

THE ENERGY BALANCE OF SHORT-ROTATION COPPICE FORESTS:  
A PARTIAL ASSESSMENT FOR GEORGIA

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Biological energy sources should be evaluated in terms of energy inputs needed to achieve various levels of biomass yields and energy outputs. Site preparation, seed or seedling production, and the establishment, cultivation, harvest, transport and conversion of the crop all necessitate energy expenditures. These inputs can include energy needed to manufacture the machinery and that needed to run it in the various production and utilization processes, produce fertilizers, and feed the labor force. They may also include environmental energy inputs like solar radiation, rain and wind energies. Outputs can be measured at several stages, such as before or after harvest, transportation, pretreatment (e.g. chipping, pelletizing, drying), or final conversion. Comprehensive energy balances for agricultural crops such as corn (Pimentel et al., 1973) and sugar cane (Hopkinson and Day, 1980) have been calculated, but relatively little is known about such balances for forest crops.

All types of biomass share certain advantages and disadvantages as energy sources. Among the most important positive, long-term aspects are that they are renewable indefinitely, cause no net change in atmospheric carbon dioxide levels and contain relatively few pollutants. Biomass is versatile in that it can be converted into a variety of liquid or gaseous fuels or directly into heat. Disadvantages of biomass include the removal of nutrients and organic matter from soils and high harvest and transport costs because the resource is generally scattered, bulky and high in moisture.

Forest tree species offer several advantages as energy crops in comparison with agricultural crops or other herbaceous plants. The perennial nature of trees offers flexibility in harvest timing and the accumulation of large amounts of biomass in the field. Trees make low nutritional demands on soils and protect them from erosion with an organic litter layer. Broadleaved species sprout from the stump or root system, obviating the need for additional site preparation or planting once they are established and thereby reducing energy inputs needed for the second or subsequent rotations. Woody materials also are less subject to deterioration in post-harvest storage than are the more succulent, herbaceous ones.

There are many different types of forest materials which can and do currently serve as alternate energy sources. They range from logging and mill residues to thinnings and stands which currently lack a market. The specific biomass production system for which I wish to develop energy input / output ratios are short-rotation coppice forests in Georgia. These consist of plantations of broadleaved tree species which are planted much like an agricultural row crop. Seedlings in our current research outplantings are spaced in rows 2.4m apart and 1.2m apart within the rows. These seedlings are allowed to grow, generally with cultural help like fertilization and weed control, until they have fully captured the site. Then they are harvested mechanically and the rootstocks, which remained in the ground after the harvest, will sprout and automatically establish the next stand. These sprouts will grow more rapidly than a new planting would because they are supported by an established rootsystem, designed for a larger plant, which has access to soil water and nutrients. Such rootstocks also act as carbohydrate reservoirs so that the new stem and leaf tissues for the reemerging stand can be developed rapidly. Generally the new stand will fully occupy the site within the first or second growing season after harvest.

For this preliminary assessment it will be necessary to combine energy inputs for a plantation established in 1978 (Steinbeck, 1979) with the energy outputs determined for a spacing, yield and rotation length experiment which was installed in 1967 (Steinbeck and May, 1971). Both plantings, however, are in similar, rolling terrain in the Piedmont province of Georgia and in the main also on the same soil series.

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GROWTH, YIELD AND COMPOSITIONAL CHARACTERISTICS OF JERUSALEM ARTICHOKE  
AS IT RELATES TO BIOMASS PRODUCTION

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Jerusalem artichoke (*Helianthus tuberosus* L.) has shown excellent potential as a carbohydrate-rich crop. Our initial investigations determined inulin and tuber yields; however, when additional studies showed that good quality pulp remained after inulin extraction and high forage yields per hectare were obtainable, the scope of our investigation was broadened to assess utilization of the total plant. Plant growth, yield and compositional characteristics of Jerusalem artichoke as they relate to biomass production will be reported.

#### Plant description and characteristics

Jerusalem artichoke is native to temperate North America and adapted to the region circumscribed by the agricultural region contiguous with the northern shore of the Great Lakes, the Red and Mississippi Rivers on the West as far South as Arkansas, eastward to the Piedmont coastal plain of the Eastern seaboard, extending from George north to Quebec. Although often referred to as wild sunflower, it differs from other native *Helianthus* species by producing perennial, fleshy tubers. Plants grow tall and upright, having either a branching or non-branching form of growth. Small yellow ray and disk florets borne at the end of main stems and branches may produce small, hard seeds although seed production is often poor. Tuber shape, size and display vary from round, knotty clusters to long, smooth single tubers.

Growth begins from tubers early in the season. Maturity is reached within 100 to 130 days. Jerusalem artichoke's moderate tolerance to spring and fall frosts extends its growing season beyond that of conventional field crops. This characteristic aids some experimental lines in achieving high tuber yields. Late maturing genotypes do not mature.

