indicated.

The total amount of coal affected during the period considered was 2986 tons with 1171 tons carbonized only and 1815 tons completely gasified. These results are based on the linkage and gasification of three pathways of 80, 90, and 100 feet, respectively, radiating from the original ignition point to three different wellbores used as air injection points. Assuming that a cylinder of coal 30 ft. in diameter was accessible to gasification for each pathway, approximately 4700 tons of maf coal were available for gasification. Therefore, the coal utilization efficiency was 63%. From Table 3 the average energy recovered from the coal affected was 58%. The product of these two efficiencies yields an overall energy

These data indicate that while the ash content varies widely with respect to depth in the seam of interest, the ratio of fixed carbon to that of volatile matter and the C/H ratio remain relatively constant.

In assessing a material balance for a UCG experiment, several assumptions must obviously be made. It is difficult to measure the total quantities of water which are gained or lost by the system. More importantly it is difficult to directly measure the amount of coal affected and the manner in which it was affected. However, excavation of previous UCG experiments and laboratory simulations have shown that the process occurs in two discrete steps: carbonization only and complete gasification. In UCG a stream of the gasification agent is passed over the surface of the coal with carbonization occurring first followed by complete gasification of the remaining char. Water from the coal itself or natural ground-water influx from the seam is present at or near the region of reaction. For practical purposes air, volatile matter from coal, char from coal, and water are present in the reaction zone where the carbonization-gasification processes occur.

Although it is not difficult to set up a material balance in theory, practical considerations of UCG make it extremely difficult to measure all of the quantities involved. Obtaining a material balance thus involves:

1. Measurement of the gasification agent (air).
2. Assuming that the material to be gasified enters the system in two discrete parts: (a) the products of carbonization of the coal at 900°C, and (b) the char remaining after carbonization.
3. Estimating the quantity of water entering the underground system.
4. Measuring the volume and composition of the products.

The application of Elder's method (1) of material balance to the Hanna #1 coal is based on a precision carbonization assay at 900°C, the results of which are listed in Table 2 along with the ultimate analysis.

TABLE 2. - Elemental distribution in coal, char and volatile matter from 100 pounds of moisture and ash free Hanna #1 Coal

Element	Coal		Char		Volatile Matter	
	wt. %	Pounds	wt. %	Pounds	wt. %	Pounds
H	6.04	6.04	0.83	0.43	11.60	5.61
C	74.33	74.33	97.02	50.34	49.82	23.93
O	16.67	16.67	0.03	0.02	34.65	16.65
N	1.94	1.94	0.93	0.48	3.04	1.46
S	1.02	1.02	1.19	0.63	0.81	0.39
Totals	100.00	100.00	100.00	51.90	99.92	48.04

TABLE 3. - Five Day Averages of Operating Data and Material Balance Results

Starting Date of 5 Day Period	Air Injection Rate (MM scf/day)	Dry Gas Production Rate (MM scf/day)	Heating Value (Btu/scf)	Tons of MAF Coal Carbonized Only (tons/day)	Tons of MAF Coal Completely Gasified (tons/day)	Total MAF Coal Affected (tons/day)	Energy Recovery Efficiency (%)
9/16/73	1.20	1.40	61	16.0	0.9	16.9	20
9/21/73	0.69	0.97	134	13.5	1.6	15.1	33
9/26/73	0.82	1.26	150	15.7	2.9	18.6	39
10/01/73	0.99	1.48	138	2.6	9.3	11.9	67
10/06/73	1.06	1.78	163	8.7	9.9	18.6	61
10/11/73	1.11	1.89	162	13.0	8.9	21.9	54
10/16/73	1.08	1.76	153	11.0	8.4	19.4	54
10/21/73	1.03	1.56	136	9.6	6.9	16.5	50
10/26/73	1.06	1.60	134	7.5	7.9	15.4	54
11/01/73	0.83	1.44	158	9.3	6.7	16.0	55
11/06/73*	0.71	1.04	112	-4.2*	8.1	--*	--*
11/11/73	1.08	1.63	132	4.2	9.3	13.5	61
11/16/73	1.23	1.79	129	6.9	9.4	16.3	55
11/21/73	1.20	1.76	129	5.9	9.5	15.4	56
11/26/73	1.36	1.91	114	4.2	10.5	14.7	57
12/01/73	1.15	1.69	125	8.4	8.4	15.2	53
12/06/73	1.09	1.57	109	3.6	8.1	11.7	56
12/11/73	1.25	1.91	136	-1.6*	13.7	--*	--*
12/16/73	1.22	1.81	126	7.2	9.0	16.2	55
12/21/73	1.29	1.86	110	0.2	11.2	11.4	69
12/26/73	1.22	1.72	103	-4.7*	12.0	--*	--*
1/01/74	0.79	1.01	75	-4.6*	7.3	--*	--*
1/06/74	0.96	1.21	68	-5.9*	8.6	--*	--*
1/11/74	0.96	1.13	52	-5.1*	7.5	--*	--*
1/16/74	0.94	1.14	70	1.4	5.5	6.9	44
1/21/74	0.78	0.77	96	3.3	3.3	6.6	44
1/26/74	0.58	1.13	125	5.7	5.3	11.0	50
2/01/74	1.09	1.84	168	7.7	11.2	18.9	63
2/06/74	1.20	1.98	176	16.9	9.2	26.1	51
2/11/74	1.39	2.14	153	7.0	13.1	20.1	62
2/16/74	1.43	2.35	187	14.4	14.4	28.8	59
2/20/74	0.69	1.66	200	28.7	13.5	42.2	42
2/24/74	2.06	2.85	118	-4.4*	20.4	--*	--*
3/01/74	1.56	2.21	117	-9.8*	18.1	--*	--*
3/06/74	1.89	2.75	128	3.2	17.2	20.4	67
3/11/74	0.66	1.48	182	-8.5*	14.3	--*	--*
3/16/74	1.51	2.25	131	-2.3*	16.0	--*	--*
3/21/74	0.10	0.34	229	-6.9*	5.5	--*	--*
3/26/74	0.00	0.05	275	--*	--*	--*	--*

* These data are not significant because abrupt variations in flow rates preclude a steady state system.

recovery efficiency of 37% based on results of this material balance calculation.

This material balance is only a chemical interpretation of the process based on many assumptions. The areal and vertical sweep efficiencies are unknown. In addition, this first experiment was designed not to optimize operating parameters but to provide preliminary information for designing other experiments to evaluate UCG feasibility. Even so, the results are encouraging. The overall energy efficiency for the period considered is higher than that achieved in any previous UCG experiment for the length of time considered here. Physical assessment will include coring and downhole measurements to better establish the sweep efficiencies and the geometry of the coal area affected. These data will give a much better idea of the overall resource utilization efficiency than the material balance calculations.

FUTURE RESEARCH

A second experiment (8) at Hanna is presently underway utilizing an oxygen blown system, an improved well linkage system, and in situ instrumentation consisting of both active and passive acoustic techniques, surface and subsurface resistivity, and in situ temperature and pressure measurements to better define the combustion zone. A "line drive" system will be initiated. This involves movement of a 60-foot long combustion front at right angles to the major natural permeability direction in the coal providing intimate contact between the gasification agent and the coal. Coal utilization efficiency should be improved over that estimated from the first UCG experiment. A target of 50% overall energy efficiency rather than the 37% estimated here for the first experiment has been set. This second experiment should lead to development of process control and process evaluation techniques as well as significantly improved process interpretation for determining the feasibility of UCG.

CONCLUSIONS

A UCG experiment has been successfully conducted in a thick seam of subbituminous western coal with encouraging results. Problems of gas leakage and the ability to link wellbores successfully have not occurred during the Hanna project so long as reverse combustion was used to link adjacent wellbores. Seam water, rather than posing a problem, appeared to be an asset in preventing gas leakage in the underground reaction system. A material balance technique based on the carbonization properties of coal has been used to estimate an energy recovery efficiency of 58% from the coal affected, a coal utilization efficiency of 63%, and an overall energy recovery efficiency of 37%. Many problems remain to be solved in UCG such as a greater degree of process control, but results of the first UCG experiment are especially encouraging even though it was not designed to optimize operating parameters. The second UCG experiment now underway should yield higher coal utilization efficiencies and offer a feasible technique for recovering energy from coal seams unsuited to current coal mining techniques.

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THE GEZRO PROCESS FOR OPEN-CYCLE HYDROGEN PRODUCTION

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Various scenarios using hydrogen as a general energy medium in the future have been proposed based upon its outstanding environmental compatibility, its ultimate derivation from an inexhaustible feedstock material (H_2O) and its high flexibility. At least until the next century, however, the overwhelming uses of hydrogen will be as a chemical feedstock, in chemical and metallurgical processing operations and the production of clean synthetic fuels. In particular, the conversion of coal into synthetic natural gas and liquefied synthetic fuels will require large amounts of hydrogen. Both present and projected demands for hydrogen require that new, higher efficiency and lower cost production methods be developed.

Currently the vast majority of hydrogen produced is made by open-cycle processes that consume natural gas, oil or other petroleum products as the feedstock material. The principal methods include steam reforming and partial oxidation both of which are followed by the shift reaction⁽¹⁾. Thermal efficiencies of such processes in terms of the combustion value of hydrogen produced compared to that of the input fossil fuels typically range from 50-80%. Only a small fraction of the hydrogen consumed presently is produced by water electrolysis in spite of the simplicity of the process, the product purity, and the good efficiency achievable in the electrolysis step itself by advanced methods (up to ~70-90%). This is due largely to the low overall efficiency (i.e., <35%) when electric generation and DC conversion steps from a base load thermal power plant are included. Much attention has recently been given to the closed cycle thermochemical decomposition of water in which heat at moderate temperatures (<1000°C) is used to carry out a series of reactions,⁽¹⁾ the net result of which is: $H_2O + H_2 + 1/2 O_2$. All other chemical intermediates in the process are recycled, ideally. Detailed analysis indicates that overall thermal efficiencies of 40-60% might be achieved. While numerous closed cycle processes have been theoretically proposed, none have yet been successfully operated in an integrated mode. Serious technical barriers, including corrosion, kinetics, system stability and design, combined with licensing uncertainties, the projected high cost of high temperature nuclear heat and process components shed serious questions on the viability of multi-step closed cycle processes for hydrogen generation, at least in this century. Thus it appears that open-cycle processes to make hydrogen will be very important for the foreseeable future.

The primary objective of this paper is to describe a new open cycle technique which will utilize coal or coal char from gasification to produce electrolytically pure hydrogen. The concept stems from our earlier high temperature fuel cell program, during which an electrolytic water dissociation cell using an oxygen ion conductive membrane was proposed⁽²⁾ and demonstrated⁽³⁾. By introducing a reducing gas at the cell anode, the voltage required to produce hydrogen from water is lowered. The new method is to use a ceramic membrane that is both an electron conductor as well as oxygen ion conductor. Thus the cell can operate in a "self-driven" mode, i.e., no

electrical driving force or electrodes are needed. Such a cell is shown schematically in Figure 1. Steam is passed over one side of the membrane while carbon monoxide is passed over the opposite side of the membrane. On the "cathode" side, the steam reacts at the surface with two electrons to yield hydrogen gas plus an oxygen ion, which is transported through the electrolyte to combine at the "anode" surface with carbon monoxide to form carbon dioxide plus two electrons. This process, operating without electrical input, has been named GEZRO. It should achieve overall thermal efficiencies, as defined earlier, of at least 60-70%.

The net reaction for the process is the well-known water gas shift reaction: $H_2O + CO = CO_2 + H_2$. Because the reactants are separated, the product hydrogen does not have to be purified with respect to CO or CO_2 . This has important implications to ammonia synthesis, for example, where CO impurity in the hydrogen acts as a catalyst poison. Also, the input carbon monoxide need not be pure. For this reason, GEZRO is particularly adaptable for integration into coal liquefaction or gasification technology. Figure 2 shows a possible cycle using gas obtained from coal which has been partially oxidized in air as the feed to GEZRO. Nitrogen from the air and coal contaminants such as sulfur also enter the GEZRO reactor; gas clean-up is accomplished subsequently at lower temperatures. On the steam side, a portion of the steam is reduced to hydrogen and the remainder is recycled. Heat exchangers, not shown in the diagram, would be used so that minimal heat input would be required. Figure 3 shows a cycle in which GEZRO is incorporated into a high BTU coal gasification scheme, such as HYGAS. In this cycle, hydrogen and steam from GEZRO are fed directly into the second stage gasifier (both hydrogen and steam are required to maintain proper heat balance in the gasifier) to react with coal and char and yield methane. The remaining char is partially burned in air to provide the input gas for GEZRO.

The GEZRO reactor can be considered as an electrochemical cell in which the cell voltage is zero (short circuit condition). For this case an effective average thermodynamic cell voltage, \bar{v} , may be defined by $\bar{v} = r\bar{j}$, where r is the electrolyte specific resistance, and \bar{j} is the average current density. Thus, r , which depends on the membrane material, and \bar{v} which is related to the driving force for the reaction (proportional to temperature and oxygen partial pressure differential) integrated over the reactor length, determine the output of the cell in terms of oxygen ions transported per unit area of membrane. For typical membrane compositions, it can be shown that by operating with countercurrent gas flows, it is theoretically possible at 800°C, to oxidize 80% of the CO to CO_2 while converting half of the input steam to hydrogen when the input steam flow rate is twice the input CO flow rate. In general, the process is expected to operate at between 700°C and 1000°C at any required pressure.

The critical problem in the development of a GEZRO reactor is the selection of a suitable membrane and our experimental program has centered in this area. Materials requirements include the following:

- (1) High oxygen ion conductivity,
- (2) High electronic conductivity,
- (3) Thermal stability,
- (4) Stability toward reactants and products,
- (5) Stability toward contaminants,
- (6) Mechanical stability and strength, and
- (7) Fabrication capability (thin and gas tight).

These properties are similar to those required by high temperature fuel cells, with the important exception that electronic conductivity, instead of being undesirable, is required. Indeed, the optimum condition for GEZRO is that the transport number for electrons (t_{e^-}) is equal to that for oxygen ions ($t_{O^{2-}}$), so that $t_{O^{2-}} = t_{e^-} = 0.5$. The severe operating environment, which includes corrosive and reactive gases (e.g., H_2S , SO_2 , COS) as well as a wide range of reducing conditions (10^{-20} atm $< P_{O_2} < 10^{-7}$ atm) at high temperatures, rules out many possible materials.

Because of its well-established use in experimental fuel cells, zirconia has been chosen as the initial candidate membrane base material. When certain oxide materials containing a cation in the +2 or +3 oxidation state are added to monoclinic ZrO_2 , the ZrO_2 is stabilized in a cubic fluorite crystal structure. The stabilization process leaves several percent oxygen ion vacancies in the structure and leads to significant ionic conduction. The ionic conductivity at a given temperature generally increases with the nature of the additive in the order $CaO < Y_2O_3 < Sc_2O_3$. The use of Y_2O_3 as a stabilizer appears attractive as a compromise between cost, long-term stability, reactivity toward sulfides, and reasonable conductivity. A maximum in the conductivity of the Y_2O_3 - ZrO_2 system occurs at about 7-8 m/o Y_2O_3 , at which point the purely ionic conductivity is about $0.1 \Omega^{-1} cm^{-1}$ at $1000^\circ C$. The addition of compatible transition metal oxides into the ionically conducting fluorite lattice is expected to introduce electronic conductivity, provided the additive goes into the structure and is not merely segregated along grain boundaries..

A program to synthesize and screen various three and four component ceramic compositions by means of microstructure analysis, electrical conductivity measurements, and transport number measurements is in progress. Table I summarizes some of the compositions which have so far been successfully prepared and which have been sintered into dense, gas-tight shapes. The sintering conditions were found to be critical in achieving good materials properties. In general, sintering was carried out at temperatures between $1500^\circ C$ and $1900^\circ C$ in an atmosphere of either air or wet hydrogen; wet hydrogen atmospheres generally approximate the oxygen partial pressures used in the GEZRO process. Oxides of Mn, Zn, Ce, U, and Fe have been successfully added to yttria-stabilized zirconia to form pure single phase materials. Additive contents have ranged from 4.1 m/o to 13.4 m/o in compositions based on 7-8 m/o Y_2O_3 -stabilized zirconia. Other preparations involving 2-20 m/o of additive, and using other transition metals have been attempted or are in progress.

Electrical conductivity measurements have been completed on several of the above compounds using a two-probe AC technique. Platinum paste electrodes (Engelhard #6082) were applied to sintered bar samples which made pressure contact with platinum foil spacers in a sample holder constructed of alumina. Measurements were carried out as a function of temperature in the range between $500^\circ C$ and $1000^\circ C$ and as a function AC frequency in the range between 400 Hz and 50 kHz, in either pure nitrogen or carbon monoxide atmospheres. Figure 4 shows the results for selected compositions. In most cases, the plot of the logarithm of conductivity (σ) vs reciprocal temperature is linear. The most conductive and the lowest activation energy (0.47 ev) material yet measured is the 7 m/o Mn_2O_3 composition. Unfortunately, a severe decrease in the conductivity resulted within 70 minutes after carbon monoxide was introduced at high temperature. Post-run

examination revealed that reduction, probably to poorly conducting Mn^{+2} oxidation state, had occurred. Both ZnO and CeO_2 additives are more promising. As shown in Figure 4 the composition containing 8.1 m/o ZnO is somewhat more conductive than the 13.4 m/o ZnO material. Measurements for the 13.4 m/o ZnO composition in carbon monoxide revealed no significant deterioration in the conductivity even after several hours exposure. Similar results were obtained in the case of 8.1 m/o CeO_2 where measurements in both CO and N_2 are shown for comparison in Figure 4; in this case, the reducing atmosphere lowered the conductivity somewhat, but there was no change in activation energy. Finally, one four component system, containing 2.8 m/o UO_2 and 7.6 m/o Fe_3O_4 , was measured since earlier work had indicated this material to be a potential mixed conductor. Although this material has been prepared in the form of dense, gas tight discs, such preparations are not always repeatable. In addition, efforts to prepare tubular shapes by means of plasma spray techniques have not led to suitably dense material.