Pest and disease problems are few. Of the diseases, Sclerotinia wilt (*Sclerotinia sclerotiorum*) is the most efficacious; however, rust, Septoria leaf spot and downy mildew are potential problems. White mold and soft rot tuber diseases may occur in storage. Unharvested tubers winter well in the soil and remain healthy until their removal in the spring. In all respects, Jerusalem artichoke is adaptable and remarkably resilient to damage which explains its high yield potential.

#### Growth functions

The growth of plant tops and tubers are influenced by the flowering process. Considerable variation in time of flowering occurs within the species, the earliest lines flowering in early July, and the latest at the end of September. When flower buds appeared, the rate of dry matter accumulation in the aerial parts decreased (Fig. 1). Maximum dry matter (DM) yields of plant tops were 12.2 T/ha and occurred after flowering. The subsequent loss of dry matter was, in part, the result of leaf senescence and abscission.

Tubers develop from stolons which enlarge with the onset of flowering (Fig.1). The number of tubers increased until 50 percent flowering occurred and subsequently declined to approximately 25 tubers/plant. During that time, the weight per tuber increased exponentially. It is hypothesized that translocation of material from some tubers, as well as leaf senescence, contributes to increasing the rate of individual tuber dry matter accumulation. Tuber yields were 283.5 g DM/plant which is equivalent to 9450 kg DM/ha (42 T/ha fresh weight). Plant growth was terminated by killing frosts.

#### Variability in forage yield and composition

Forage composition changes with advancing maturity (Table 1). Protein decreased continually, but between week 6 and 7 there was a significant reduction. Conversely, the ADF and lignin fractions increased between weeks 7 and 8. These changes were associated with cessation of flowering. Cellulose and ash contents remained relatively constant throughout the sampling period.

Considerable variation in dry matter yield and forage composition exists among accessions (Table 2). High forage yielding lines generally were those which flowered late. All accessions were harvested when flowering began so the variability in DM content was not influenced by stage of maturity. Rather, DM content appeared to be associated with prevailing climatic conditions at time of harvest. The low yielding line (NC10-50) is a leafy, relatively fine stemmed accession having the highest protein and lowest ADF and lignin contents among all accessions evaluated. The greatest amount of protein, ADF and lignin in the respective high accession was 1.8, 2.1 and 3.4 times that of the low value accession. Based on the magnitude of variability, it appears that forage composition could be readily improved through plant breeding.

#### Variability in tuber yield and composition

Total reducing sugar (TRS) content and fructose: glucose (F/G) ratios were used to estimate inulin content and its molecular size. Actual inulin content and molecular size found in Jerusalem artichoke is not clearly understood, but research is currently underway at a western Canadian university to identify degree of polymerization and the changes which occur during tuberization and later during storage.

Ontogenetic changes in carbohydrate content and composition were recorded in two Jerusalem artichoke accessions (Table 3). The native Manitoba accession had a higher average TRS content and a wider range of values over the sampling period than the higher yielding Russian accession. A trend toward lower reducing sugar content and percent fructose was evident in the native strain, whereas TRS content remained relatively constant in the Russian line.

The duration and conditions of storage alter carbohydrate and DM content of the tubers (Table 4). Holding the tubers at 3°C and 75% relative humidity for eight weeks allowed some dehydration of the tubers and the greatest reduction in TRS content. Freezing the tubers caused a small increase in DM content, but the least reduction in TRS of those storage treatments imposed.

The variability in carbohydrate content among several selected accessions ranged from 13.2 to 27.7 percent when harvested late in the season (Table 5). Fructose: glucose ratios also differed, but no relationship existed between high TRS yields and high F/G ratios. In another study to determine composition of the carbohydrate-extracted pulp, significant variability was identified for NDF, ADF, acid-detergent lignin and ether extract (Table 6). Neither protein nor digestible energy varied greatly; however, the levels found indicates that the pulp has good

feeding value. Amino acid analysis revealed that lysine and methionine contents in the pulp are high (Table 7). Protein quality is considered to be very good.

It is evident that considerable variability in yield and carbohydrate content exists within the species although accessions high in carbohydrate often produce low yields. A small breeding effort showed interesting results. As summarized in table 8, high TRS lines crossed with intermediate carbohydrate-high yielding branching and non-branching lines (standards) produced significant ranges in percent TRS, fructose and protein. This suggests that rapid progress could be made when plant utilization is determined and plant breeding objectives are established.

#### Production requirements

The highest Jerusalem artichoke yields of 75 tonnes/ha (34 T/ac) occurred in a year when temperatures were below normal and precipitation above normal. Since tubers contain approximately 87.5 percent water, yield is highly dependent on soil water potential throughout the growing season and particularly during tuberization. Production requirements for Jerusalem artichoke are similar to potatoes. Generally, the requirements are:

- soils; sandy-loam, sandy clay loam
- fertilizers (kg/ha); N-90, P<sub>2</sub>O<sub>5</sub> - 56, K20-50  
(or according to regional potato recommendations)
- weed control; inter-row cultivation
- fungicide; (possibly)
- pesticides; (none required to date)

Estimated energy requirements for producing the crop are derived using data by Southwell and Rothwell (1978). The data are presented in terms of energy resource depletion (ERD). Distinction is made between fossil fuel and total energy resources consumed in producing the crop (Table 9). ERD is based on calorific values of fuel used (converted from BTU's) times the supply system efficiency factor (i.e., the actual plus energy absorbed in the supply system as losses or expenditures).

Stating Jerusalem artichoke forage and tuber yields in terms of alcohol production, each respective component would yield 4580 and 2880 l/ha (Table 10). The energy output of each is 1181 X 10<sup>6</sup> kcal/ha from the tubers and 1176 X 10<sup>6</sup> kcal/ha from the forage component.

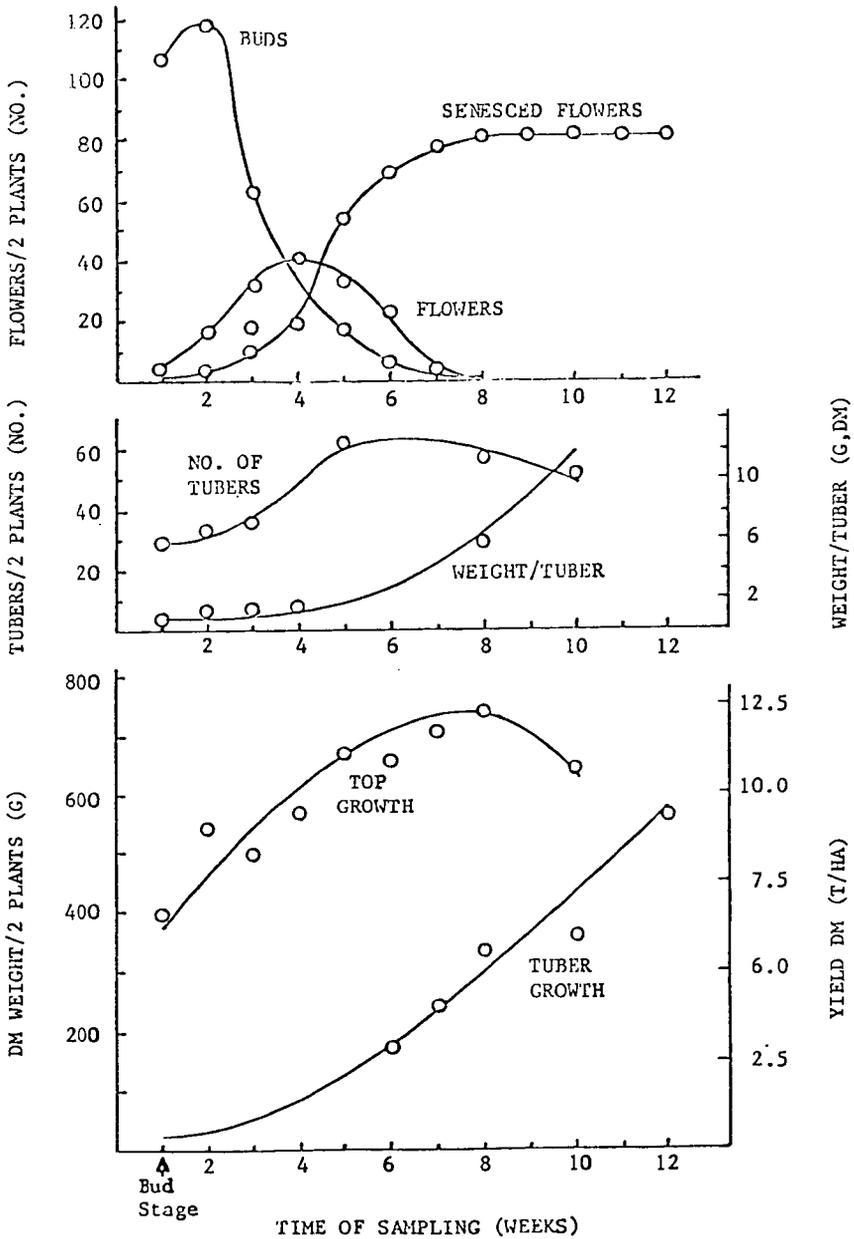


FIGURE 1 -- Flowering pattern and growth rates of tubers and plant tops sampled at weekly intervals beginning at the bud stage.