Measurement of transport numbers for oxygen ions and electrons for the above and other potential materials, is also underway. These measurements are being made by the emf-technique in which the voltage generated by differing known oxygen partial pressures on either side of a disc sample is measured and compared with the theoretical voltage obtained for pure oxygen ion conduction.

Table I

<u>Additive*</u>	<u>m/o</u>	<u>Sintering Temperature Time, Atmosphere to Produce Dense Sample</u>
ZnO	8.1	1510°, 5 hr., air
	13.4	1510°, 5 hr., air
	8.1	1700°, 5 hr., wet H_2
CeO_2	8.1	1510°, 5 hr., air
	8.1	1500°, 5 hr., wet H_2
	4.1	1510°, 5 hr., air
Mn_2O_3	7.0	1510°, 5 hr., air
UO_2/Fe_3O_4	2.8/7.6	1900°, 16-1/2 hr., wet H_2

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*All compositons based on 7-8 m/o Y_2O_3 -stabilized ZrO_2 .

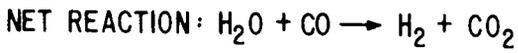
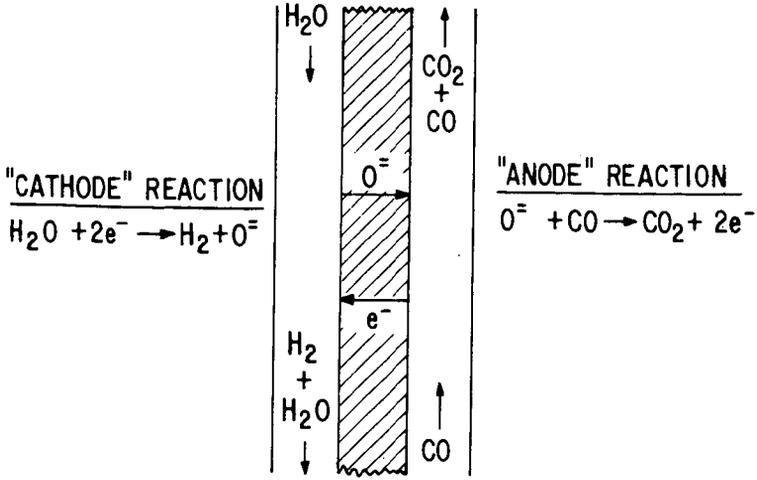


FIG. 1

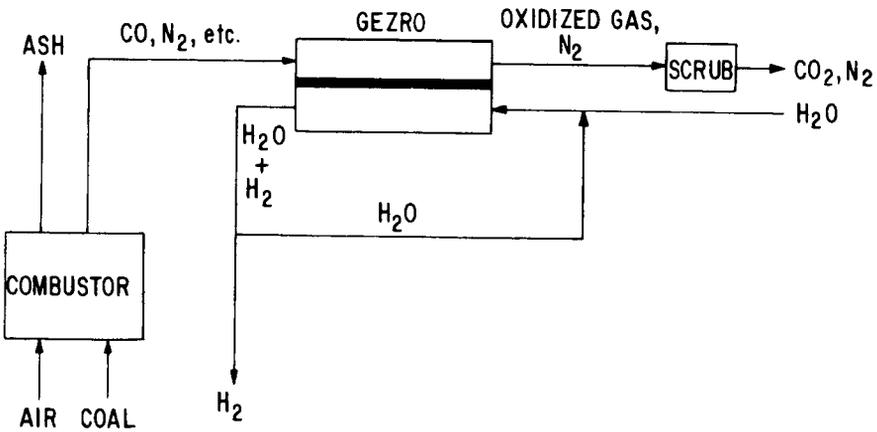


FIG. 2

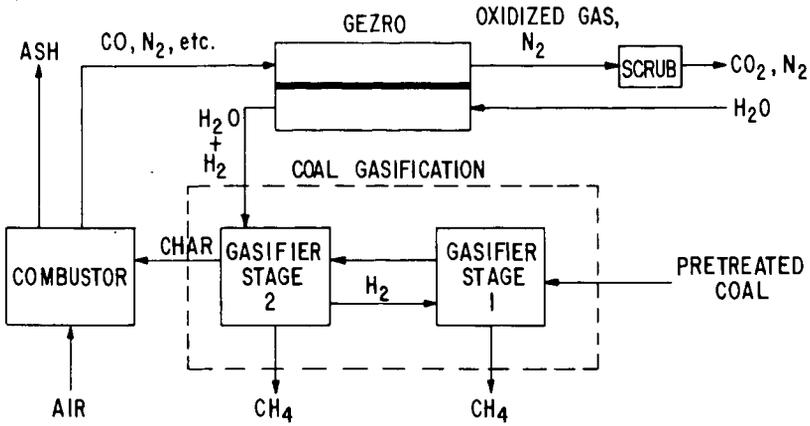


FIG. 3

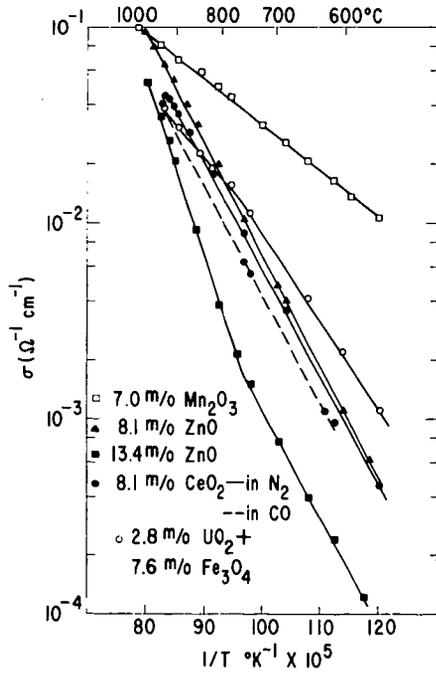


FIG. 4

DESIGN OF A WOOD WASTE-TO-OIL PILOT PLANT

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The Pittsburgh Energy Research Center of the U.S. Bureau of Mines has, for a number of years, been involved in programs for the conversion of coal to fuel oil. One such process, based on the findings of Fischer & Schrader¹ that low-rank coals could be hydrogenated with carbon monoxide and steam, is currently being developed. An interesting and significant offshoot of this work was the observation that lignin, cellulosic materials, and plastics could be converted to oil by the same chemical processing. Thus, the potential exists for the disposal of vast amounts of environmental pollutants and the creation of a replenishable energy source. Estimates indicate that the equivalent of one billion tons of dry, mineral matter-free organic waste will be generated in the U.S. in 1974. The energy value of this waste is $12-16 \times 10^{15}$ Btu or approximately 17 pct of the total estimated 1974 energy consumption in the country. Basically the waste-to-oil process involves the reaction of carbon monoxide and steam with organic waste material in the presence of sodium carbonate catalyst at temperatures of 250°-400° C and 2,000-4,000 psig pressure. The technical feasibility of the process was demonstrated in batch autoclave and bench-scale continuous process unit runs^{2,3}; the results and observations from this work was the basis for the design of a pilot plant for converting 1-3 tons per day of wood chips to oil. This pilot unit is currently being constructed on the site of the Bureau of Mines Metallurgical Station at Albany, Oregon. An overall process-flow diagram is presented in Figure 1.

Wood Chips Drying and Grinding

The wood chips (1/4" x 2" x 2" maximum size) will be withdrawn from the storage bin by the table feeder and fed into a rotary dryer where the moisture content will be reduced from 45 to 4 wt pct. The dry chips will be pulverized to -50 mesh in a hammermill and then conveyed pneumatically in an inert gas stream to the wood flour surge bin.

Feed Systems

The area of principal difficulty encountered in the operation of the bench-scale continuous units was the feeding of the wood oil slurry into the reactor. This problem is caused by the fibrous nature of the cellulosic waste material and its low-bulk density. Accordingly, three separate feed systems were designed into the wood-to-oil pilot plant; namely,

1. Wood-oil slurry feed
2. Pretreated wood-oil slurry feed
3. Solids feed

In the wood-oil slurry feed system, the pulverized wood will be continuously mixed with some of the product oil to form a slurry containing 30 wt pct solids. This slurry, which is extremely stiff, will be injected into the reactor feed lines by a high-pressure plunger pump with special check valves to minimize fouling.

The pretreated wood-oil slurry system is very similar to the wood-oil slurry feed technique with the exception that the raw wood chips will first undergo a partial carbonization to increase their bulk density. Hopefully, slurries of greater than 30 wt pct concentration of wood can be prepared through this technique. The pretreatment will involve heating the raw wood chips with some additional water to 500° F in a closed vessel. A pressure of approximately 700 psig will be developed from the steam. After process conditions have been maintained for a fixed time period, the pretreater and its contents will be cooled to 150° F by means of an external pump loop and an air cooled heat exchanger. The pretreated wood will then be separated from the water by vacuum filtration, dried, pulverized to -50 mesh, mixed with recycle oil, and fed to the reactor as described previously.

Direct solids feeding of wood flour will be accomplished by a lock-hopper system. This method of operation permits the greatest throughput per reactor volume but is quite complex and difficult to operate. Basically the feed system consists of two pressure-balanced lock hoppers which will be used alternately. The process gas, carbon monoxide, must be used to pressurize the feed system because of partial pressure considerations; i.e., the partial pressure of the carbon monoxide in the reactor would be reduced considerably if inert gas were used to pressurize the lock hoppers. Metering of the solids will be effected by a rotary feeder installed on the exit side of each lock hopper. During operations, a lock hopper at atmospheric pressure will be filled with -50 mesh wood flour from the storage bin. The unit will then be pressurized to operating pressure and the solids fed to reactor via the rotary feeder. When a lock hopper is empty, the pressure in the vessel is reduced to atmospheric by first venting to a carbon monoxide surge tank and finally to a flare stack. The surge tank, which is not shown in figure 1, is used to capture most of the carbon monoxide from the lock hopper for re-compression and reuse in the next cycle. In this feed system, recycle oil will be pumped separately into the reactor so that the desired ratio of wood-to-oil can be maintained.

Catalysts and Process Gas

Sodium carbonate solution will be prepared and pumped continuously into the reactor by means of a high-pressure plunger pump.

Carbon monoxide process gas will be taken from 35,000 scf tube trailers and compressed to operating pressure in a non-lubricated, non-contaminating diaphragm-type compressor. The compressed process gas will be preheated in a gas-gas interchanger and sparged into the reactor. Later, synthesis gases of various H₂:CO molar ratios will be used as the process gas.

Reaction and Subsequent Processing

The reaction will take place continuously at temperatures in the range of 250°-400° C and pressures of 1,500 to 4,000 psig. The liquid flow from the reactor will be cooled to 200° C in an air-cooled bottoms cooler and pressure reduction will be effected by a pressure reducing valve operating on a reactor liquid level controller. As the pressure is reduced, some liquid will flash and the remaining will be collected in a bottoms tank and then pumped to a centrifuge where oil and water are separated. The oil will then be filtered to remove any solids and transferred to a hold tank. Residual gases from the flash tank will

be measured, analyzed continuously for carbon monoxide, carbon dioxide, and hydrogen and flared in the flare stack.

The reactor off-gases will be cooled in a gas-gas interchanger and then undergo a pressure reduction by means of a reducing valve operating on a pressure controller. The gas will then be cooled to 80° C in an off-gas cooler, measured, analyzed continuously for carbon monoxide, carbon dioxide, and hydrogen, and finally flared.

The plant has the capability of producing 3 barrels of oil per day from wood waste. The product oil will be collected in an oil hold tank and then transferred to 55-gallon drums. Routine product oil analysis will include water and solids content, benzene solubles and insolubles, asphaltenes, viscosity, and heating value. Present plans call for the processing of other organic waste products upon completion of the wood-to-oil program.

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Photosynthesis as a Model for Photochemical Hydrogen Generation

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Introduction

Using solar radiation as an energy source has been considered for years, and a large number of attempts have been made to harness this seemingly "free" and clean energy directly. Most of the successful techniques rely on the heating effect of long wavelengths or on direct photovoltaic production of an electric current. Attempts at conversion of solar radiation to a chemically stored form of energy have been largely unsuccessful for one or a number of the following reasons: 1) the energy of a single photon of most of the light which reaches the earth's surface is insufficient to bring about a reasonably endothermic reaction; 2) the stored reaction products tend to recombine too readily before they should; 3) the reaction products do not combine readily enough at the desired time; 4) the reactants or reaction products are highly corrosive, toxic, expensive or otherwise difficult to work with; 5) since only a weakly endothermic photochemical reaction can be brought about, a large volume of reaction products must be stored for use during dark periods.

We have recently begun a feasibility study on a closed-cycle photochemical process for splitting water into hydrogen and oxygen. The novelty of the proposed method lies in the fact that the energy of two photon captures is added together in the cycle just as plants add photon energies during photosynthesis. In this way, a highly endothermic reaction, such as the photolysis of water, can be brought about by photons of relatively low energy and the five problems just mentioned can be largely eliminated. Hydrogen is an especially interesting reaction product, as many recent articles have pointed out, because it can be burned to produce heat, used in a fuel cell to produce electricity directly, or used as a chemical feedstock for coal liquefaction, etc.

Energetics of Photolysis and the Solar Spectrum

At 25°C, the free energy change for the conversion of liquid water to oxygen and hydrogen is 56.7 kcal/mole (1.23 electron volts). However, from the relationship $E = hc/\lambda$, one can calculate that only photons of a wavelength less than about 504 nm will have sufficient energy to do this and only about 15% of the incident solar energy at the earth's surface satisfies this criterion. (See Figure 1). The differential curve, which shows absorption bands for H₂O, O₂, etc., is taken from Levine *et al.* (1). An integrated curve also is shown. Even a 100% efficient conversion process would fail to be of much interest. If two equally energetic photons could funnel their energies into one reaction, though, the wavelength limit would be doubled and about 64% of the incident radiation could be utilized. A three-photon process in which the energy requirement is equally divided would result in a wavelength limit of 1512 nm, and about 84% of the incident radiation would be suitable.

The efficiency of such conversion processes as well as the fraction of the spectrum which can be utilized must, of course, also be

considered. To do this we can construct from Figure 1 a second plot (Figure 2) which decomposes the energy flux as a function of wavelength into photon flux vs. wavelength relationships, both differential and integral. We will next assume that the amount of energy which can be captured from any given photon is no more than that of the least energetic photon in whatever photon population we are considering. Such an assumption is quite realistic and parallels what we would expect to obtain in a photochemical excitation process. (The manufacturers of solar cells face a similar dilemma. To capture a larger fraction of the solar spectrum, they must decrease the band gap and thus the output voltage of the cell.) By multiplying the integral photon flux at a given wavelength by this minimum photon energy and comparing with integral energies found from Fig. 1, we can find a conversion efficiency and also an efficiency based on the total solar energy flux. For the single photon process, these efficiencies are 90% of the photons with sufficient energy, but only about 10% relative to the whole spectrum. For a two-photon process the efficiencies are 67% for the population (up to 1008 nm) and 37% for the entire spectrum. For three photons, the population efficiency (for wavelengths to 1512 nm) has dropped to 52% because so little energy is extracted from each photon, that the spectrum efficiency increases only to 38%. As an alternate to drawing each of the two or three photons from the same population, we can divide the total population into two (or more) sub-populations, a short wavelength high energy band and a long wavelength low energy band. Since we have already found that two-photon processes can use a reasonably large fraction of the spectrum, we will henceforth limit ourselves to such schemes. We also will assume that the low wavelength limit is set low enough to capture all of the high energy photons. The efficiency of a two-photon process depends on two factors: the upper wavelength cutoff point for the entire population, λ_u , and the wavelength, λ_c , at which the change from one sub-population to another takes place. The overall efficiency can be limited by too few photons in the high energy band, too few in the low energy band, or insufficient photon energy in the low energy band to make up a total of 56.7 kcal/mole. Using the data in Figures 1 and 2, the influence of λ_u and λ_c on efficiency has been calculated and is shown in Figure 3. Efficiency is a rather strong function of λ_c which determines the number of photons in each band. For wavelengths below 1008 nm, the peak efficiency corresponds exactly to the efficiency obtained by drawing photons from the same population because each photon has at least half of the required energy. However, it is now possible to use photons beyond 1008 nm by dividing the energy unequally. An interesting result which emerges is that a new upper wavelength limit of 1280 nm exists. Beyond this point the photon energies are insufficient even though the total number of photons is increased. At this wavelength and the optimum λ_c of 830 nm the efficiency is 59% of the whole spectrum and 75% of the photon population absorbed, a considerable improvement over the two-photon efficiencies obtained from a single population division. In closing this section we should point out that we have completely neglected fluorescence, competing reactions, etc. which produce non-unitary quantum yields. Actual efficiencies may be considerably lower than those which we have given here.

The Photosynthetic Cycle

Having decided that a two-photon process can efficiently capture a significant fraction of the solar radiation, particularly if wavelengths up to 1280 nm can be used and different populations are chosen

for each of the two photons, we now consider how to couple their energy. The cycle is very similar to that involved in photosynthesis, so a brief description of nature's scheme as it is presently understood, will be given first (see Figure 4) (2, 3, 4).

Chlorophyll a 670 is a pigment which when photochemically excited forms a strong oxidant (chl a^{+670}) and a weak reductant (reduced plastoquinone). The strong oxidant regenerates the original chl a 670 by an unknown series of reactions (collectively called the Hill Reaction) which ultimately extract an electron from water in the presence of Mn^{++} and Cl^- , liberating oxygen gas and hydrogen ions. The plastoquinone regenerates itself by contributing its electron to a chain of cytochrome compounds. As the electron falls toward a more oxidized state, part of its energy is trapped by converting ADP (adenosine diphosphate) to ATP (adenosine triphosphate) an energy source molecule used in cellular reactions. The electron eventually winds up in a compound called plastocyanin. This entire scheme of photon trapping and electron transport reactions is referred to a photosystem II.

The second series of reactions is called photosystem I. A pigment P700 is excited by the second photon, contributing its electron to an unknown compound X and thereby creating a very strong reductant. The weak oxidant, P700^+ returns to its original state by extracting the electron from plastocyanin. The compound X contributes its excess electron to a slightly less strong reductant, ferredoxin. The reducing energy of ferredoxin is used to create a second type of energy storage and transport molecule, NADPH, from NADP. This compound then supplies the energy to create carbohydrates from carbon dioxide and carry out other endothermic cellular reactions.