Table 1. Change in composition and content of Jerusalem artichoke forage sampled at weekly intervals following the flower bud stage of development

Plant Fraction	Sampling Period (Weeks)											
	1 <sup>a</sup>	2	3	4	5	6	7	8	9	10	11	12
Protein (% DM)	18.0	17.0	15.0	14.3	13.5	12.5	9.7	9.7	7.9	6.2		
ADF (% DM)	35.3	31.8	33.9	31.1	32.1	35.5	35.4	40.9	45.6	46.6		
Lignin (% DM)	6.21	6.0	7.2	6.1	6.3	6.9	6.7	7.8	9.4	8.9		
Cellulose (% DM)	23.0	23.2	22.3	22.3	23.6	23.9	24.2	-	-	-		
Ash (% DM)	2.1	2.0	2.2	2.3	2.3	2.4	2.3	-	-	-		

<sup>a</sup> Bud stage

Table 2. Forage content of crude protein (CP), acid-detergent fiber (ADF) lignin (Lig) content of selected Jerusalem artichoke accessions sampled at early flowering or prior to frost.

Accession	DM	DM	C P	ADF	Lig
	Yield	Content			
	(t/ha)	(%)	-----% of Total DM -----		
NC 10- 5	9.81	32	11.96	52.21	11.40
8	31.78	28	13.85	45.76	8.48
9	8.35	35	10.72	50.69	12.02
13	14.67	38	15.95	42.16	12.77
18	7.26	40	11.92	44.14	7.69
44	22.97	22	9.54	34.37	7.10
50	2.30	23	17.28	25.21	3.78
60	26.04	31	13.21	40.25	7.21

Table 3. The effect of harvest dates on the content and composition of reducing sugars in fresh tubers of two strains of Jerusalem artichoke.

Strain	Harvest date	Reducing sugar %	Fructose %	Glucose %	F/G ratio	
Manitoba	Sept. 28	21.5	87.6	9.1	9.6	
	Oct. 12	23.3	80.9	12.5	6.5	
		21.8	81.8	12.0	6.8	
		19.9	78.7	13.2	6.0	
		22.7	74.3	16.1	4.6	
	Nov. 2	18.5	78.9	12.6	6.3	
		16.5	76.0	13.6	5.6	
		MEAN	20.6	79.7	12.7	6.5
	Russian	Sept. 28	14.5	82.4	11.2	7.4
		Oct. 12	18.7	78.7	12.9	6.1
16.8			76.8	14.4	5.3	
16.2			74.9	14.8	5.1	
19.9			74.1	14.6	5.1	
Nov. 2		13.8	79.2	11.8	6.7	
		18.4	71.8	14.9	4.8	
		MEAN	16.9	76.8	13.5	5.8

Table 4. Dry matter and total reducing sugar (TRS) content in Jerusalem artichoke tubers stored at different temperatures and relative humidity levels.

	Storage Time and Conditions			
	0 Weeks	8 Weeks		
		3°C/95%RH	3°C/75%RH	-40°C/Ambient RH
Dry Matter (%)	25.8	25.5	28.2	26.5
TRS (% of DM)	78.4	66.7	62.9	72.5

Table 5. Content and composition of reducing sugars in fresh tubers of six strains of Jerusalem artichoke harvested on October 23, 1972.

Strain	Reducing sugar %	Fructose %	Glucose %	F/G ratio
MS #1	27.7	75.3	14.9	5.1
MN #5	20.7	74.7	15.1	4.9
HMR #1	17.1	78.2	13.4	5.8
HMR #2	18.6	71.0	16.1	4.4
HMR #3	17.3	75.2	16.0	4.7
Commercial	13.2	80.6	12.3	6.6

Table 6. Composition of several experimental Jerusalem artichoke accessions.

Accession	Digestible Energy	C P	NDF	ADF	AD Lig	Ether Extract
	Mcal/kg (DM)		-----% of DM-----			
Morden #5	3.509	26.9	47.8	34.4	1.43	3.9
Perron	3.551	26.7	45.1	42.8	2.62	2.9
Branching	3.603	25.6	47.6	38.1	0.92	3.3
Non-Branching	3.563	25.4	50.4	38.1	0.60	3.2

Table 7. Amino acid analysis of inulin-extracted Jerusalem artichoke pulp.

Amino Acid	Content (g/100g Sample N)	Amino Acid	Content (g/100g Sample N)	Amino Acid	Content (g/100g Sample N)
Lys.	48.98	Ser.	30.42	Meth.	11.79
His.	13.08	Glut.	71.43	Iso	30.80
NH <sub>3</sub>	12.67	Pro.	21.83	Leu	46.45
Arg.	31.70	Gly	32.01	Tyr.	22.37
Asp.	59.52	Ala	35.44	Phe	28.63
Thr	33.36	Vil	38.31		

Moisture 5.9%  
 Protein (D.B., N X 5.7) 16.16%  
 Recovery 86.9%

Table 8. Variability in percent total reducing sugar (TRS), fructose (F) and protein among Jerusalem artichoke advanced selection and new crosses compared to standard branching and non-branching types.

	No. of or Comparisons	Range (%)		
		TRS	F	Prot.
Adv. selections	21	17.4-22.4	68.0-80.4	23.1-27.0
New crosses	41	10.66-22.8	65.9-80.1	21.0-30.3
Branching (standard)		21.2	75.3	25.6
Non-branching (standard)		20.3	75.5	25.4

Table 9. Energy requirements in terms of energy resource depletion (ERD) of fossil fuel (FF) and total (T) to produce 1 hectare of Jerusalem artichoke\*

Energy inputs/ha	ERD (FF)	ERD (T)
	( $10^3$ K cal)	
Cultivation	81	83
Planting	171	174
Fertilizer**	2327	2402
Inter-row cultivation (2)	145	146
Fungicide	184	193
Sprout inhibition	148	160
Harvesting - tops ***	311	317
- tubers	767	780
Hauling to storage	878	878
Total	5012	5133

\* Potato production energy requirements by category according to Southwell, P. H. and T. M. Rothwell.

\*\* Fertilizer rates (kg/ha) in Manitoba: N - 90;  $P_2O_5$  - 56;  $K_2O$  - 50.

\*\*\* Assumes values similar to corn silage.

Table 10. Theoretical yields of ethyl alcohol from several crops  
(Manitoba yield basis)

Crop	Plant part	Yield		ETOH l/ha
		Fresh wt.	Carbohydrate	
		-----kg/ha-----		
J. artichoke	Tuber	42000	7088	4580
Sugar beet	Root	33600	4930	3185
Corn	Grain	6700	4150	2680
Wheat	Grain	3360	2240	1447

## Carbon and Light Limitation in Mass Algal Culture

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### INTRODUCTION

A variety of potential applications for mass algal culture are often proposed. The suggested uses for algal biomass include use as fertilizers, raw material for extracted commercial chemicals, animal or human protein supplements either directly, or indirectly through incorporation into aquaculture systems, as well as energy via conversion to methane gas (1). In spite of the apparent potential usefulness of algal biomass and years of research centered around understanding algal growth in both laboratory and field culture, mass algal culture has not yet been commercially realized to any large extent.

The primary reason for this lack of success lies in the complexity of the process of large scale algal culture. Attempts at modelling the species' specific responses of algal culture has been attempted with varying degrees of success (2-6). The continued development of such models will likely be the only successful means of answering the many questions concerning optimum design and operation of future algal culture.

Most mathematical models describing algal growth revolve around three central sub-models. These sub-models attempt to define the growth of a particular alga as a function of the important environment parameters; nutrient concentration, light levels and temperature. These models attempt to simulate the response of algal cell production as a function of these three factors. Although simple in concept, because of the many possible limiting nutrients, multitudes of possible dominating algal species, combined with interaction between the three central variables, the resultant models become extremely detailed and complex. However, in the situation of high density algae culture, it is often the case that two factors, in particular, become most important in controlling production. The supply of inorganic carbon at a sufficient rate and concentration to meet algal carbon uptake rates and the availability of sufficient light intensity to supply the energy needs of the growing culture, are often suggested as controlling net cell productivities (1,7,11).

For these reasons, attention has been directed at understanding more fully the situation of light and inorganic carbon limitation of algal growth. It is the purpose of this discussion to examine the nature of the carbon limited response of algae and to combine a quantitative model of this behavior with models describing the carbonate equilibrium chemistry and flow-through algal culture. These relationships will be examined under both non-light and light limiting conditions.

### PREDICTING THE RESPONSE OF A CARBON LIMITED CONTINUOUS ALGAL CULTURE

#### I. Algal Response to $\text{CO}_2\text{f}$

Over the years considerable controversy has developed over the interpretations of data concerning the uptake of the various forms of inorganic carbon by unicellular algae (4,7,8,9,10,12). Early investigators felt that most algae were capable of using either dissolved carbon dioxide ( $\text{CO}_2\text{f}$ ) or bicarbonate ( $\text{HCO}_3^-$ ) as a carbon source.

The basis for the belief in  $\text{HCO}_3^-$  uptake was centered on observations of algal culture growth to pH values as high as 11.0. Since in vitro studies on the  $\text{KSCO}_2$  of the enzyme Ribulose diphosphate carboxydismutase yielded values as high as  $10^{-4}$  moles/liter, it was felt that the  $\text{CO}_2$  concentrations in high pH cultures ( $10^{-6}$  -  $10^{-8}$  m/l)

was simply too low to supply to carbon needs of the growing culture (9).

Goldman (12) on the other hand suggested that the interconversion of one carbon form to another was much more rapid than was the carbon uptake rate of a growing algal culture. This led him to conclude that carbon limited response of an algal culture may best be represented as a Monod model of the specific growth rate vs. the total carbon concentration ( $C_T$ ). He further suggests that this relationship must be modified by effects of culture pH.