The Proposed Photolytic Cycle

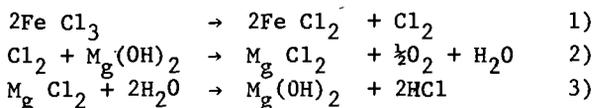
The cycle shown in Figure 5 is quite similar in principle to photosynthesis. Specific dyes are shown, but these are for convenience only and their choice was dictated primarily by what has already been described in the literature. Corresponding to photosystem II is a scheme based on the dye methylene blue. Excited by a photon, it extracts an electron from Fe^{++} forming the colorless leucomethylene blue and Fe^{+++} . (Actually the reaction occurs in two steps and 2 electrons are transported.) This reaction is well documented in the literature (5). We then postulate that a carrier molecule, such as one or more cytochromes, would extract the electron and carry it to a second system containing a dye such as acridine.

Upon photon excitation, the acridine is converted to an acridan. Unlike the methylene blue system, there is little or no tendency for the reaction to spontaneously reverse itself. Leucomethylene blue plus Fe^{+++} tend to react and regenerate the ferrous ion plus original dye. Although to our knowledge cytochromes have not been tried as electron donors for acridine, a wide variety of compounds including allylthiourea, isopropyl alcohol, ethanol, toluene, ethylene diamine tetraacetic acid, and ascorbate are effective (6, 7), so the carrier and donor molecules probably will not be too critical.

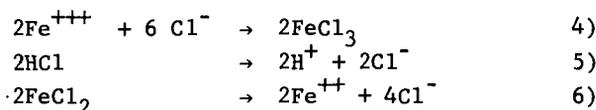
The reduced acridan molecule has a redox potential more negative than that of the hydrogen electrode. It is therefore thermodynamically capable of producing hydrogen gas given a source of protons. We postulate that it will be quite easy to use the energy of the reduced acridan to reduce one of the viologens (methyl viologen,

benzyl viologen, etc.) which is slightly less negative in redox potential than the acridan. It is known that reduced viologen molecules plus protons will regenerate the oxidized viologen, liberating hydrogen gas, in the presence of the enzyme hydrogenase (8).

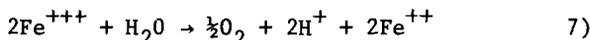
The scheme as shown is incomplete because the electron has been obtained by the conversion of Fe^{++} to Fe^{+++} and the proton source has not been shown. Obviously the Hill Reaction would be the ideal answer to this problem, but since it is unknown, we will borrow a few reactions from a proposed thermochemical hydrogen cycle to illustrate how the problem could be handled with known reactions (9):



The temperatures at which these reactions proceed are 300°C, 50 to 90°C, and 350°C respectively. Now we add three simple reactions representing crystallization and dissolution of a gas and solid:



The net result of all six reactions is therefore



Our cycle is therefore closed, the ferric ion returned to ferrous ion, oxygen liberated, and the hydrogen ions needed for hydrogen production are supplied. Such an additional set of reactions could be supplied with low grade heat from photons not used in the primary photochemical reactions.

An important consideration in successfully carrying out all of the foregoing reactions is obviously separation of the various steps. Ferric ion, a strong oxidant, certainly would react very vigorously and rapidly with the acridan or viologen, strong reductants. Fortunately, coupling the dyes and even the hydrogenase enzyme to a solid surface presents little difficulty, so the circulation of fluids over beds of solid material can be carried out readily. This is one simple expedient to separate the reactants, but of course there are others too.

In summary, an examination of the mechanisms involved in photosynthesis, of previous work on photosensitive synthetic dyes, and of some pertinent theory suggest that it should be possible to split water into hydrogen and oxygen with moderate efficiency using a significant fraction of the photons in sunlight. Considerable experimental work is needed to verify the possibility of coupling certain steps in the suggested sequence and to determine the ease with which individual reactions could be segregated to prevent undesirable energy "short-circuiting" reactions.

Acknowledgment

We are pleased to acknowledge support of this work by the National Science Foundation (Grant GK43641).

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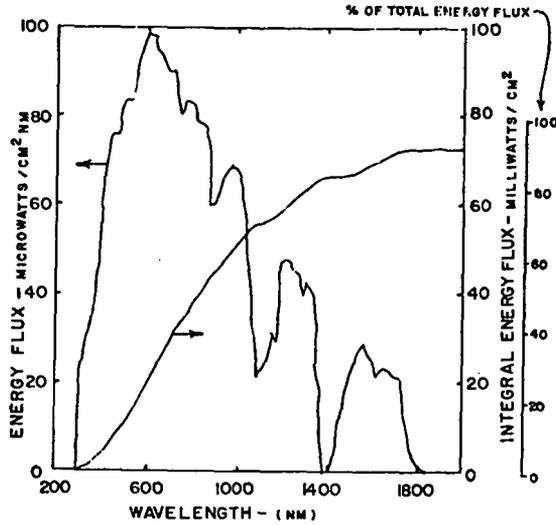


Figure 1. Solar Energy Flux at the Earth's surface (1) between 200 and 2000 nm and the integrated flux curve. About 10 percent of the total radiation has a wavelength greater than 2000 nm and is not shown.

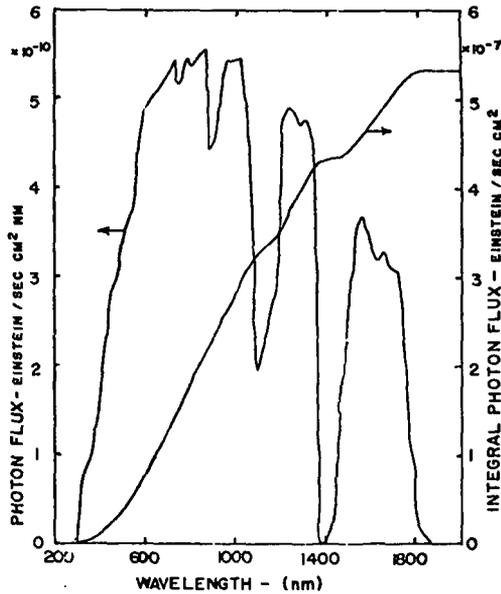


Figure 2. Photon Flux at the Earth's surface, differential and integral. This data was derived from Fig.1 using $E = h\nu$.

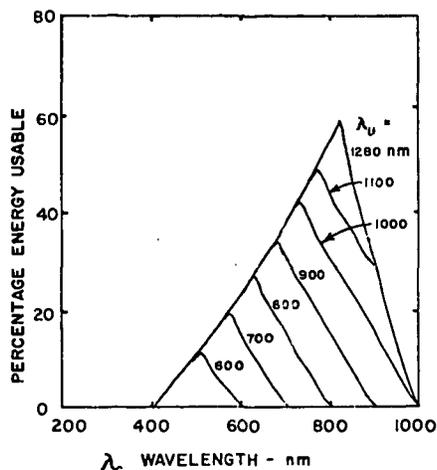


Figure 3. Percentage of the total Solar Flux which can be used in a two-photon process in which each photon is drawn from a different population. The upper cutoff wavelength (λ_u) is a parameter and the wavelength at which the change (λ_c) is the independent variable.

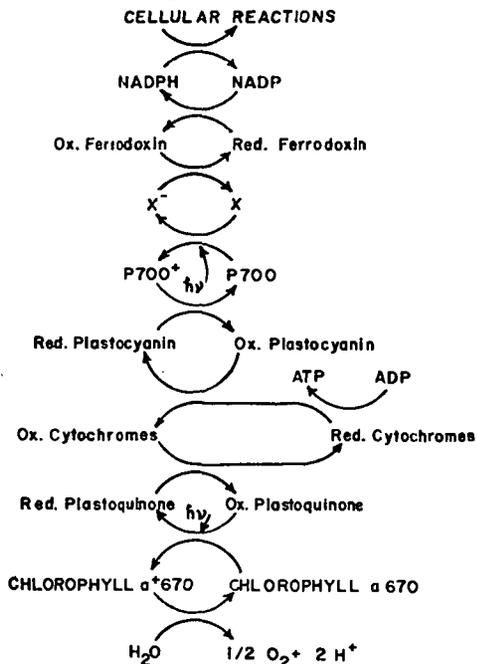


Figure 4. The coupled reactions of photosynthesis as presently understood.

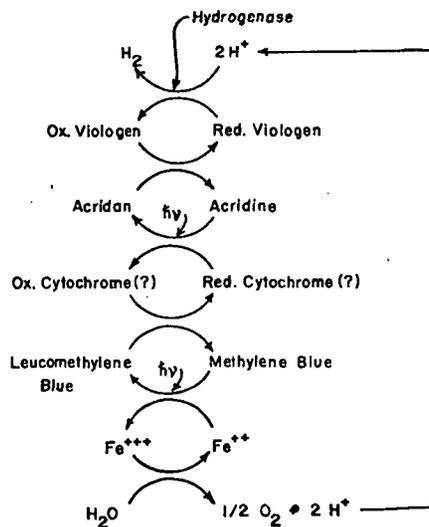


Figure 5.

The proposed photochemical cycle to split water. The ferric to ferrous conversion with attendant release of oxygen is discussed in the text.

Symposium on Unusual Fuels Production
 Division of Fuel Chemistry
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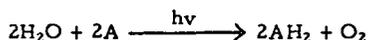
April 6-11, 1975
 Philadelphia, Pennsylvania

BIOPHOTOLYSIS OF WATER TO HYDROGEN AND OXYGEN

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The concept of the biophotolysis of water with the formation of oxygen and hydrogen is the bringing together of two biological fields of scientific endeavor, each of which has made phenomenal progress during the last decade or two. The two areas of progress referred to are: (1) a greater understanding of the molecular events which occur in photosynthesis, and (2) a greater understanding of molecular events in microbial metabolism. Although thermodynamically feasible, heretofore not much thought has been given to the possibility of biophotolysis.

The photosynthetic apparatus which consists of two photosystems operating in series can, by capturing two quanta of radiant energy, place an electron from the water-oxygen couple (+0.8 volts pH 7.0) to a negative value as much as -0.7 volt which is 0.3 volts more negative than the hydrogen electrode. A minimum of eight quanta of radiant energy are required for the following photosynthetic equation:



where A is an electron acceptor (Hill reagent). A variety of compounds may serve as Hill reagents. For the purpose of employing these photosynthetic electrons for the reduction of protons to hydrogen by the action of a bacterial hydrogenase, the acceptor must have an oxidation-reduction potential near the potential of the hydrogen electrode and in its reduced state serve as a substrate for the hydrogenase. Several anaerobic non-photosynthetic and photosynthetic bacteria form hydrogen during some of their metabolic processes. Usually the immediate precursor of electrons for the reduction of protons as catalyzed by these hydrogenases is reduced ferredoxin, a small molecular weight iron-sulfur protein. A similar species of protein although smaller in molecular weight is in the normal pathway of electron transfer in the photosynthetic apparatus. In this latter case the reduced ferredoxin reduces

triphosphopyridine nucleotide (TPN) which in turn is the source of electrons for the reduction of carbon dioxide to plant materials. With some anaerobic bacteria it has been demonstrated that reduced TPN can reduce ferredoxin with sufficient kinetics in spite of the unfavorable thermodynamic barrier of approximately 0.1 volt. The electrons of reduced ferredoxin are the precursors of hydrogen as catalyzed by the bacterial hydrogenase.

The first experiments which demonstrated the biophotolysis of water to oxygen and hydrogen consisted of a two-stage reaction mixture. The first stage employed the classical method of San Pietro and colleagues who demonstrated that spinach chloroplasts could photosynthetically reduce TPN by the oxidation of water, providing ferredoxin was present. Five μ moles of TPNH were prepared and added to the second mixture containing the components listed in Table 1.

Table 1

HYDROGEN FORMATION FROM TPNH
-- NO GENERATING SYSTEM

	<u>per ml</u>
Tris buffer pH 7.6	100.0 μ moles
Glutathione (SH)	2.0 μ moles
TPNH	5.0 μ moles
Na pyruvate	20.0 μ moles
DPN	1.0 μ moles
Lactic dehydrogenase	9 units
<i>C. kluveri</i> hydrogenase	0.4 ml
Ferredoxin	500 μ g

Total volume 10 ml, argon atmosphere, temp. 35°C

	<u>Hydrogen evolved</u> (μ moles)
15 min	3.2
30 min	3.2
45 min	3.2

The important components for this discussion are TPNH, the bacterial hydrogenase preparation from *Clostridium kluveri* and buffer. At the bottom of the table is given the quantity of hydrogen evolved from TPNH. Control experiments demonstrated that hydrogen evolution was totally dependent upon the presence of TPNH. The quantity of hydrogen is less

than the TPNH added but it could be shown that the activity of the hydrogenase was lost shortly after the beginning of the experiment. A general characteristic of hydrogenases is that they are labile, particularly to the presence of oxygen. In this case, although the experiment was conducted under an atmosphere of argon, the oxidized TPN formed from the oxidation of TPNH to hydrogen inactivated the enzyme.

In an attempt to overcome the inhibition by TPN of hydrogenase activity and the thermodynamic barrier between TPNH and the hydrogen electrode in these anaerobic bacteria, we investigated the probability of employing photosynthetic bacteria. Photosynthetic bacteria although they cannot use water as an electron source use reduced organic or inorganic substances for photosynthetic electron donors and in many cases can form hydrogen photosynthetically from these substrates. Rhodospseudomonas capsulata, a photosynthetic bacterium, can form copious quantities of hydrogen from malate under anaerobic conditions providing no elemental nitrogen or fixed forms of inorganic nitrogen are present. The photochemical systems present in spinach chloroplasts are also labile, having a short-lived mechanism for forming TPNH. The photosystems present in the blue-green alga, Anacystis nidulans, were therefore employed. Freshly harvested cells of the alga are impermeable to most organic substrates. Lyophilization under appropriate conditions render the cells permeable to several substances including TPN and photosystems I and II remain active and reasonably stable. These cells were employed to prepare reduced TPN (TPNH) photosynthetically, using water as the electron donor. No reduction of TPN occurred in the dark or in the presence of 1,1 dimethyl-3-(3,4 dichlorophenyl) urea (diuron), a specific inhibitor for photosystem II.

Lyophilized cells of R. capsulata are permeable to reduced TPN and contain a very active malate dehydrogenase. These cells by well known biochemical reactions can reduce oxalacetate to malate with the reduced TPN. In contrast to freshly harvested cells the lyophilized cells cannot photosynthetically form hydrogen from malate. With a mixture of freshly harvested cells and the lyophilized cells, small quantities of oxalacetate and substrate amounts of reduced TPN (obtained photosynthetically with the algae) hydrogen was obtained photosynthetically in quantities equivalent to the amount of reduced TPN added. For example, with 10 μ moles of TPNH, 20 mg (dry weight) freshly harvested R. capsulata, and 5.0 mg lyophilized cells in a total volume of 2 ml under an atmosphere of argon and exposed to 22,000 lux of white light, 10 μ moles of hydrogen were obtained in 45 minutes.

The events may be summarized as follows:



Omitting the microorganisms and electron carriers, the sum of the equations become:



In a one-stage experiment, by combining the following components: 40.0 mg Anacystis nidulans, 2.5 μ moles TPN, 50.0 mg (dry weight) freshly harvested R. capsulata, 12.0 mg lyophilized R. capsulata in a total volume of 5 ml under an atmosphere of argon with 175,000 lux of white light, 2 μ moles of hydrogen were formed in 30 minutes. Apparently the hydrogenase of the photosynthetic bacterium is sufficiently stable to the oxygen liberated by the photosynthetic activity of algae to form hydrogen from the photosynthetically formed TPNH.

The experiments cited here as well as other conclusively show that hydrogen can be formed by the biophotolysis of water.

A LONG-RANGE APPROACH TO THE NATURAL GAS SHORTAGE UTILIZING NONFOSSIL RENEWABLE CARBON

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INTRODUCTION

The production of substitute natural gas (SNG) from petroleum liquids, coal, and oil shale to alleviate the natural gas shortage has received considerable developmental effort. Commercial SNG processes based on these fossil feeds will undoubtedly play important roles in the future of the U.S. gas industry and help to maintain it as a methane marketer over the next few decades. But fossil feeds for the production of SNG are still finite natural resources, and ultimately depletion will occur. A very promising long-range practical solution to this problem is to convert a major source of continuously renewable nonfossil carbon to SNG.^{1,2}

One source of nonfossil carbon that has been considered is organic wastes.³ The growing environmental and pollution problems caused by the generation of organic wastes in the United States provides an opportunity to combine improved waste-disposal technology, for recycling valuable waste components into the economy, with energy recovery in the form of SNG. Table 1 summarizes the results of a recent study to survey the various types of organic wastes generated in the United States and the amounts that are collected and available for conversion to synfuels.⁴ At SNG yields per ton of dry waste of 10,000 cubic feet, about 8.8 trillion cubic feet of SNG could be produced each year if all of the wastes could be processed. This is obviously not possible; all of the wastes could not be collected for this purpose even if laws were passed requiring total collection and a concerted effort were made to achieve it. However, if total collection did occur, the amount of SNG that could be produced would still fall far short of the U.S. annual demand for natural gas, which is currently about 24 trillion cubic feet. Organic wastes offer a significant source of supplemental synfuels, but are not the total answer to fossil fuel depletion. Another source of nonfossil renewable carbon must be utilized.

The most promising source of this carbon is water- and land-based biomass produced from ambient carbon dioxide and solar energy by photosynthesis.^{1,2} Biomass is defined as all growing organic matter, such as plants, trees, grasses, and algae, and, in a real sense, is perpetually renewable. The production of SNG from low-cash-value, high-fuel-value biomass would offer a major, controllable, nonpolluting, storable source of fossil fuel substitutes. It has been estimated that 146 billion tons of biomass, most of which is wild and not controlled by man, is produced on the earth each year,⁵ so at the same SNG yield used for organic wastes above, about 1.6% of this amount of biomass would provide enough raw material to meet all of our natural gas demand. With the advanced state of U.S. agricultural practice, it is conceivable that the conversion of solar energy to SNG via biomass could be achieved to establish what might be called "A Perpetual Methane Economy."

The concept of A Perpetual Methane Economy reduces itself to the development of suitable methods for planting, growing, harvesting, transporting, and converting biomass to SNG. The purpose of this paper is to review the important factors related to the development of this concept. Although liquid fuels and syncrudes can also be produced from biomass,² they are not included in the review.

Table 1. ESTIMATES OF AVAILABLE ORGANIC WASTES, 1971

Source	Total Organic Wastes Generated	Organic Solids Available
	10 ⁶ tons/yr	
Manure	200	26.0
Urban Refuse	129	71.0
Logging and Wood Manufacturing Residues	55	5.0
Agriculture Crops and Food Wastes	390	22.6
Industrial Wastes	44	5.2
Municipal Sewage Solids	12	1.5
Miscellaneous Organic Wastes	50	5.0
Total	880	136.3
Net Oil Potential, 10 ⁶ bbl	1098	170
Net Gas for Fuel Potential, 10 ¹² CF	8.8	1.36

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SYSTEM DESIGN

The overall design of a biomass-to-SNG system depends on several parameters such as the type, size, number, and location of the biomass growth and processing areas. In the ideal case, the SNG production plants would be located in or near the biomass growth areas to minimize the cost of transporting the harvested biomass to the plants, all the nonfuel effluents of which are recycled to the growth areas. If this kind of "synfuel plantation" could be developed, it would be equivalent to an isolated system with inputs of solar radiation, air, carbon dioxide, and minimal water, and one output, SNG. A schematic design of such a system is depicted in Figure 1. The nutrients are kept within the ideal system so that the addition of external fertilizers and other materials is not necessary. Also, the environmental and disposal problems are eliminated.

Onsite production of synfuel from the biomass would be facilitated in land-based synfuel plantations and near water-based growth areas where the natural water currents might function as a transport vehicle for the biomass to move it to the conversion plant sites. The gasification plants would be strategically located onshore with respect to biomass supply, recycling, and SNG transmission or transportation facilities.

The achievement of optimum system designs will be necessary to make the manufacture of SNG from biomass a commercial reality. The scope and size of commercial SNG plantations alone will demand careful planning and total integration of each operation because any errors in design will result in operating difficulties that can seriously affect the continuity of production, efficiencies, and economics.

The risks in such a large venture will have to be minimized by evolutionary development in a logical sequence of steps, such as system synthesis, preliminary analysis, small-scale demonstration, second-stage analysis, moderate- to large-scale demonstration over a prolonged time period, final analysis and system optimization, and full-scale commercialization. The business and political problems associated with each system cannot be overlooked either, because any new industry of

this magnitude will undoubtedly have its quota of skeptics among those who can benefit from the technology. The development program must produce the information needed to prove the viability of the concept beyond any doubt.

BIOMASS PRODUCTION

In the last few decades, the production of biomass for foodstuffs applications has been significantly improved through the use of modern techniques and equipment. Higher yields and more nutritious strains of crops have been developed as a result of these advanced methods, and much of the information could be applied to the development of low-cash-value, high-fuel-value biomass for SNG production. Also, our basic knowledge of photosynthesis has advanced so that specific biomass crops and growth methods can be optimized together to improve production.

A broad range of biomass production technology is available because the crops can either be land- or water-based. Suitable crops might include certain land-based, high-yield grasses and water-based algae, which can be grown in either fresh water or seawater. The goal of any program undertaken to develop and select the best biomass forms for SNG manufacture is to choose the highest yield, highest fuel-value crops that require minimum labor during planting, growth, and harvesting, and that not only survive but thrive in most climates. Also, it is desirable to use crops that have no large-scale markets as foodstuffs or materials. As expected, no one crop meets all of the desired characteristics, but, fortunately, numerous biomass species meet many of the idealized requirements.

A preliminary assessment of biomass production as it relates to SNG has been performed, and a few in-depth studies are in progress to assist in the selection of optimum biomass forms.^{1,6} Some of the important parameters that were studied included biochemical energy transfer classification, solar energy capture efficiency, growth rate and cycles, yields, nutrient needs, water needs, carbon content and fuel value, insolation, temperature, and rainfall. These studies have attempted to quantify the relationship of these parameters and their importance in selecting the proper biomass types and production methods. It is not the purpose of this paper to review this information in detail; instead, the major conclusions will be summarized.

One major conclusion is that it appears sufficient yields of certain plants can be obtained to provide suitable raw material for conversion to large quantities of SNG. Examples of biomass that may prove to be optimum crops include land crops of Sudangrass, napiergrass, sorghum, sugarcane, sunflower, kenaf, and eucalyptus, sycamore, and poplar trees; freshwater crops of water hyacinth and the unicellular algae, Chlorella and Scenedesmus; and seawater crops such as Macrocystis pyrifera (giant kelp). Several of these crops are capable of production at yields of 20 to 30 tons dry organic matter/acre-year, and some have been reported to be produced at yields over 60 tons/acre-year. Also, the fuel values generally range from about 5000 to 8000 Btu/dry lb. These crops are believed suitable for SNG production.

Another important conclusion from these studies is that relatively large areas of land or water are needed to grow enough biomass to supply the U.S. fuel needs. For example, at a yield of 50 tons/acre-year of dry biomass, about 169,000 square miles are required at an overall thermal efficiency of conversion of 35% to SNG to replace all of the U.S. natural gas demand with SNG as indicated in Table 2.¹ This area corresponds to a square 411 miles on each edge and might be considered to be a major roadblock to commercialization of a biomass-to-synfuel industry. But, on further examination, it does not seem to be an insurmountable barrier, especially when considered in light of the problem solved. First, this area is about 5.6% of the Lower-48-State area. Idle farmland and deserts comprise about 6.4% of the Lower 48 States now. When compared with the surface areas of the oceans, a small portion of which might be devoted to biomass production, a

411-mile square seems to be an insignificant part of the whole. Also, it is possible to conceive of combined foodstuffs and biomass-for-fuel production, so some growth areas might serve dual functions. In some cases, symbiotic relationships might lead to further improvement in both biomass forms. Finally, it should be realized that the preliminary studies that have been made are based primarily on existing information. Major improvements in yield, fuel value, and other important properties might emanate from field-test programs.

Table 2. POTENTIAL SNG PRODUCTION FROM BIOMASS*

PERCENT OF PRESENT DEMAND [†]	AVERAGE AREA REQUIRED, sq miles		
	10 ton/acre-yr	25 ton/acre-yr	50 ton/acre-yr
1.66	12,000	5,000	2,800
10	72,000	30,100	17,000
50	361,500	150,500	84,500
100	723,000	301,000	169,000

*Based on indicated dry yields at overall thermal efficiency of conversion to SNG of 35% and fuel value of 6500 Btu/dry lb.

[†]Calculations based on annual demand of 22×10^{12} cubic feet.

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No field tests of any significant size are yet in progress to optimize biomass production methods and specific biomass crops for SNG manufacture. However, the U.S. Navy has announced plans to begin such a program with giant kelp off the California coast.⁷

BIOMASS CONVERSION TO SNG

Methane can be produced from biomass by digestion, pyrolysis, and hydrogasification as shown in Figure 2. Digestion is a biological process that occurs in the absence of oxygen and in the presence of anaerobic organisms at ambient pressures and at temperatures of 95^oto150^oF. The biomass is supplied to the anaerobic digesters as a water slurry and is converted to an intermediate-Btu gas (450 to 800 Btu/cubic foot) that is essentially a two-component gas containing methane and carbon dioxide. This product is easily upgraded to pipeline gas (SNG) by removal of carbon dioxide in conventional amine scrubbers or by other methods. IGT's BiogasTM Process (Figure 3) is an example of such processes.³

Biomass can also be converted to SNG by pyrolysis. Pyrolysis consists of thermal decomposition of the feed at low pressure in the 900^o to 1700^oF range. However, the initial product gas is generally a low-Btu gas (100 to 450 Btu/cubic foot) that contains low concentrations of methane and higher concentrations of carbon monoxide, carbon dioxide, and hydrogen. In addition, by-products of char and oxygenated liquids are formed; these are often used to supply the heat for the pyrolysis units. If SNG is the desired end product, the pyrolysis gas must first be adjusted in composition by "shifting" the molar ratio of hydrogen to carbon monoxide in a shift converter to about 3:1, which corresponds to the stoichiometric ratio needed to convert the carbon monoxide to methane in the methanator. The gas is then scrubbed to remove carbon dioxide, and the resulting gas, which contains methane, carbon monoxide, and hydrogen, is methanated to yield SNG. The process developed by West Virginia University for solid-waste pyrolysis should also be suitable for biomass pyrolysis.⁸

In the hydrogasification process, part of the biomass feed is first converted to hydrogen by partial oxidation or steam-reforming followed by shifting to increase the hydrogen content as high as

possible. The hydrogen-rich gas is then reacted with the remaining biomass at 500^o to 1500^oF and 500 to 2500 psi to hydrogenate it and yield a product gas high in methane. The gas is then upgraded to SNG by shifting, scrubbing, and methanating as in the pyrolysis process.

As might be expected, each of these three processes is not energetically suitable for all types of biomass. Some types of biomass, especially those in the water-based category, usually contain large quantities of intracellular water, as high as 90 to 95%. If this type of feed is pyrolyzed or hydrogasified, the water must be removed before thermal treatment, or a large amount of feed energy is consumed in the process simply in driving off the water before gasification.¹ The curves in Figure 4 illustrate the effect of moisture content on the energy available for conversion of heat-dried biomass to SNG. For example, if a biomass containing 70% moisture is heat-dried to a moisture content of 30%, only 62% of the energy content is available for conversion to SNG. Anaerobic digestion is preferred for those feeds high in moisture because the process requires large amounts of water. Air-drying of biomass is the most economical drying method if it is needed.

Table 3 lists representative examples that have been reported of methane-containing products made from various biomass plants. Available information on actual experimental data is limited because the biomass-to-synfuels concept has only recently begun to receive attention. Only a few research groups are developing data at present, but the data base is expected to expand rapidly in the near future.

Table 3. EXAMPLES OF FUEL GAS PRODUCTION FROM BIOMASS

Biomass	Conversion		Fuel Products ^a
	Reaction	Approximate Conditions	
Pine Bark ⁹	Pyrolysis	900 ^o C, ambient pressure	Low-Btu gas, char, oil ^b
Rice Straw ⁹	Pyrolysis	200 ^o -700 ^o C, ambient pressure	Low-Btu gas, char, oil ^b
Cellulose (Refuse) ¹⁰	Hydrogasification	540 ^o C, 1000 psi	High-Btu gas (after -CO ₂), char
Wood (Excelsior), Paper ¹¹	Digestion	30 ^o C, 30 days	Intermediate-Btu gas
Grass ¹²	Digestion	48 ^o C, 10-28 days	Intermediate-Btu gas
Water Hyacinth ^{c, 12}	Digestion ^d	48 ^o C, 28 days	Intermediate-Btu gas
Seaweed Algae ^{e, 12}	Digestion	33 ^o and 48 ^o C, 20-50 days	Intermediate-Btu gas
Unicellular Algae ^{f, 13}	Digestion	35 ^o and 55 ^o C, 30 days	Intermediate-Btu gas

^aLow-Btu gas, 100-450 Btu/CF; intermediate-Btu gas, 450-800 Btu/CF; high-Btu gas, >800 Btu/CF.

^bMinor product.

^c*Eichhornia crassipes*.

^dAfter caustic treatment.

^e*Macrocystis pyrifera*; commonly called giant kelp; grown in seawater.

^fPrincipally *Scenedesmus* spp. and *Chlorella* spp.; grown in fresh water.

ECONOMICS AND ENERGETICS

The economics of biomass conversion to SNG are in a preliminary stage of development. However, some idea of the cost structure can be obtained from existing information. Table 4 illustrates the energy cost of several selected biomass species. With the exception of the edible portion of corn,

whose energy cost was calculated from current market prices, the price range varies from \$0.42 to \$1.88/million Btu, which places biomass energy in a range competitive with the current costs of fossil fuel energy. Of course, the cost of converting biomass to SNG must be added to the biomass energy costs.

Table 4. SELECTED COST ESTIMATES OF BIOMASS ENERGY

Biomass	Yield, dry tons/acre-yr	Fuel Value, Btu/dry lb	Estimated Cost, \$/10 ⁶ Btu
Corn	2.27*	6,500*	9.70 [†]
Corn Silage ¹⁵	15.9	6,500	1.31
Corn Silage ¹⁵	6.5	6,500	1.88
Conifer ¹⁵	—	7,000	1.25-1.75
Poplar ¹⁵	10	7,800	0.90-1.00
Sugarcane ⁶	25	7,500	0.63
Kenaf ⁶	20	7,500	0.61
Kenaf ⁶	6	7,500	1.40
Land or Water Based ¹	20	8,000	0.79-1.46 [‡]
Land or Water Based ¹	50	8,000	0.42-0.87 [‡]
Land Based ⁶	30	7,500	0.65

*Assumed values based on current yield and market information.¹⁴

[†]Calculated from assumed values and market price of \$3.53 per bushel of No. 2 yellow corn (Chicago).¹⁴

[‡]Calculated from Table 11 in Reference 1.

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A few cost estimates have been reported on the conversion of biomass to SNG as shown in Table 5. There is a wide diversity of plant sizes, conversion efficiencies, and capital requirements in this particular tabulation, but the SNG price ranges from only \$0.73 to \$3.50/million Btu. One of the available SNG-from-coal projections is also included in this table for comparison.

An interesting factor in the production of biomass alluded to in Table 4 concerns the energy budget of the system, i.e., the total energy into the system and the product energy returned. Few studies of this type have been made. One of the in-depth studies computed the energy budget of U.S. corn production and included all of the nonsolar energy inputs into the system such as electric power, equipment fuels, and the energy needed to manufacture ammonia fertilizer which is made primarily from natural-gas-derived synthesis gas.¹⁷ Some of the information developed in this study has been converted to thermal energy production efficiency (energy in/energy out) and nonsolar energy input/lb of corn produced and plotted versus year (Figure 5). Less energy was expended to produce a pound of corn in 1940, which means that the energy input is utilized less efficiently today.

This kind of energy budget treatment is directly related to SNG because one of the important factors that has largely been ignored in the development of new energy supplies concerns the net

Table 5. PRELIMINARY COST ESTIMATES OF BIOMASS-DERIVED SNG

Biomass	Biomass Yield, dry ton/acre-yr	Biomass Fuel Value, Btu/dry lb	Gasification Process	SNG Production, CF/day	Area Required, acre	Eff. % ^b	Capital Requirement, \$	SNG Cost, \$/10 ⁶ Btu
Land or Water Based ¹	20	8,000	Digestion	1.0×10^{12} ^a	3.26×10^6	35	1.6×10^9	1.10-1.77
Land or Water Based ¹	50	8,000	Digestion	1.0×10^{12} ^a	1.30×10^6	35	0.98×10^9	0.73-1.17
Giant Kelp, Floating ^{1b}	2.8 ^b	5,160 ^c	Digestion	3.56×10^{12} ^d	64.0×10^6	70	5.0×10^9	2.48
Giant Kelp, Anchored ^{1c}	49	5,160	Digestion	19.2×10^{12}	22.4×10^6	62	105×10^9	3.50
Land Based ^b	30	7,500	Air Dry, Pyrolysis	76.0×10^{12} ^a	89.6×10^3	69	0.325×10^9	2.09
Coal ^e	-	-	Hydro- gasification	250×10^6	-	-	0.350×10^9	1.61

^aBiomass is assumed to be gasified onsite at growth area, transportation costs of biomass and SNG not included.

^bCalculated from referenced area of 250 miles x 400 miles in which it was estimated that 80% of kelp is harvested.

^cCalculated from referenced information which indicates kelp yield of 1.8×10^8 dry tons/yr, conversion of 70% of its energy content to SNG, and SNG yield of 1.3×10^3 CF/yr.

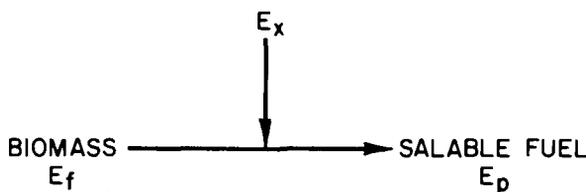
^dAs liquefied SNG.

^eCalculated from ratio of energy produced as SNG and fuel value of biomass feed: $100 E_p/E_f$.

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energetics of the system. * Valid comparisons of different systems cannot result from only synfuel cost estimates and capital and operating cost projections; these factors do not necessarily correlate with net energy production. Nor can valid comparisons be made simply by calculating the thermal efficiency or the energy in and out of a process. All of the energy inputs involved in planting, harvesting, transportation, fuel production, and recycling of product streams should be considered. It is essential that these factors be lumped together with economics in the fully integrated system. Since the primary objective is to produce new fuel supplies, more fossil fuel substitutes must be produced as salable end products than the fossil fuels consumed in the system. Even then, the selection of the best of several systems is a difficult one to make.

For example, let E_f , E_x , and E_p represent the energy content of the dry biomass, the sum of the external nonsolar energy inputs into the total system, and the energy content of salable fuels, respectively. Diagrammatically, the system can be represented as follows:



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Then the ratio, $(E_p - E_x)/E_x$, which can be termed the Net Energy Production Ratio, indicates how much more (or less) salable fuel energy is produced than that consumed in the integrated system if the external energy consumed is replaced, and it is assumed that the biomass feed energy is zero. This is a reasonable assumption because the energy value of the biomass is derived essentially 100% from solar radiation. Net Energy Production Ratios greater than zero indicate that an amount of energy equivalent to the sum of the external energy inputs and an additional energy increment of salable fuel are produced; the larger the ratio, the larger the increment. The ratio $100 E_p/E_f$ is the Fuel Yield Efficiency and is a measure of how much biomass energy is diverted to other than salable fuels in the system. The ratio $100 E_p/(E_f + E_x)$ is the overall Fuel Production Efficiency of the system.

*The rationale presented here is also applicable to synfuels from fossil feeds.

In Table 6, a comparison of selected end product costs, as either SNG or biomass energy, and the calculated Net Energy Production Ratio for each end product is presented. A correlation exists between these ratios and the biomass energy costs listed, namely, the higher the energy cost, the lower the ratio. However, the corresponding correlation does not apply to the listed SNG cases. The Net Energy Production Ratio is therefore a useful tool when considered together with the energy costs to evaluate synfuel systems and, especially, to bring out the importance of the external energy inputs.