Recent work by Brune (15) has, however, led to the continued development of yet another model first proposed by King (7). The basis for this model exists in an array of experiments in which the batch growth of laboratory cultures of various freshwater algae were studied. The typical behavior of these cultures is illustrated in Figures 1-5. It was found that for these cultures growing over a wide range of pH (7-11) the carbon limited growth response could best be modelled as a Monod fit of  $\mu$  vs.  $CO_{2f}$  (Figure 1). In contrast to this, fits of  $\mu$  to  $HCO_3^-$  (Figure 2) or  $\mu$  to  $C_T$  (Figure 3) yielded plots atypical of what is considered normal microbial response to limiting nutrient levels.

In an attempt to quantify any effects from varying culture pH on this relationship, several cultures were grown in which the initial culture alkalinity was varied. The net result of this modification was the observation of  $\mu$  at similar  $CO_{2f}$  concentrations but at differing pH values. A sample of the data (Figure 4) did indicate an effect, which was first interpreted as a suppression of growth rate by increased culture pH. However, attempts to relate  $\mu$  to pH did not prove particularly successful. On the other hand, a strong correlation was discovered between the  $K_{SCO_2}$  of the algal response and the ionic strength of the growth medium. It was later discovered that this effect could be reproduced independently of pH by increasing the ionic strength of the growth medium with additions of NaCl (Figure 5).

Thus, to date, the simplest model capable of simulating the carbon limited algal response over the widest possible combinations of environmental conditions appears to be a Monod fit of  $\mu$  vs.  $CO_{2f}$  modified by increasing  $K_{SCO_2}$  with increasing culture ionic strength. For the algae examined thus far, culture pH over a wide range appears to have little, if any, effect on this relationship.

The importance of this model is realized when this biological response is combined with equations describing the carbonate equilibrium chemistry to produce a powerful predictive model of algal culture behavior.

## II. Combining the Biological, Physical and Chemical Responses

Given that the specific growth rate ( $\mu$ ) of a carbon limited algal culture can be defined as:

$$\mu = \frac{\mu_{\max} (CO_{2f})}{K_S + (CO_{2f})} \quad 1)$$

In addition in a continuous flow algal culture, an algal cell mass balance gives (12);

$$\frac{dx}{dt} = DX_1 - DX_2 + \mu X_2 - K_d X_2 \quad 2)$$

At steady state ( $dx/dt = 0$ ) and in the case of a rapidly growing culture with the decay rate ( $K_d$ ) taken as zero, and with the influent cell concentration ( $X_1$ ) also zero, this equation reduces to:

$$\mu = D = 1/\theta \quad 3)$$

Therefore, the above relationship suggests that once the dilution rate (D) of a continuous algal culture is fixed and steady state is achieved, the specific growth rate is also fixed. The  $CO_2$  concentration of the effluent can then be obtained from the combination of equations 1 and 3;

$$[CO_2]_2 = \frac{K_{SCO_2}}{\frac{\mu_{max}}{D} - 1} \quad 4)$$

If the buffering capacity of the culture media is dominated by the  $CO_2$ -carbonate-bicarbonate system and if the influent pH and total titratable alkalinity are known, then the cell concentration and pH of the effluent can be obtained by combining equation 4 with the carbonate equilibrium equations given by Stumm;

$$\text{algal biomass} = X_A = C_{T_1} - C_{T_2} \quad 5)$$

$$\text{where: } C_{T_1} = \frac{[ALK] + [H^+] - [OH^-]}{\alpha_1 + 2\alpha_2} \quad 6)$$

The  $C_{T_2}$  concentration (effluent) is determined by  $\mu_{max}$ , D and  $K_{SCO_2}$  and is given by:

$$C_{T_2} = \frac{[CO_2]}{\alpha_0} = \left[ \frac{K_{SCO_2}}{\left( \frac{\mu_{max}}{D} - 1 \right)} \right] \left[ \frac{1}{\alpha_0} \right] \quad 7)$$

therefore:

$$[CO_2]_2 = \left( \frac{[ALK] + [H^+] - [OH^-]}{\alpha_1 + 2\alpha_2} \right) (\alpha_0) \quad 8)$$

Since alkalinity is unaffected by algal growth (except for minor modification; see Brewer 14) and is known, and since  $[CO_2]_2$  is determined by D,  $\mu_{max}$  and  $K_{SCO_2}$  and are also known, the effluent culture pH can be obtained. The solution is in the form of a 4th order equation and given by Ricci (17). The predicted culture pH for a hypothetical algae (a composite of pooled data) with a  $\mu_{max}$  of  $0.10 \text{ hr}^{-1}$  and  $K_{SCO_2}$  ranging from  $0.17 \times 10^{-6} \text{ m/l}$  to  $8.1 \times 10^{-6} \text{ m/l}$  (depending on ionic strength) is given in Figure 7.