Table 6. COMPARISON OF ESTIMATED END PRODUCT COST AND NET ENERGY PRODUCTION RATIO

Biomass	Conversion Process	Fuel Efficiency Yield, % ^a	End Product	End Product Cost, \$/10 ⁶ Btu	Net Energy Production Ratio ^b
Rice (U.S.A.) ^{18, 19}	None	-	Rice	26.70 ^c	0.67 to 0.80 ^e
Corn (U.S.A.) ¹⁷	None	-	Corn	9.70 ^d	1.82 ^f
Giant Kelp, Floating ¹⁶	Digestion	70	LNG	2.48	5.07 ^g
Land Based ⁶	None	-	Biomass	0.65	17.40 ^h
Land Based ⁶	Air Dry, Pyrolysis	69	SNG	2.09	2.34 ⁱ
Land or Water Based ²⁰	Digestion	35	SNG	0.73 to 1.77	3.79 ^j

^a100 E_p/E_r

^b(E_p - E_x)/E_x

^cAverage price of \$20.00/100 lb and 7500 Btu/dry lb assumed.

^dFrom Table 4.

^eCalculated from References 18 and 19 that state that 1/5 to 1/3 of energy input returned as end product. NEPR = (0.2 - 1.0)/1.0, and (0.33 - 1.0)/1.0.

^fCalculated from in-depth analysis in Reference 17 for year 1970 that states that 2.82 kcal returned/kcal input; NEPR = (2.82 - 1.0)/1.0.

^gCalculated from Table 1 in Reference 6 utilizing reported estimate that 16.48% of end product fuel content consumed by system; NEPR = (1.0 - 0.1648)/0.1648.

^hCalculated from Table 5, p. 51, in Reference 6, using reported estimate that total energy yield for case analyzed was 45 X 10⁷ Btu out and 2.45 X 10⁷ Btu consumed; NEPR = (45 - 2.45)/2.45.

ⁱCalculated from conditions assumed in Reference 6: 5.6% biomass energy content required as energy input in growth phase, 15.0% of biomass energy content required as energy input on gasification, and Fuel Yield Efficiency of 69.0%; NEPR = (0.69 - 0.206)/0.206.

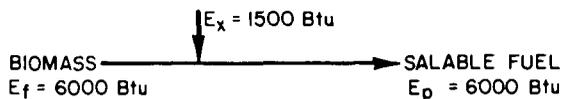
^jCalculated from conditions assumed in Reference 20 for waste conversion in which 2.7% of feed energy equivalent required as external energy input on gasification, Fuel Yield Efficiency is 35%, and assuming 5.6% of biomass energy content is required as energy input in growth phase as in Reference 6; NEPR = (0.35 - 0.073)/0.073.

8-124-2161

For biomass having an energy content of 6000 Btu/dry lb, a plot of Net Energy Production Ratio versus the total external energy input as a percentage of the feed energy equivalent (100 E_x/E_r) provides the two curves shown in Figure 6 for Fuel Yield Efficiencies of 66.6% and 100%. If the following two systems selected from Figure 6 are compared, which is preferred?

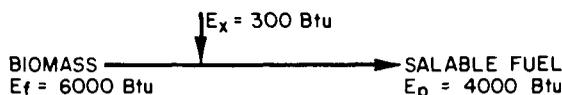
Is the first system preferable because it has a higher Fuel Production Efficiency, or is the second system preferable because it has a higher Net Energy Production Ratio? Consideration of this kind of information in conjunction with economics is necessary to make an intelligent choice. Also, in this simplified treatment, the boundary is not drawn regarding the size of the system. Thus, tractors may be used to plant and harvest biomass. The fuel requirements of the tractors are certainly part of E_x, but is the energy expended in manufacturing the tractors also part of E_x? In-depth studies are necessary to decide these questions.

ENERGETICS OF TWO SELECTED SYSTEMS



$$(E_p - E_x)/E_x = 3.0$$

$$100 E_p/(E_f + E_x) = 80\%$$



$$(E_p - E_x)/E_x = 12.3$$

$$100 E_p/(E_f + E_x) = 63\%$$

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SUMMARY

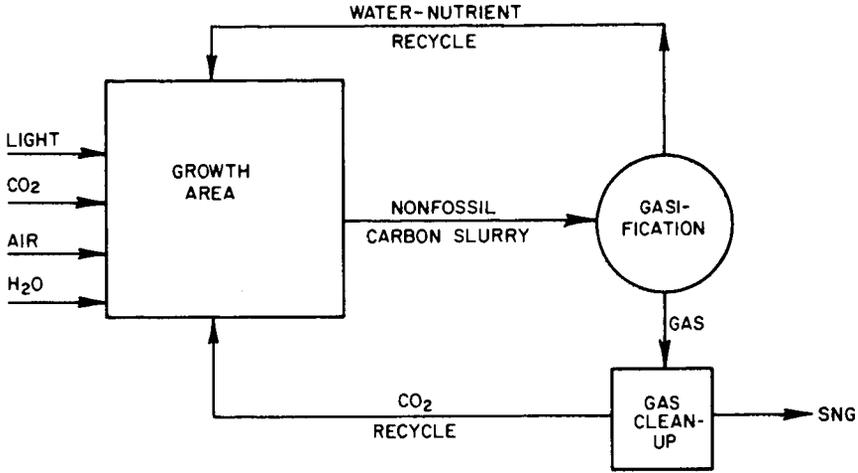
The concept reviewed in this paper to attain A Perpetual Methane Economy by conversion of biomass to SNG is technically feasible. After suitable development, the commercialization of an SNG industry using low-cash-value, high-fuel-value biomass raw materials will probably be economically attractive and permit conservation of our valuable fossil fuel reserves. Since the basic technology is already on hand, large-scale programs to refine the technology and to develop intergrated systems should be started without delay before fossil fuel depletion causes greater energy supply problems.

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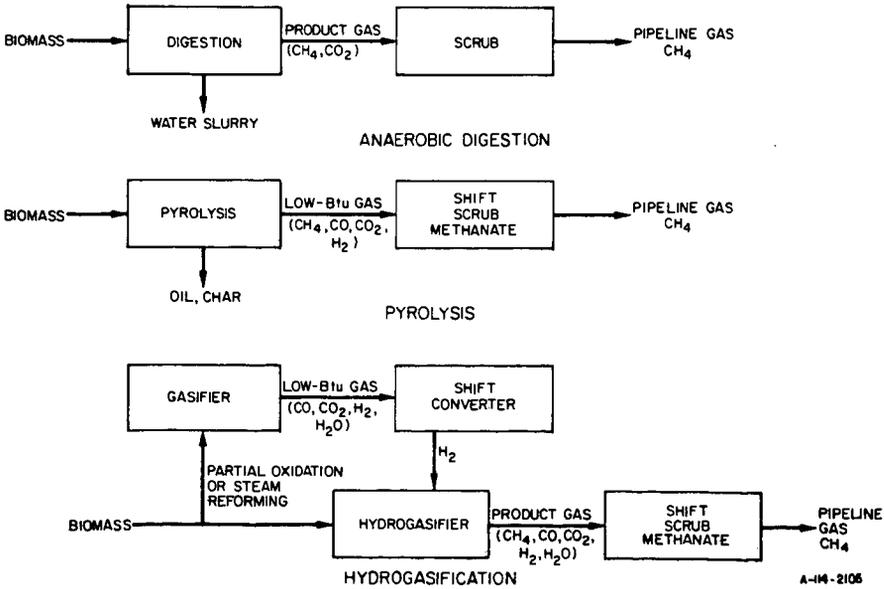
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FIG. 1. SCHEMATIC DIAGRAM OF BIOMASS-TO-SNG SYSTEM



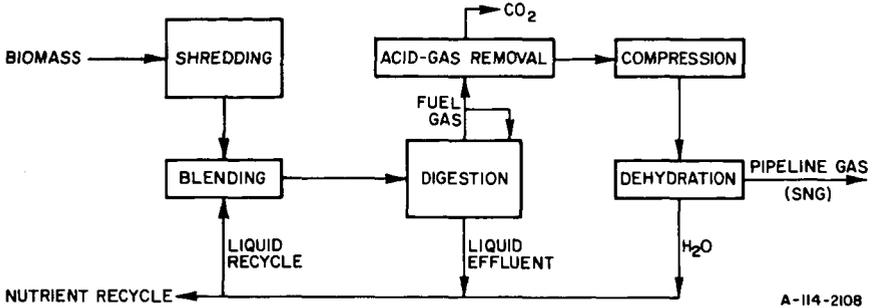
A-53-762

FIG. 2. SCHEMATIC DIAGRAM OF THE THREE PRINCIPAL METHODS OF METHANE PRODUCTION FROM BIOMASS



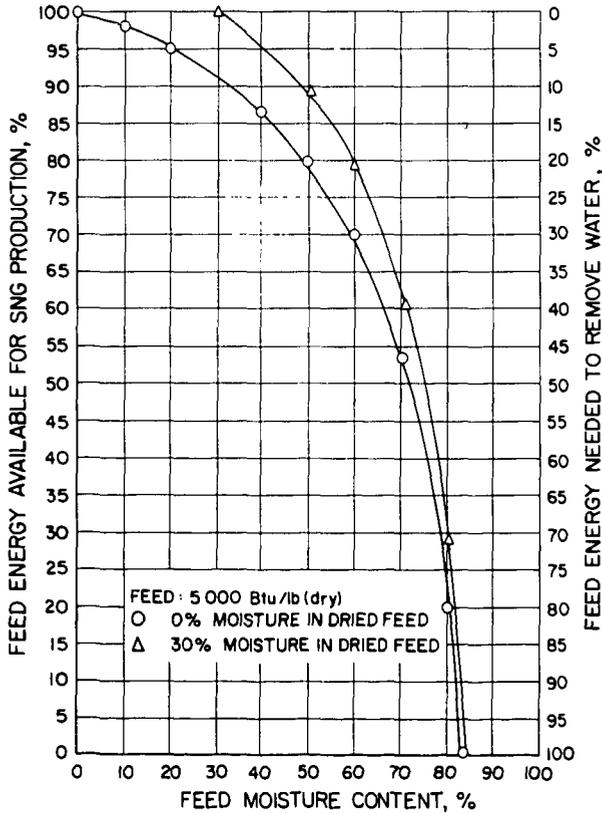
A-14-2106

Fig. 3. EXAMPLE OF BIOGAS™ PROCESS DESIGN USING BIOMASS FEEDS



A-114-2108

Fig. 4. EFFECT OF FEED MOISTURE CONTENT ON ENERGY AVAILABLE FOR SNG PRODUCTION



A-114-2110

Fig. 5. THERMAL ENERGY PRODUCTION EFFICIENCY AND ENERGY INPUT FOR U.S. CORN FROM 1945 TO 1970

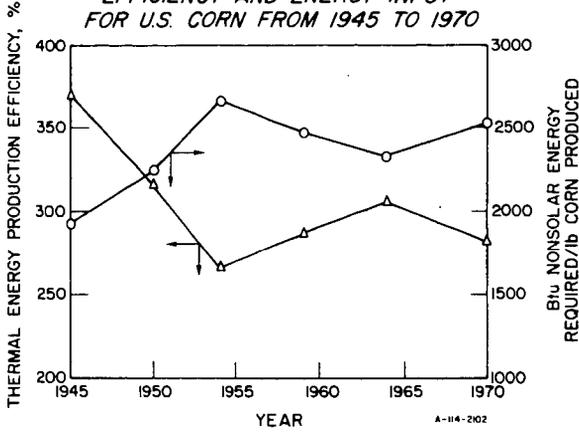
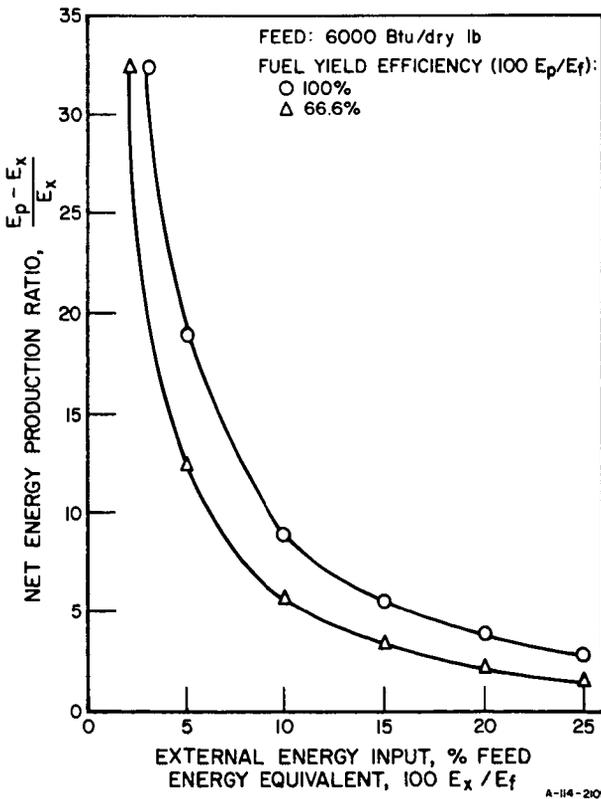


Fig. 6. NET ENERGY PRODUCTION RATIO vs. EXTERNAL ENERGY INPUT



METHANOL OR AMMONIA PRODUCTION FROM SOLID WASTES
BY THE CITY OF SEATTLE

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I. INTRODUCTION

Solid waste disposal on an acceptable environmental and cost basis is one of the most nagging, costly, and unpleasant problems facing Seattle and other cities in America. Escalating costs for disposal labor and transportation and the difficulty of finding suitable landfill sites has caused what was simply an unhandy problem a decade ago to become a major problem for the City.

In the 1960's, the federal government and industry began to emphasize development of major new alternatives to the historic methods of solid waste disposal. A number of new handling and disposal methods have reached development maturity and are available for application. The past decade has also seen widespread acceptance of the fact that affluence and waste need no longer be synonymous. Terms like "recycling" and "urban ore" typify a changing attitude toward what was once simply garbage. Public demands for environmental reform, prudent land use, and economy in public services, have all simultaneously crested in a time of fuel cost increases, power shortages, and a recognition that terrestrial resources are finite.

In this context, the Mayor of Seattle and the Chairman of the Utilities Committee of the Seattle City Council, in December of 1973, commissioned the Engineering and Lighting Departments of Seattle to aggressively undertake a program of utilizing the latent material and energy potential of Seattle's municipal solid wastes.

In May of 1974, an interdepartmental report appropriately titled *SEATTLE'S SOLID WASTES...AN UNTAPPED RESOURCE* (1) was presented to the Mayor with the revelation that of numerous solid waste disposal options, the conversion of solid waste to methanol, as suggested by T. Reed (2,3), appeared to be the most environmentally advantageous and economical. Table 1 summarizes the comparative economic findings of the Seattle study.

Briefly stated, all practical disposal alternatives except conversion to methanol or to a bulk confetti-like air-classified fuel, were found to be as costly or more costly for Seattle than continued waste disposal in landfills. It was later found that the bulk fuel alternative is impractical, leaving methanol production as the most promising alternative from an economic standpoint. Conversion of waste into methanol may also be a method for achieving fuel independence for the City's motor fleet and a modest reduction of air pollution from City vehicles. These potential benefits, plus the opportunity for eliminating dependence on landfills, except for inert materials, caused the City to undertake more intensive investigations of the feasibility of solid waste conversion.

In June of 1974, the Seattle firm of Mathematical Sciences Northwest, Inc. (MSNW), was retained to do an intensive study of the technical feasibility, economics, and environmental impact of conversion of Seattle solid waste to methanol, and use of methanol as a vehicle fuel. (4) The MSNW study confirmed that the proposed conversion process was technically feasible; however, neither the quantity of methanol produced nor the system economics were found to be as attractive as

initially believed. Nevertheless, the process still showed promise as being superior to landfill. In addition, the study disclosed an opportunity for using the same basic technologies for the manufacture of ammonia. These findings, plus further verification that methanol is a potentially practical automotive fuel (5,6,7), have caused the City of Seattle to intensify project planning.

II. PROCESS DESCRIPTION

The process as envisioned for the City consists of grinding the solid waste to make it more convenient to convey and pyrolyze. Following coarse grinding, ferrous materials are removed magnetically, following which the remaining residues--paper, wood, glass, yard wastes, domestic wastes, organics, and plastics--are charged into a pyrolysis system.

There are several pyrolysis systems currently being developed. One system that is in the late stages of large scale and successful demonstration is the Union Carbide Corporation's Purox system (8). In this system, solid waste is charged into the top of a structure similar to a blast furnace. As the solid waste migrates downward, it is heated by rising gases generated from the oxidation of residues at the bottom of the vessel. This hot gas permeates upward through the solid waste, providing the necessary heat for the conversion of the cellulosic materials into additional carbon monoxide plus hydrogen. The gas leaving the top of the reactor, which consists largely of carbon monoxide, hydrogen, and water vapor, is then processed through a closed gas-cleaning system in which water and other impurities are trapped. The product gas leaving the system consists of approximately two-parts carbon monoxide to one-part hydrogen plus impurities.

The first step for subsequent treatment of the gas as currently envisioned is an absorption process to remove sulfur compounds and convert the sulfur to its elemental state. This is to be done for pollution control reasons and to protect the catalysts used in subsequent synthesis operations. The objective of this step should be to achieve a gas concentration of 0.5 ppm or less sulfur. Following this step, a water-gas shift is employed to alter the carbon monoxide-hydrogen ratio. In this traditional process, steam is added to the gas stream in the presence of a catalyst and under appropriate pressure and temperature conditions. The quantity of hydrogen and carbon dioxide in the inlet clean gas is approximately doubled and halved, respectively, so that the shifted gas has a composition of about one-part carbon monoxide to two-parts hydrogen, the stoichiometric ratio required for methanol synthesis. The amount of carbon dioxide produced in the shift reaction is large and must be purged down prior to the synthesis step.

The product synthesis step, while requiring complex equipment, is relatively straightforward. Under conditions of heat and pressure and in the presence of a catalyst, the carbon monoxide and hydrogen are spontaneously combined into methanol. Alternatively, the shift reactor may be designed to more completely shift carbon monoxide in the inlet gas to carbon dioxide and hydrogen. The hydrogen, in combination with nitrogen, may then be reacted by the traditional method, using catalysts, to produce ammonia gas. By-product nitrogen resulting from oxygen production in the head-end pyrolysis step is more than sufficient to meet the requirements of ammonia synthesis in this case.

The product yields computed in this study were 370 pounds of methanol per ton of solid waste, or 445 pounds of ammonia per ton of solid waste. On an annual basis, these amounts represent potential yields of approximately 100,000 tons of methanol per year (31-million gallons per year) or 120,000 tons of ammonia per year, starting from 550,000 tons per year of municipal solid waste. While these amounts of chemical products seem large to city government, they represent only a small percentage of national production for these products. What is of interest, of course, is that they represent potential revenues with which to reduce the future cost of solid waste disposal.

Both the methanol and ammonia processes are established commercial processes. The raw material now used for their manufacture is primarily natural gas. In the context of fuel conservation, then, the production of chemical methanol or ammonia from solid waste represents conservation of natural gas which might otherwise have been used for these products. The Btu content of the products was found to exceed the external energy required by a factor of 2.5 to 3.0, depending on the product. This factor is measured at the plant boundary; the overall energy balance of the process may be positive or negative, depending upon the ultimate product uses and related thermal efficiencies.

III. PROJECT ECONOMICS

Solid waste disposal - not chemical production - is the project's primary purpose. Therefore, the project financial target to equal or beat is the combined cost of long-haul transport and sanitary landfill operations. In Seattle, this combined cost is currently \$4.90 per ton and projected to increase significantly by 1978. The indifference point for this project is that situation prevailing when the pyrolysis facility and the chemical synthesis plant operate at an annual net cost of \$3.3 million per year (1978). This will be the cost to the City if landfill disposal is continued. From a project accounting standpoint, a revenue credit can be made to the project for disposal service in an amount equal to what conventional disposal would have cost. This credit is expressed in Table 2 as a "disposal gain" of \$3.3 million.

Obviously, the financial feasibility of the project is dependent upon product prices. Based on late 1974 prices (\$0.38/gallon for methanol and \$150/ton for ammonia), one may postulate that with the diminishing supply and rising cost of natural gas (the usual feedstock for such plants), either plant alternative offers the definite possibility of significantly bettering the marginal economics indicated above. For example, a price of \$0.44/gallon for methanol or \$130/ton for ammonia would entirely offset the disposal gain, yielding free solid waste disposal (1978). Even more favorable prices were developed using assumed escalation values over the entire project lifetime. Such expectations are not unrealistic and should leave an attractive profit margin for any industrial participant in the project. The reliability of solid waste supply and the potential advantage of City financing of the project makes it a potentially attractive product source for the private sector. In assessing product risk, one must consider preservation of the cellulose content of solid waste. If that content were to decrease as a result of paper being extracted from the solid waste supply stream, product production would suffer. A decrease in cellulose feed results in more than a proportional loss in the methanol or ammonia production rate.

IV. CITY BENEFITS AND CONSIDERATIONS

Solid waste disposal cost is a major consideration to any city contemplating a change in its disposal system. Most professionals in solid waste management view any change as inevitably more costly simply because until recent years, that has been the history of the industry.

Recent rapid changes in the economics of energy--the rising cost and scarcity of fuel for long-haul disposal plus the greater opportunities for entering the energy marketplace as an energy producer--have begun to change that traditional view of disposal economics. This is occurring at a time when public attitudes toward landfill disposal are bordering on hostility because of the environmental and land use compromises that characterize such operations.

Another lesson learned by city governments during the 1973/1974 oil shortage is that public services are dependent on automotive fuel. The City of Seattle, for example, found itself with only 60 percent of its usual gasoline for City

fleet use, and in the minds of many City officials, the situation bordered on one of City government being unable to provide adequate public services. With this memory still fresh in mind and with the possibility of future fuel supply interruptions and even higher fuel prices, there is genuine appeal to the concept of City fuel independence by way of fleet conversion to 100 percent methanol made from municipal solid wastes. Studies performed to date indicate technical feasibility and a need for a fleet testing program to define vehicle conversion requirements and to confirm estimated vehicle performance parameters.

A modest reduction in urban air pollution is another benefit that can be realized from the utilization of methanol as an automotive fuel. (5,6) While the improvement may be minor, it is nevertheless a step in the right direction.

Clearly, there are significant incentives and benefits inherent in a solid waste disposal process that yields either methanol or ammonia.

- Cessation or reduction of landfill disposal.
- Potentially attractive economics.
- City fuel independence and reliability of public services.
- Fuel conservation.
- Reduced urban air pollution.

Preliminary studies show that the recovery plant can be sited next to one of the City's large transfer stations. Neutralization of several plant waste liquid streams will be required for discharge into the regional liquid waste system. Current air pollution standards can be met and noise levels are not expected to exceed 65 dBA at the plant boundary, a level of noise within proposed City standards.

V. SYSTEM APPLICABILITY ELSEWHERE

The question frequently arises as to possible widespread use of "The Seattle Concept." In an earlier paper (9), one of the authors projected the potential national benefits of converting municipal wastes to methanol in terms of equivalent automotive fuel and imported crude oil. That projection assumed that 70 percent of all municipal solid waste could ultimately find its way into conversion to methanol and, that product yield (if all were used as automotive fuel) could displace 150-million barrels per year of imported crude oil, for a national balance of trade saving in excess of a billion dollars per year. Aside from the fact that calculated product yields were probably too high, there is legitimate reason to question whether such wide use of the process is likely to be undertaken.

The environmental and energy appeal of converting wastes to methanol or ammonia tend to confuse the practical realities of solid waste disposal. The energy profile of every city is different, and conversion of waste to these products is not likely to be the best solution in every case. The use of solid waste for steam and power generation is an established technology, and where pulverized coal is now used in existing urban plants on a year-around basis, it makes economic and environmental sense to follow the lead of the City of St. Louis and the Union Electric Company where pulverized and air-classified solid waste fuel is suspension-fired in base-load electric utility boilers. Similarly, the Baltimore Landguard installation, where steam is generated from a pyrolysis process and displaces steam that would otherwise have been generated by burning oil in an urban power plant, makes both financial and environmental sense. (10) In both of these cities, electric power demands are heavy during the Summer when solid waste generation is greatest. Also, fossil-powered plants are located close to the source of solid waste. In situations such as these, the economics of producing methanol or ammonia may be less attractive than steam or power generation, at least in the

near future. In arid areas where there is ample land for landfill disposal and the hazards of leachate are minimal, relatively little incentive may exist--except the ethical matter of resource conservation--for a city to undertake any energy recovery system, particularly one as unfamiliar to the lay public as conversion to methanol or ammonia. The studies on which this paper are based also considered the possibility of installing facilities to pyrolyze solid waste coupled with sale of the clean gas for direct fuel use, thus avoiding the expense of chemical synthesis plant installation. In this case, markets for the clean gas were not identified. In other locales, where customers for the fuel gas exist close to the pyrolysis plant, this solution may prove optimal. Clearly, every city must determine the best solution in the light of its own particular circumstance.

Seattle is situated in a region that utilizes methanol in its wood products industry and ammonia for agriculture. Electric utility loads are minimum in Summer when solid waste generation is maximum and, in most years, hydropower is more than adequate to satisfy demands for electricity through much of the year. Therefore, a process leading to the generation of electricity does not appear to be competitive at this time. Moreover, large close-in fossil-fuel power plants suitable for solid waste combustion are nonexistent. Another factor that enhances the economics of methanol or ammonia conversion processes in this area is that both products are imported at considerable cost (methanol from the Gulf Coast, ammonia from Alaska). Also, ammonia and related fertilizer products are dependent primarily on natural gas which is experiencing dramatic price increases and declining availability. Simply stated, Seattle's situation appears to be tailor-made for the concept of converting solid waste to either methanol or ammonia.

VI. SUMMARY

The utilization of municipal solid waste as feedstock for the manufacture of either methanol or ammonia has been found to be technically feasible for the City of Seattle. Further effort is underway to confirm the initial findings of economic feasibility. Such an installation should reduce future disposal costs while simultaneously providing the City with a source of methanol for City motor fleet use. The use of methanol for vehicle fuel will assure continuity of public services during periods of fuel shortages and aid in reducing urban air pollution. After diverting 6,000,000 gallons per year of methanol for City fleet use, 25,000,000 gallons per year of methanol, or 100,000 tons per year of ammonia can be made available for marketing through existing commercial channels. The suitability of this process for other cities depends upon local energy and product markets which must be carefully analyzed on a case-by-case basis.

The list of those academic and industry people who willingly and generously shared their knowledge and offered encouragement for this project, especially during its embryonic stages, would be too long to include here. This opportunity is taken to extend appreciation to them as a group for their important contributions to the Seattle studies.

TABLE 1
SUMMARY OF DISPOSAL ALTERNATIVES¹

SYSTEM ALTERNATIVE (1)	NET OVERALL DISPOSAL COST \$/TON (2)
A. Unprocessed Solid Waste Steam-Electric Plant	-16.10
B. Processed Solid Waste Steam-Electric Plant	-13.77
C. Processed Solid Waste/Pulverized Coal Steam-Electric Plant 60,000 KW	-15.62
D. Processed Solid Waste/Pulverized Coal Steam-Electric Plant 100,000 KW	-18.62
E. Processed Solid Waste/Pulverized Coal Steam-Electric Plant 200,000 KW	-25.97
F. Processed Solid Waste/Existing Coal Fired Steam-Electric Plant (Centralia, Washington)	- 6.30
G. Unprocessed Solid Waste Steam Plant (Steam Only)	- 8.15
H. Processed Solid Waste Steam Plant (Steam Only)	- 7.62
I. Processed Solid Waste Pyrolysis Gas Turbine-Electric Plant	-11.07
J-1. Limited Solid Waste Processing Pyrolysis-Oxidation-Gas Turbine-Electric Plant	-10.92
J-2. Processed Solid Waste Pyrolysis-Oxidation-Gas Turbine-Electric Plant	- 9.97
K-1. Limited Solid Waste Processing Pyrolysis-Oxidation System for Methanol Production	- 0.32
K-2. Processed Solid Waste Pyrolysis-Oxidation System for Methanol Production	+ 0.63
L. Processed Solid Waste as a Marketable Fuel	+ 1.03*
M. Unprocessed Solid Waste Landfill Disposal No Energy Recovery	- 7.90

¹City of Seattle, "Seattle's Solid Waste...An Untapped Resource," May, 1974.

*NOTE: Does not include haul cost.

TABLE 2

MARGINAL OR "BREAK-EVEN" ECONOMICS OF SEATTLE SOLID WASTE
METHANOL OR AMMONIA PROJECT (1978)

(1)	METHANOL PLANT (2)	AMMONIA PLANT (3)
Plant Nominal Product Size	300 T/Day	350 T/Day
Annual Product Yield	100,000 T/Year (31,000,000 Ga1/Yr)	120,000 T/Year
<u>CAPITAL COST¹</u>	\$ 56,000,000	\$ 65,000,000
Debt Service ²	6,600,000	7,500,000
Operation and Maintenance	<u>7,100,000</u>	<u>8,100,000</u>
<u>FIRST-YEAR COSTS</u>	\$ 13,700,000	\$ 15,600,000
Product Sales	\$ 10,400,000	\$ 12,300,000
Disposal Gain ³	<u>3,300,000</u>	<u>3,300,000</u>
	\$ 13,700,000	\$ 15,600,000
Marginal (Break-Even) Product Price, First Year	33.6¢/Ga1	\$103/Ton

¹Gasifiers, gas cleanup, shift process, synthesis plant, site, tankage, and associated facilities.

²15-year life, 8% interest.

³Disposal cost for equivalent transport and landfill.

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- (10) The Landguard process is a proprietary process of the Monsanto Corporation of St. Louis, Missouri.

PRODUCTION OF ETHANOL AND VEGETABLE
PROTEIN BY GRAIN FERMENTATION

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INTRODUCTION

Since the end of World War II the use of synthetic ethanol for industrial purposes in the United States has grown at a steady pace displacing ethanol produced by the fermentation of grain and molasses. In 1970 less than 5% of the U.S. industrial ethanol was produced by fermentation. Because of FDA regulations that require ethanol for human consumption be produced by the fermentation of grain, fruit or sugar, the synthetic ethanol industry has not penetrated the beverage market. In 1972 approximately 37 million bushels of grain were fermented to produce 94.2 million gallons of ethanol expressed as 200°proof (100%) alcohol. During the same year approximately 241 million gallons of ethanol (as 200°proof) were produced synthetically from ethylene and ethyl sulfate. The bulk of the ethanol consumed by industry outside of the United States is produced by fermentation of fruit, grain, and molasses. In 1972, 800 million gallons of fermentation ethanol (as 200°proof) were consumed by industry outside of the U.S.A.

Synthetic ethanol has had a very stable price history. Between 1959 and 1969 the price was 52¢/gallon for 190°proof alcohol. In 1970 the price increased to 54¢/gallon and remained there into 1973. 200°proof synthetic ethanol typically costs 7¢/gallon more than 190°proof. These prices are quoted without the federal beverage alcohol tax.

The dramatic increase in the price of energy which came about in late 1973 has caused the price of ethylene to increase sharply. This in turn has caused a substantial price increase for synthetic ethyl alcohol. An estimate of the 1974 price for synthetic ethanol is shown in Table I. The increase in fuel prices added 10.3¢/gallon to the alcohol cost and the increase in the price of ethylene has added another 28.7¢/gallon to the cost bringing the 1974 price to \$1/gallon. Actual quotations on tank car prices of synthetic ethanol have been difficult to obtain. Two major producers of synthetic ethanol, Exxon Corporation and Tennessee Eastman, have announced that their synthetic ethanol plants would be shut down at the end of 1974. These plants represent about 22% of the U.S. synthetic ethanol production capacity.

The price of ethanol produced by fermentation in the beverage trade is not generally available. A rough estimate can be made if we consider that a fifth of 80°proof vodka sells for as little as \$2.79 including the federal alcohol tax. If one deducts the taxes and, recognizing that vodka is only a 40% blend of ethanol and water, corrects the price to pure ethanol he obtains about \$10/gallon. Recognizing that bottling, packaging, shipping and distribution expenses are significant, it might be reasonable to assume that the fermentation ethanol as 200°proof alcohol is worth at least \$1/gallon

in the distillery storage tanks. This is comparable to the current price estimated for synthetic ethanol.

Because ethanol produced by both processes is chemically equivalent and now cost the same, fermentation ethanol need no longer be limited to the beverage market. Furthermore, with the potential for recovering a valuable protein concentrate from the by-products of fermentation alcohol manufacture it now appears that fermentation ethanol can actually become cheaper than synthetic ethanol. With increasing fuel prices and increased world demand for protein sources fermentation ethanol may have the potential for being produced at a price based on its fuel properties which will make it attractive as a blending component in automotive fuel.

PRODUCTION OF ETHANOL BY GRAIN FERMENTATION

The process for the production of ethanol by the fermentation of grain is well established. Starch containing grains such as wheat; corn, milo, etc. are ground to expose the interior of the kernel and cooked to gelatinize the natural starches. The cooked grain is cooled and an enzyme is added to convert the starch to sugar. The sugars are then fermented to ethanol anaerobically with yeast and the alcohol recovered from the mixture by fractional distillation.

Two by-products result from this fermentation process, carbon dioxide and distillers dried grains with solubles. The distillers dried grains represent the insoluble materials in the original grain such as fiber, ash, and protein. The soluble components such as unconverted starch and soluble proteins are concentrated and dried with the distillers dried grains to yield this by-product. The distillers dried grains plus solubles (DDG&S) are a desirable high protein content (25-30%) cattle feed. In 1972 slightly more than 400 thousand tons of DDG&S were produced and in 1973 their average selling price was \$117/ton. The carbon dioxide produced is of high purity and if a market is available this gas can be sold at \$2/ton or more at atmospheric pressure.

The cost of converting grain into 200°proof ethanol is about 28.6¢/gallon of alcohol. This cost includes utilities, labor, supervision, maintenance, etc. but does not include the cost of the grain nor depreciation. The investment for an alcohol plant to produce 20 million gallons/year of 200°proof ethanol from milo (a feed grain belonging to the corn family) is approximately \$18 million. Milo contains about 70% starch and a typical price that agricultural economists estimate in the next 12 months is \$2.29/bushel at a moisture content of 15.5 weight per cent. The process would also produce 174 tons/day of carbon dioxide and about 218 tons/day of DDG&S at a 14% moisture content.

Table III shows an economic evaluation for the production of 20 million gallons/year of 200°proof ethanol from 21,490 Bu/day of milo. With ethanol valued at \$1/gallon and distillers dried grains at \$120/ton, the total annual income from such a plant is \$29.68 million. The expenses for such a plant include the cost of milo, and the conversion cost. These total \$23.68 million per year. This then gives a profit of \$6 million/year before depreciation and taxes which in turn gives a payout of 3 years for the investment of \$18 million.

RECOVERY OF PROTEIN FROM DDG&S

As mentioned above, the DDG&S contains between 25% and 30% protein depending on the protein content of the original grain. A portion of this protein may be solubilized by treating the DDG&S with a pH greater than 11.0. If the pH is then lowered to about 4.0 a sizable portion of the protein will precipitate. The process equipment requirements are not complex. The amino acid profile of the protein concentrate depends to a great extent on that of the original grain.

Table III contains an economic evaluation for a process to produce 20 million gallons/year of 200° proof ethanol and to recover 66,200 lb/day of protein concentrate (85% protein) from the distillers dried grains and solubles. In this case the value of the DDG&S is reduced to \$90/ton after the protein has been removed. The protein concentrate has been estimated by an agricultural economist to have a value in the human food market of about 60¢/lb. The incremental investment for the protein plant is \$4 million and the conversion cost for recovery of the protein is \$1.09 million per year. The value placed on ethanol in this case is that which will provide a three year payout on the total investment for the alcohol plant plus the protein plant i.e. a profit of \$7,370,000/year. From the figures shown in Table III it can be seen that the 20 million gallons per year of ethanol must bring an income of \$11,600,000/year or 58¢/gallon.