As can be seen, the tendency toward higher culture pH as a result of increasing alkalinity is eventually overpowered by the decreasing ability of the algae to extract  $CO_2$  to low levels at the increased ionic strength due to higher alkalinity levels. The net result; at high alkalinity, continuous cultures will stabilize at lower pH values at a given detention time. Support for the theoretical model has been obtained in the form of data from actual continuous cultures of the alga *Scenedesmus quadricauda*. As can be seen (Figure 6) the form of the curve is as predicted.

The important implications of this model are summarized in Figures 8 and 9. If culture pH is allowed to drift without control, a large percentage of total carbon in the influent medium will not be utilized. At the detention time giving optimum production (Figure 8) the carbon utilization will range from only 10 to 30% depending on culture alkalinity. Therefore, attempts to increase carbon supply by alkalinity addition alone (as  $NaHCO_3$ ) will not provide for efficient utilization of inorganic carbon. PH control through acid addition would markedly improve the situation; however, the costs of continuous acid addition combined with dangers of instability produced by destroying the

culture buffering capacity do not favor this technique.

Apparently the only effective means of maintaining carbon supply through pH control will be through CO<sub>2</sub> addition. Unfortunately, the low CO<sub>2</sub> content of air makes aeration a very energy intensive means of CO<sub>2</sub> transfer. An alternative method which has been utilized for years in sewage treatment lagoons is the supply of CO<sub>2</sub> from bacterial degradation of waste organics. However, nothing comes free and so it is in this case; the price being the loss of algal productivity by shading of light from the added bacterial biomass.

LIGHT LIMITED ALGAL CULTURE

Once the carbon limitation of the algal culture is removed, the culture will respond by increasing cell density until another factor finally limits cell production. In many cases this factor will be the availability of light. Pipes (18) demonstrated that net algal cell production in a light limited culture is independent of culture detention time. Thus the algal cell density (X) is a linear function of detention time (θ);

$$X \cong \frac{K\theta}{V} \tag{9}$$

Smith (19) showed that the overall productivity (P) could be related to the biological response of the alga to limiting light and the incipient light levels by the equation;

$$P = \frac{\alpha I}{(1 + (\frac{I}{P_m})^2)^{1/2}} \tag{10}$$

Using the integrated form of this equation given by Groden (20), with values of the extinction coefficient of algal biomass from Lehman (3) ( $\epsilon = 1.2 \times 10^{-7}$  l/cell-m) the response of the cell density of a shallow light limited culture of an alga with  $P_{max} = 0.10 \text{ hr}^{-1}$ ,  $I_0 = 5000 \text{ fc}$ , to increasing detention time is given in Figure 10 (computer generated solutions to equation 10). As seen in this figure, cell density responses linearly to hydraulic detention time as predicted by the earlier equation from Pipes. The ideal behavior illustrated in this figure will be modified by many factors; of prime importance will be the additional light shading by the added bacterial biomass and the effects of bacterial CO<sub>2</sub> production. The bacterial biomass present may be predicted from equations describing the decay of influent BOD;

$$\text{where } BOD_E = BOD_I 10^{-kt} \tag{11}$$

The bacteria biomass may be predicted from equations given by Lawrence and McCarty (16);

$$X_B = Y_B \frac{(BOD_I - BOD_E)}{1 + k_b \theta} \tag{12}$$

and the rate of supply of CO<sub>2</sub> from the bacterial decomposition of the incoming BOD;

$$\frac{d[CO_2]}{dt} = -C_1 \frac{d[BOD]}{dt} \tag{13}$$

Using these equations Figure 10 is modified to account for added bacterial biomass and CO<sub>2</sub> production and the resultant modifications are presented in Figures 12 and

13. Assuming a strong waste influent with a BOD of 500 mg/l, a yield coefficient  $Y = 0.55$ , decay rate  $b = 0.55$ ,  $C_1 = 0.018$  milli-moles  $\text{CO}_2/\text{mg}$  BOD oxidized and a coefficient of extinction of light from the bacterial biomass the same as for the algal biomass, the effects of the added bacterial biomass are illustrated in Figure 13. Perhaps the most important result of this effect can be seen as the requirement for longer and longer detention time at increasing depth to achieve a stable algal cell population. This effect is due solely to the slower algal growth rate as a result of lowered average light levels per unit of algal biomass.