ETHANOL IN GASOLINE

As a component in gasoline anhydrous ethanol has a blending octane number of 123. If the differential value between 94 octane regular gasoline and 100 octane supreme gasoline is 2¢/gallon at the wholesale level then ethanol as a blending component in gasoline is worth 9.7¢/gallon more than the price of 94 octane regular. This in turn means that when the wholesale price of regular gasoline excluding state and federal taxes is 48.3¢/gallon ethanol at 58¢ per gallon can be used as an economical blending component based on its fuel properties. Allowing for a 35¢ mark-up to retail price and adding 12.5¢/gallon state and federal taxes we come to a retail price of 77.7¢/gallon of gasoline at the pump as being consistent with an alcohol price of 58¢/gallon at the distillery. Table II is a comparison of price (including taxes) of 94 O.N. regular gasoline at the pump with the alcohol price at the distillery which is necessary for anhydrous ethanol to be an economical gasoline blending component.

CONCLUSIONS

Based on laboratory studies it has been shown that protein of a quality suitable for human consumption can be extracted from vegetable materials such as distillers dried grains and solubles, the by-product of the production of ethanol by grain fermentation. Economic evaluations of the investment and operating cost requirements for the production of anhydrous ethanol from grain and the recovery of protein concentrate from distillers dried grains and solubles indicates that the protein recovery can reduce the selling price of alcohol without adversely affecting the return on investment. In the case where milo was used as the feed grain to the fermentation process the selling price of anhydrous ethanol could be reduced from \$1/gallon to 58¢/gal. while maintaining a 3 year payout on investment. If ethanol were

available at 58¢/gallon it would be economical to use as a blending component in gasoline if the price of regular gasoline at the pump including state and federal taxes were 77.7¢/gallon. Lower grain prices would permit lower ethanol costs which in turn would make the ethanol attractive at lower gasoline prices. Recovery of the protein concentrate from the distillers dried grains results in an increase of about 46% in the total amount of protein produced over feeding the grain directly to cattle. The energy deficit associated with farming and fermentation ethanol production has been shown elsewhere to be less than that associated with ethanol production from light gases via ethylene.

Table I
Current Price Estimate
For Synthetic Ethanol

Base Price in 1972	61.0¢/gal
Increase in Fuel Prices of 90¢/million Btu	10.3
Increase in Ethylene Price from 3¢/lb to 10¢/lb	<u>28.7</u>
1974 Price	<u><u>\$1.00/gal</u></u>

Table II
Value of Ethanol as
a Gasoline Component

<u>Gasoline</u> 94 O.N. Reg. (Incl. Tax)	<u>Ethanol Value</u> at the Distillery
52¢/gal	39.0¢/gal
60	44.9
80	59.7
100	74.5

Table III

Economic Evaluation for the Production
of 20 Million Gallons per year of 200°Proof Ethanol

	<u>Without Protein Recovery</u>	<u>With Protein Recovery</u>
Feed: Milo (Bu/Day)	21,490	21,490
Products: Ethanol (Gal/yr)		20,000,000
Distillers Dried Grains & Solubles (Ton/Day)	218	180
Carbon Dioxide (Ton/Day)	174	174
Protein (Lb/Day)	---	66,200
Income: Ethanol	@ \$1/gal	@ 58¢/gal
DDG&S	@ \$120/ton	@ \$90/ton
CO ₂	@ \$2/ton	@ \$2/ton
Protein	---	@ 60¢/lb
Total Income	<u>\$20,000,000/yr</u> 9,550,000	<u>\$11,600,000/yr</u> 5,910,000
Expenses: Milo	@ \$2.29/Bu	@ \$2.29/Bu
Conversion Cost	<u>130,000</u>	<u>130,000</u>
Total Expenses	\$29,680,000	\$32,140,000
Profit: Before Taxes and Depreciation	<u>\$17,960,000/yr</u> 5,720,000	<u>\$17,960,000/yr</u> 6,810,000
Capital Investment:	\$23,680,000	\$24,770,000
Payout: Before Taxes and Depreciation	\$ 6,000,000/yr	\$ 7,370,000/yr
	\$18,000,000	\$22,000,000
	3.0 yrs	3.0 yrs

THE USE OF METHANOL AS A MOTOR VEHICLE FUEL

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I. Blends of Methanol and Gasoline as Motor Vehicle Fuels

The use of methanol has been suggested as a means of extending the nation's supply of liquid fuels. The transportation sector of the economy is one of the largest users of liquid fuels today, and several investigations have been made of the possibility of blending portions of methanol with gasoline to extend the supply of that fuel. The data reported from several of these investigations together with the particular experiences encountered have been gathered together in a report prepared for the City of Seattle by Mathematical Sciences Northwest, Inc. The sections of this report are summarized here together with pertinent references.

Fuel Consumption (1, 2, 3, 4, 5, 6, 7, 9, 14, 17, 18)

The energy content of methanol is less than that of gasoline (8640 Btu/lb vs 19,080 Btu/lb) so that higher fuel consumption would be theoretically predicted for blends of methanol and gasoline than for straight gasoline. However, these blends will burn more satisfactorily at sub-stoichiometric fuel to air ratios than will gasoline, and this fact together with their better anti-knock qualities and cooler, more efficient engine operation may offset this theoretical prediction. Depending upon the automobile engine tested, fuel economy has been shown to be improved slightly or slightly decreased by the addition of methanol to form blended fuels. Since the blend contains less Btu per gallon, there is a slight but significant increase in efficiency of operation on a mile per Btu basis. This increase is generally reported, and may be of importance economically depending upon the comparative prices of gasoline and methanol on a dollars per million Btu basis.

Power or Acceleration (6,8,9,10,14)

The high latent heat of vaporization of the methanol (474 Btu/lb vs 141 Btu/lb for octane) cools the air charge of an engine and increases its density. This causes an increase in volumetric efficiency and available power from an engine. However, the methanol also lowers the combustion temperature in the cylinder, resulting in lower combustion efficiency. It has been shown that the addition of practical amounts of methanol to gasoline should not appreciably affect the power output of an unmodified automobile engine.

Vapor Pressure (9, 11, 13, 14, 18)

Because of the disruption of hydrogen bonding in methanol when it is mixed with a hydrocarbon, the vapor pressure of a mixture of methanol and gasoline deviates greatly from ideal behavior as predicted by Raoult's Law, exhibiting a much higher vapor pressure than would be expected. This excess vapor pressure can lead to vapor lock problems, difficulties with hot starts, stalling, hesitation, and poor

acceleration. The evaluation of these problems is highly subjective, however. This question will be discussed after three more factors affecting driveability are mentioned.

Solubility (2,6,7,8,9,11,15,17)

Another factor affecting the driveability of an automobile fueled with a methanol-gasoline blend is the degree of solubility of the methanol in the base gasoline. Methanol is least soluble in paraffins and naphthenes, and more soluble in aromatics and unsaturates. Therefore, the amount of aromatics in the base gasoline greatly affects the degree to which the methanol will blend. At lower temperatures the solubility of methanol in gasoline is decreased. Operation in sub-freezing environments will be a problem, and suitable solubilizers such as higher alcohols will have to be added to the fuel.

Separation (1, 3, 4,6,7,9,11,14,15,17,19,20,21,22,23,24)

The presence of very small amounts of water can cause methanol-gasoline mixtures to separate into gasoline and water-alcohol phases. These separate phases are vastly different in their combustion properties. Some of the aromatics from the base gasoline will also separate with the alcohol-water leaving the gasoline phase very low in octane number. The separation becomes more pronounced at low temperatures so that the primary effect will be very difficult, if not impossible, cold starting and stalling in cold weather. As with solubility the properties of the blend are dependent upon the aromatic content of the base gasoline. As the methanol fraction increases in a blend so does the water tolerance. The presence of higher alcohols in the blend increases its water tolerance. The problem of phase separation of methanol-gasoline blends can be a serious one. The solution may lie in the addition of higher alcohols to the blend.

Octane Number (1,3,6,7,8,9,11,14,15,17,18,20,21,28)

Pure methanol has a very high blending octane value (BOV). This number reflects the fact that the blending of methanol with gasoline is a very effective method of increasing the octane number of the fuel. The effect is less pronounced in newer automobiles. The elimination of knocking has been demonstrated as the result of this effect. Higher compression ratios may be utilized and the attendant increases in fuel economy realized. The effective increase in octane number depends upon the octane number of the base gasoline used in the blend. Methanol is more effective in raising the octane number of an originally lower octane number fuel. One of the most interesting effects of this octane number boost is the possibility of replacing tetra-ethyl-lead as an anti-knock compound in gasoline with a low percentage of methanol in a blend, helping to minimize lead pollution. The substitution of methanol for TEL in gasolines as an anti-knock agent will prevent the accidental poisoning of catalytic mufflers by lead.

Subjective Road Tests (1,3,6,7,8,14,15,17,19,20,24,25,29)

The overall effect upon driveability resulting from the properties of methanol gasoline blends that were discussed in the preceding

sections can only be assessed through subjective fleet tests in which some qualitative judgments of overall driveability are given by drivers of automobiles in actual field tests. These qualitative judgments can only be subjective, and as such are open to the effects of bias; however, care is taken (blinds) to minimize these effects.

One specific area that has been investigated is the effect upon cold starting. Difficult cold starting has been predicted. Cold start problems are decreased by the addition of higher alcohols to the fuel. Subjective judgments of the effects of methanol blends used as fuels on driveability seem as mixed as the driver's assessments of automobiles themselves. Perhaps it can be safely stated that the substitution of a 7 percent blend of methanol would exhibit enough beneficial effects to overshadow most detrimental effects. However, this number depends strongly upon the specific automobile considered and the severity of the cold weather to be encountered in service.

Corrosion and Compatibility (1,2,6,7,9,11,13,14,15,17,24,26,27,29)

The automotive fuel system has been developed for the use of petroleum distillates and the substitution of blends of methanol for fuels opens the possibility of corrosion of fuel system parts. The gasket materials and elastomer seals used in the automotive fuel system must also be examined for compatibility with methanol fuel blends. Several test programs have been carried out in this area, and also observations have been made of the effects of corrosion during most of the fleet tests that have been performed.

Methanol and methanol blends have been seen to attack the terne plating on automobile fuel tanks. Deterioration of copper, aluminum and magnesium has also been reported.

There appear to be serious corrosion and compatibility problems associated with the use of methanol blends in some automobile fuel systems. There are similar problems when pure methanol is used as a fuel; however, the greater problem is experienced with blends primarily because of the water separation problem. The corrosion and compatibility problems listed above are not universally observed, however. It appears as if the severity of the corrosion and compatibility problem depends strongly upon the particular vehicle and fuel system being considered. Certain specific problems such as those with methacrylate fuel filters and Viton float valve seats can be identified; however, it is very difficult to generalize further.

Modifications and Reliability (1,3,6,8,11,14,15,21,24)

One of the beneficial aspects of the use of methanol as a blend with gasoline should be the fact that engine modifications are not necessary. The degree of adherence to this dictum depends upon the percentage of methanol considered, the age of the automobile, and the tolerance of the driver. Problems of driveability that point to the necessity of equipment modifications increase with methanol concentration. Older, richer cars are more tolerant of the leaning effect of methanol blends. Equipment reliability has not been sufficiently examined in the time scale of the experiments that have been carried out, except for the corrosion problems mentioned in the previous section. Further testing needs to be done before sufficient data are

available to make valid conclusions concerning equipment reliability.

Emissions

One of the most beneficial effects of the use of methanol blends as automotive fuels is the reduction in the emission of air pollutants afforded. This reduction, together with the octane number boost, has been the motivating factor in most of the investigations of the use of methanol blends as automotive fuels.

Carbon Monoxide Emissions (2,3,5,6,8,14,21,23,24,25,30)

The emission of carbon monoxide (CO) from an automotive engine is decreased when methanol blends are substituted for straight gasoline as a fuel without vehicle modifications because of the leaning effect of the blend and the more complete burning of the fuel that is afforded. The blending of methanol with gasoline has been shown to decrease the emissions of carbon monoxide in the vehicle exhaust if the vehicle is unmodified and allowed to take advantage of the leaner operation possible with methanol blends. Indeed, the fact that the engine need not be modified for the use of methanol blends is one of the motivating factors for the use of such blends and should be considered a ground-rule for vehicle testing in which the use of blends is investigated. Comparison of the data with the Federal Standards points out the fact that the use of methanol blends will not obviate the incorporation of catalytic converters in order to meet the 1977 standard for CO emissions.

Hydrocarbon Emissions (2,5,6,9,14,21,24,30,31)

The effect of the use of methanol blends as fuels upon the emissions of hydrocarbons is not as easily discerned as the effect upon carbon monoxide emissions. Part of the reason can be found in the fact that the constituents of "unburned fuel" in the case of methanol are different than those for gasoline. Considerable care must be taken in the hydrocarbon emission measurement procedure to account for all of these constituents that may be present.

When methanol blends are used as fuels, the possibility of increased emissions of formaldehyde in the exhaust exists. The use of methanol blends as a motor fuel has, in many cases, been shown to decrease the hydrocarbon emissions slightly as compared to the use of gasoline. This effect is caused by the leaner operation afforded by the use of methanol blends in the unmodified automobile. The beneficial effect is not as pronounced or reproducible as the decrease in carbon monoxide emissions when methanol blends are used. The levels of HC emissions were not lowered enough to meet the 1977 Federal Standards and the use of a catalytic converter will be necessary to meet these standards.

Oxides of Nitrogen Emissions (2,5,6,14,21,25,30)

The effect of the use of methanol blends upon the emission of oxides of nitrogen (NO_x) from a motor vehicle is pronounced, although not uniform from vehicle to vehicle. Nitrogen oxide emissions are maximized for the operation of a motor vehicle engine under conditions near stoichiometric combustion. Therefore, if the vehicle is originally adjusted to operate at or near an equivalence ratio of unity on gasoline and not modified when a methanol blend is substituted, the

leaning effect of the blend should reduce the NO_x emissions. If the vehicle originally operated fuel rich, however, this same leaning effect should increase the NO_x emissions.

When used in an unmodified vehicle, methanol blends have been shown to decrease nitrogen oxide emissions when the vehicle was of recent vintage, operating at or near stoichiometric conditions on gasoline. Tests on vehicles as old as 1970 showed such an effect; however, tests on a 1967 vehicle which originally operated fuel rich showed an increase in NO_x emissions. The blending of methanol into motor fuel has not reduced NO_x emissions below the 1977 Federal Standard, and the use of emission control devices will be necessary.

II. Pure Methanol as a Motor Vehicle Fuel

The use of either analytic or commercial grade methanol or methyl-fuel alone as a fuel for motor vehicles has also been suggested. As described in the preceding section, there are many problems associated with the use of blends of methanol and gasoline as a motor fuel, principally in the area of phase separation caused by the presence of water and the attendant alterations necessitated in the fuel distribution system. The separation problem is eliminated when pure methanol is used as a vehicle fuel; however, when this is done certain modifications to the vehicle itself become necessary. These modifications are considered to be more feasible particularly in the case where pure methanol is considered as the fuel for fleets of vehicles.

Economy (5,8,11,14,17,18,20,22,24,25,27,32,33,34,35,36,37)

Methanol possesses the lowest heating value of all the alcohols because it contains a higher percentage of oxygen by weight. Its heating value per gallon and per pound is approximately one-half that of gasoline. Theoretically, for the same performance, it should require twice as much methanol as gasoline per mile in the same vehicle. However, the high octane number, low volatility, high heat of vaporization and low heat of combustion of methanol can be put to good use in raising the thermal efficiency of engines. Because of the greater thermal efficiency afforded with the use of methanol, the number of miles travelled per BTU can be greater for methanol than for gasoline. As a result, the cost per mile can be lower for methanol fuel than for gasoline.

The use of methanol as a motor fuel has been shown to increase the thermal efficiency of internal combustion engines normally fuelled with gasoline. This increase is due to the possibility of using methanol at much leaner equivalence ratios and the possibility of utilizing higher compression ratios, as well as the elimination of certain emission controls that are deleterious to fuel economy. This increase in efficiency has been shown to be approximately 20 percent. Assuming that methanol is priced on an equal cost per BTU basis as gasoline, these savings will be reflected in the costs per mile to operate an equivalent vehicle.

Power (11,14,17,20,24,27,32,34,35,36,37,38)

For a stoichiometrically correct air to fuel ratio (6.45 for methanol, 15.3 for gasoline) the energy densities of the fuels are very nearly equal (94.5 BTU/ft³ for methanol, 95.5 BTU/ft³ for gasoline) indicating that equal power can be extracted from comparable engines using these fuels. Methanol will extract more brake-mean-effective pressure from an engine than will gasoline because of the increased volumetric efficiency afforded by the cooler methanol charge.

Equal power output has been achieved with methanol in an engine usually operated on gasoline when stoichiometric mixtures were used. Power

output has been raised significantly above that for gasoline when richer mixtures were used; however, to gain the benefits in economy afforded by the lower lean misfire limit of methanol, this excess in power will have to be forfeited and possibly a slight loss in power sustained. For equivalent exhaust emissions, the methanol fueled engine has been shown to exhibit significantly higher power than the emission control equipped gasoline engine.

Driveability

Several of the driveability problems associated with the use of blends of methanol and gasoline are eliminated when pure methanol is used as a fuel; however, there remain problems associated with the vaporization properties of pure methanol as compared with those of gasoline.

Vapor Pressure (17,18,19,20,27,36,37)

The vaporization characteristics of pure methanol have caused some problems when it is used as a motor fuel. Its high heat of vaporization requires an enhanced supply of heat to the intake manifold in order to assure adequate mixture distribution to the cylinders. Its lower vapor pressure has made cold starting difficult and may necessitate the use of high volatility additives during this phase of the vehicle operation. Its low boiling point requires careful attention to keeping the fuel lines and carburetor shielded from excess heat. All of these problems have been encountered and several solutions developed.

Driveability (1,15,17,24,27,36)

The power output of a vehicle fueled with pure methanol can be equivalent to a comparable gasoline fueled vehicle, and the solubility and separability problems of blends do not exist for pure methanol fuels. Most of the subjective evaluations of the driveability of vehicles fueled with pure methanol have focused on the problems associated with cold starting of such vehicles.

The higher heat of vaporization of methanol together with the requirement of over twice as much methanol as gasoline for the same amount of air to form a stoichiometric mixture require that much more heat be supplied to the intake manifold to avoid cold starting and acceleration problems. Several solutions to these problems have been proposed. It is possible to add high vapor pressure liquids or gases such as butane either generally or preferably only during cold start situations. Either gasoline or LPG could be injected at cold starts to accomplish the same effect. Aside from the cold start problem, the performance of the methanol fueled vehicle has been shown to be equivalent to a gasoline fueled vehicle.

Pure Fuel-Corrosion and Compatibility (1,6,14,17,26)

Several corrosion and compatibility problems associated with the use of methanol in blends with gasoline as a motor fuel have been described. There has been much less experience reported concerning the use of pure methanol as a motor fuel. Many of the problems encountered with the use of blends may also appear during pure fuel use, but this has not been proven by experience. Significant corrosion occurs after water causes separation of gasoline and methanol-water phases in blends. Much of this corrosion may be caused by the water in the lower phase. This separation does not take place when pure methanol is utilized as a motor fuel. Water is highly soluble in pure methanol and any traces found in the fuel system will be taken into the solution. The compatibility

problems associated with the use of pure methanol as a motor fuel have been more extensively investigated. It may be expected that compatibility problems between pure methanol and Viton fuel system elements, metacrylate fuel filters and possibly certain types of fuel pump diaphragms and gaskets may exist.

The limited experience with the use of pure methanol as a motor fuel has uncovered some compatibility problems with certain fuel system components. Some test vehicles have suffered no corrosion or compatibility problems, and others have required alterations to avoid them. There is a need for further fleet testing in which the problems of corrosion and materials compatibility with pure methanol motor fuel are more completely investigated. It will only be through the experience gained during such fleet tests that all of these problems can be uncovered.

Pure Fuel-Performance-Reliability and Conversions (1,5, 8,12,13,14,15,17,20,27,31,36,37,39,40)

The reliability of motor vehicles that have been converted to operation on pure methanol fuel has proven to be as high as that of comparable gasoline fueled vehicles in several cases. The conversions necessary to enable a vehicle to operate with pure methanol as a fuel can be divided into two phases. Because the energy per cubic foot of stoichiometric mixtures of methanol and gasoline fuels is very similar, the modifications necessary to convert a conventional gasoline engine to pure methanol fuel are relatively simple. These conversions, to enable the use of pure methanol fuel in conventional engines will be called first phase conversions. Such conversions involve changes to the carburetor, intake manifold, fuel system, and spark advance curve and do not require major engine modifications. This phase of engine modification may be easily carried out on a fleet of automobiles and has been done in several cases. In addition, major engine modifications such as an increase in the compression ratio may be made in order to take advantage of the higher octane number of methanol in order to produce better thermal efficiency and an increase in fuel mileage. These modifications constitute a second phase of possible engine conversions. No full scale tests of such conversions have been reported.

Some modifications will be necessary to convert a conventional engine from gasoline to methanol fuel. Larger carburetor jets will be needed to provide the richer mixtures necessary, and larger fuel tanks will be needed to provide the same range of operation. It is also anticipated that some elastomeric seals in the fuel system may have to be changed depending upon their compatibility with methanol. Viton is the only material that has specifically caused problems in this area. Evaporative control cannisters and metacrylate fuel filters will have to be changed. Carburetor or fuel tank substitutions may be necessary on certain vehicles because of corrosion problems. The possible corrosion and compatibility problems are not well defined and require an enlarged fleet test program to uncover them. Some means of assuring fuel vaporization and even distribution to the cylinders will have to be provided. This can be accomplished by placing heat exchangers in the intake manifold or by the adoption of a fuel injection system. Provisions will be necessary to assist in cold starting engines at ambient temperatures below 55 °F. This can be accomplished by the injection of butane, propane, acetone, ethyl ether, gasoline, or LPG during the starting procedure. The adoption of fuel injection would benefit in this area as well. Depending upon the particular vehicle and its fuel system layout there may be problems with vapor lock

during hot operation. The installation of an electric fuel pump should eliminate these.

Carbon Monoxide Emissions (1,5,17,20,25,27,31,32,
35,36,40,41,42)

Since the methanol molecule has no carbon to carbon bonds and already contains one oxygen atom, the reaction kinetics for complete oxidation of this fuel are theoretically less complex than those for gasoline and the intermediate reaction products that form exhaust emissions are more readily eliminated from the exhaust system. In addition, it has been shown earlier that methanol fuelled vehicles will operate satisfactorily at much leaner mixture ratios. Therefore, it may be expected that vehicles fueled by pure methanol, especially those equipped with catalytic muffler will emit less carbon monoxide than comparable gasoline fuelled vehicles. This reduction has been measured except in those cases in which operation was fuel-rich. The extended fuel-rich warm-up period necessary with methanol fuelled vehicles appreciably raises their CO emissions. The installation of a catalytic converter has been shown to reduce CO emissions below the 1977 Federal Standard.

Hydrocarbon Emissions (1,5,14,15,17,18,20,27,32,
34,35,36,38,40,41)

Several tests have been performed on methanol fuelled vehicles from which the emissions of hydrocarbons and unburned fuel have been reported. Some hydrocarbons emitted in the exhaust of methanol fuelled vehicles are different than those emitted by gasoline fuelled vehicles and adequate provisions must be made to insure that the recording equipment accurately measures their presence. The major component of unburned fuel in the exhaust has been found to be methanol which is technically not a hydrocarbon at all; however, the emissions of unburned fuel are generally reported under the heading of hydrocarbon emissions.

The leaner operation afforded by the use of methanol fuel should lead to lower hydrocarbon (HC) emissions. The emissions of hydrocarbons and unburned fuel from engines fuelled by methanol have been shown to be lower than those fuelled by gasoline during hot start emissions tests. Because of the longer warm-up period under fuel rich operation which is necessary with methanol fuel, the HC emissions from methanol fuel were higher than those from gasoline during cold start tests. The use of a catalytic muffler was found to be necessary in order to meet the 1977 Federal HC Standard. There are no aromatics emitted among the hydrocarbons in the exhaust of a methanol fuelled vehicle, and there is correspondingly less carcinogenic risk from these emissions. It is also expected that the total reactivity caused by the unburned fuel for the formation of photochemical air pollution is much lower for a methanol fuelled vehicle than for gasoline.

Oxides of Nitrogen Emissions (1,5,14,15,17,18,20,27,32,33,
34,35,36,37,38,40,41,42)

The emissions of oxides of nitrogen (NO_x) in the exhausts of methanol fuelled vehicles have been demonstrated to be very low; lower than the NO_x emissions of comparable gasoline fuelled vehicles. Emission levels below the 1977 Federal NO_x standard have been demonstrated with methanol fuelled vehicles without the use of emission control equipment. Results have shown no increase in NO_x emissions during cold start tests. Calculations have shown that the peak Otto cycle temperature of methanol fuel is lower than that of iso-octane. The lower combustion temperature of methanol contributes to the depression of NO_x emissions from methanol fueled vehicles. The higher flame velocity

exhibited by methanol as compared to that of gasoline allows the use of later spark timing which also results in lower NO_x emissions. Since emissions of NO_x peak at stoichiometric conditions of operation, the lower lean misfire limit exhibited by methanol permits lower NO_x emissions by allowing operation at much leaner mixture ratios than gasoline.

Aldehyde Emissions (1,18,27,32,35,36,38,41)

Aldehydes form a class of potential air pollutants that are not presently covered by Federal Standards. The presence of certain aldehydes, principally formaldehyde and acetaldehyde has been measured in the exhaust of methanol fuelled engines. Aldehyde emissions from automobiles have not been measured as extensively as those of other air pollutants. There exists no Federal Standard for aldehyde emissions. The level of aldehyde emissions from methanol fuelled vehicles seems to be a sensitive function of the air to fuel mixture ratios. Some tests have shown that the aldehyde emission level from methanol fuelled vehicles is no higher than the level from comparable gasoline fuelled vehicles. Others have shown increased aldehyde emissions when methanol is substituted for gasoline as a fuel. There is a need for further testing of both methanol fuelled vehicles and gasoline fuelled vehicles, however, before any definite conclusions can be drawn. The use of a catalytic muffler has been shown to considerably reduce the aldehyde emissions of methanol fuelled automobiles.

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PERFORMANCE OF AN ETHANOL-GASOLINE BLEND
IN AUTOMOBILES AND LIGHT TRUCKS

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INTRODUCTION

The proposal that ethanol be used as a blending component in automotive fuel is almost as old as the automobile itself. In 1907 the U.S. Department of Agriculture published a report entitled "Use of Alcohol and Gasoline in Farm Engines" (5). Over the intervening years many laboratories tests on the performance of stationary automobile engines operating on ethanol-gasoline mixtures have been reported in the literature. In 1964 a series of papers on the use of ethanol and hydrocarbon motor fuels were published (4) by the SAE. In 1971 the American Petroleum Institute prepared a review of alcohol fuel studies (1). The most recent comprehensive laboratory study was that work done by Dr. H.B. Mathur in connection with his Ph.D. thesis in New Delhi, India (2). Mitre Corp. prepared a new survey (3) of alcohol fuel technology in 1974 including both ethanol and methanol.

To date no statistically designed fleet test of ethanol-gasoline mixtures have been reported in the literature. Contact with automotive and petroleum companies indicate that they too know of no such comprehensive test. Because of the knowledge to be gained from a well designed program, a two million mile road test using a mixture of 10% ethanol-90% unleaded gasoline was designed by the authors and is now in progress.

TEST PROGRAM

The Nebraska two million mile ethanol-gasoline road test program is being conducted with 36 vehicles supplied by the Nebraska Department of Roads and is being financed by the Nebraska Agriculture Products Industrial Utilization Committee. The fuel being tested is a mixture of 10% anhydrous ethanol and 90% unleaded regular grade gasoline. This blend is known by the name GASOHOL. The gasohol is being blended for the test program by the Cooperative Refiners Assoc. in Phillipsburg, Kansas. The no-lead base gasoline used in the preparation of the gasohol is the same no-lead which they market through their normal outlets.

The objectives of the two million mile road test are to obtain the following information:

1. The quantitative effect on fuel consumption of the addition of sufficient anhydrous ethanol to produce a 10% solution by volume with unleaded gasoline meeting specifications for sale after 30 June, 1974.
2. The quantitative effect of this ethanol addition on cylinder wear.
3. The quantitative effect of this ethanol addition on exhaust gas composition.

4. The qualitative effect of this ethanol addition on engine valves.
5. The qualitative effect of this ethanol addition on spark plugs.
6. The qualitative effect of this ethanol addition on the exhaust system.
7. The drivers comments on the effect of this ethanol addition on general vehicle performance.

The quantitative information is being gathered in sufficient quantity and in such a way as to allow statistical analysis of the reliability and significance of the data. The test is to extend over a period of 10-15 months. The qualitative observations are being made sufficiently often to establish any visible trends.

The road test program is making use of a total of 36 vehicles; 10 half-ton pickup trucks and 26 passenger cars. These vehicles are located in three different parts of the state of Nebraska i.e. Lincoln, North Platte, and Sidney. The reason for including vehicles in these three cities is to incorporate into the test an effect for altitude. Lincoln has an altitude of 1160 feet above sea level, North Platte is 3000 feet and Sidney is 4300 feet. Table I summarizes information on the year, make, and model of vehicles included in the test program. As the Department of Roads acquires additional 1974 and 1975 vehicles, some of these will be added to the test program.

The vehicles have been divided into three groups; those vehicles which will run on gasohol only for the entire life of the test program, those vehicles which will run on unleaded fuel only during the entire program and those which will be changed from one fuel to the other about midway through the test program. Table I includes the fuel assignment of each of these vehicles.

Those vehicles running on gasohol fuel will obtain their fuel from new storage tanks which have been buried at state service stations in Lincoln, North Platte and Sidney. Special care has been taken to insure that the tanks remain dry through the initial cleaning and by continued observation of the contents. To date no special driers have been needed on the vents. The drivers of those vehicles running on no-lead gasoline buy their fuel at local commercial outlets since the state service stations do not have facilities for storing and dispensing an additional no-lead grade. Data on the number of gallons of gasoline added to each vehicle and the corresponding odometer reading is maintained by each driver and sent weekly on a standard form to the authors for processing.

VEHICLE MAINTENANCE AND INSPECTION

All normal vehicles maintenance such as oil change, lubrication, etc. is carried out on the test vehicles in the same fashion as other vehicles belonging to the Department of Roads. In addition, each 90 days (+ 5 days) from the beginning of the test program a visual inspection is made of the exhaust system on each vehicle. Spark plugs are checked and the compression on all vehicles is also measured. On straight six cylinder engines cylinders two and four are checked while on eight-cylinder engines, three and six are checked. Any V-6

engines in the program have the middle cylinder of each bank checked.

On 10 of the Lincoln vehicles there will be additional inspections made. These include the visual inspection of valves and seats on all cylinders and the measurement of the diameter on all cylinders. In this case six micrometer readings are made at approximately equal spacings on the circumference of the cylinder and at approximately the center of the piston travel. The vehicles undergoing these inspections have been indicated in Table I. One of the objectives of this test is to obtain quantitative information on the exhaust gas composition of vehicles powered with gasohol and with no-lead gasoline. An analytical procedure for obtaining detailed component analyses of exhaust gases using a high resolution mass spectrometer has been developed for the authors by Dr. Michael L. Gross in the Analytical Section of the Department of Chemistry at the University of Nebraska. All exhaust gas samples in this program are being obtained from Lincoln based cars. A fitting has been installed on 10 of the test cars to permit attaching a vacuum gauge to the engine manifold while the exhaust samples are being gathered. The samples themselves are taken from the exhaust pipe and lead through a stainless steel pipe and plastic hose to a set of sample bags in the rear seat of the car. In this way the exhaust samples can be gathered over an extended period of time (typically five minutes) while the car is being driven at a constant speed and a constant load as indicated by the vacuum gauge. Earlier tests with small samples which were gathered in a matter of seconds showed too much variability and uncertainty about the exact speed and vacuum when the sample was caught. The vehicles from which exhaust gas samples are being taken are indicated in Table I.

It is also planned to include standard EPA emissions tests in this test program. These will be obtained through an outside laboratory and will include the usual schedule of warm up and driving in a climate controlled dynamometer.

DATA PROCESSING

Based on the results of preliminary testing of about 250,000 miles, a computer program has been developed to process the fuel consumption and mileage data. Through the use of linear regression it has been found that the significant factors in the fuel consumption are the driver, the vehicles, average daily temperature, average relative humidity and maintenance schedule. Tire pressure while known to be significant cannot be accounted for. Normal fluctuations in atmospheric pressure, precipitation, and visibility were not found to be significant. When the significant factors have been accounted for in the fuel consumption the significance of the residuals will be tested for the unleaded gasoline and gasohol fuel. With the data available from the vehicles it is expected that we will have results with a confidence limit of 99+% for a fuel consumption of + 0.1 miles per gallon. Data are processed weekly and quarterly reports are issued to the Nebraska Agricultural Products Industrial Utilization Committee.

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TABLE I

Vehicles, Fuels and Tests in
2 Million Mile Gasohol Road Test Program

<u>Model Year</u>	<u>Vehicle Make and Type</u>	<u>Location</u>	<u>Fuel (Note)</u>	<u>Valve & Cylinder Inspections</u>	<u>Exhaust Gas Analyses</u>
1973	IHC ½T Pickup	Lincoln	A	Yes	Yes
1973	IHC ½T Pickup	Lincoln	U	Yes	Yes
1973	IHC ½T Pickup	No Platte	U/A	No	No
1973	IHC ½T Pickup	Sidney	A	No	No
1974	Dodge ½T Pickup	Lincoln	A	No	Yes
1974	Dodge ½T Pickup	Lincoln	U	No	No
1974	Dodge ½T Pickup	Lincoln	A/U	Yes	No
1974	Dodge ½T Pickup	Lincoln	U/A	Yes	No
1974	Dodge ½T Pickup	No Platte	A/U	No	No
1974	Dodge ½T Pickup	Sidney	A	No	No
1974	Dodge Coronet	Lincoln	A	Yes	No
1974	Dodge Coronet	Lincoln	A	No	Yes
1974	Dodge Coronet	Lincoln	U	Yes	Yes
1974	Dodge Coronet	Lincoln	A/U	No	Yes
1974	Dodge Coronet	Lincoln	A/U	No	No
1974	Dodge Coronet	Lincoln	U/A	No	Yes
1974	Dodge Coronet	Lincoln	U/A	No	No
1974	Dodge Coronet	No Platte	A/U	No	No
1973	AM Ambassador	Lincoln	A	Yes	No
1973	AM Ambassador	Lincoln	U	Yes	No
1973	AM Ambassador	Lincoln	A/U	Yes	Yes
1973	AM Ambassador	Lincoln	U/A	Yes	Yes
1973	AM Ambassador	No Platte	U/A	No	No
1973	AM Ambassador	Sidney	A	No	No
1972	AM Ambassador	Lincoln	A	No	No

TABLE I (Con't)

<u>Model Year</u>	<u>Vehicle Make and Type</u>	<u>Location</u>	<u>Fuel (Note)</u>	<u>Valve & Cylinder Inspections</u>	<u>Exhaust Gas Analyses</u>
1972	AM Ambassador	Lincoln	U	No	No
1972	AM Matador	Lincoln	A	No	Yes
1972	AM Matador	Lincoln	A	No	No
1972	AM Matador	Lincoln	U	No	No
1972	AM Matador	Lincoln	A/U	No	No
1972	AM Matador	Lincoln	U/A	No	No
1972	AM Matador	No Platte	U/A	No	No
1972	AM Matador	Sidney	A	No	No
1973	Plymouth Fury III	No Platte	A/U	No	No
1974	Passenger Car (To be Rec'd)	No Platte	A	No	No
1974	Passenger Car (To be Rec'd)	Sidney	A	No	No

Note: A - Vehicle to be run on alcohol blended fuel only
 U - Vehicle to be run on unleaded fuel only
 A/U - Vehicle to be run initially on alcohol blended fuel and then unleaded fuel
 U/A - Vehicle to be run initially on unleaded fuel and then alcohol blended fuel