The final upper limit on cell biomass will again come through carbon limitation and this added effect is combined with the shading effect to produce Figures 11 and 13. These figures illustrate these combined effects on culture pH and algal cell biomass. When bacterial  $\text{CO}_2$  production exceeds algal  $\text{CO}_2$  fixation the effect will be to drive the pH below the atmospheric equilibrium pH. The lowest level that pH will fall to will depend on the rate at which  $\text{CO}_2$  transports across the water surface and exits from the culture. At a steady state pH;

$$\frac{d \text{CO}_2}{dt} = \frac{\text{net } \text{CO}_2}{\text{production}} = K_{La} (\text{CO}_{2S} - \text{CO}_2)$$

On the other hand, if algal  $\text{CO}_2$  uptake exceeds bacterial  $\text{CO}_2$  production, the culture pH will rise according to the carbonate equilibrium chemistry and carbon uptake behavior of the algae as detailed in equation 8. Unfortunately, because of low atmospheric  $\text{CO}_2$  levels,  $\text{CO}_2$  input (unless aggressively supplied) from surface transport will not usually create a significant pH stabilizing effect as will  $\text{CO}_2$  transport out of the solution. The total algal cell biomass will respond by increasing in density with increasing detention time until, as a result of the pH rise, the  $\text{CO}_{2f}$  concentration again limits cell production. The effect of either increasing culture depth or increased influent BOD levels will both delay the onset of carbon limitation and increase the detention time for a stable algal biomass population.

#### LIGHT AND $\text{CO}_2$ MODELS AS A PREDICTIVE TOOL

The model presented here considers only the case of carbon and light limited growth of algal culture. It is, of course, an over-simplification of complex algal-bacterial culture; rather, this model is viewed as a starting point for a more comprehensive model which will be developed to include the important modifiers of the relationships presented here. Of particular importance will be additions to the chemical model to account for various non-carbonate buffers such as ammonia, phosphates, borates, etc. Field determination of the many empirical constants must be made, as well as an assessment of the validity of applying the laboratory derived kinetic data to field situations.

Although the model may be simplistic in nature, the power of a simple carbon and light limitation model in predicting, in general, responses of field algal culture should not be dismissed. Observations of algal cell production from a recent pilot study (21) indicate that the theoretical behavior describes reasonably well the actual culture responses (Figure 14). Although complicated by changing influent BOD loading rates used in this study, the observations of cell density compare well with predicted light and carbon limited values. The culture pH, which was observed to rise to 10 in shallow cultures, and level off at 8.0-9.0 in deeper cultures, while dropping to 7.6 in the bacterial cultures, behaves as predicted by the  $\text{CO}_{2f}$  limitation model. A simple yet often unappreciated corollary of the carbon model suggests that whenever culture pH rises above the atmospheric equilibrium value, external carbon is not being supplied at a rate fast enough to meet the algal carbon fixation rate, thus the culture obtains the needed carbon by extracting it from the carbonate system. Unless this situation is carefully controlled, the pH may stabilize at values which yield  $\text{CO}_{2f}$  concentrations that will limit algal grow rates.

## EXTRACTING ENERGY FROM ALGAL CULTURE; RECYCLING CARBON

An attempt has been made to quantitatively show the importance of  $\text{CO}_2$  concentration in controlling algal cell production. One promising method of  $\text{CO}_2$  - pH control is through careful section of detention time, influent BOD, and depth of a combined algal-bacterial culture.

Even though bacterial decomposition of organics to  $\text{CO}_2$ , followed by  $\text{CO}_2$  fixation by algae, does not represent a net organic carbon fixation, it can be used to obtain a net energy fixation. This may be particularly applicable to the situation in which algal biomass is converted to methane gas via anaerobic digestion. The resulting  $\text{CO}_2$  from gas combustion and the low energy short chain organics in the digester effluent represent a recyclable carbon supply to be returned to the algal ponds. In this situation the importance of proper balancing of algal  $\text{CO}_2$  uptake against bacterial  $\text{CO}_2$  production cannot be over-emphasized. An imbalance in either direction will result in a loss of efficiency in carbon utilization. Proper selection of the control parameters will likely come through continued development and refinement of models such as presented here.

### SUMMARY

The carbon limited kinetic responses of various fast growing algal species have been summarized. These results suggest that the growth responses of many algae used in mass culture may best be represented as a Monod fit the specific growth rate ( $\mu$ ) to the free carbon dioxide concentration ( $\text{CO}_2$ ). The environmental modifiers of primary importance appear to be light levels, temperature and the ionic strength of the growth media.

The various mathematical models describing the algal biological response to limiting  $\text{CO}_2$  concentration, the carbonate equilibrium chemistry and the physical configuration of a flow-through microbial culture are combined to yield equations which predict the pH, total carbon concentration ( $C_T$ ) and algal cell concentration of a continuous algal culture, given a  $\mu_{\text{max}}$  and  $K_{\text{SCO}_2}$  for the alga of interest. This model is further used to illustrate the under-utilization of inorganic carbon in mass algal cultures in which the pH is uncontrolled.

One method of pH control in such cultures involves the utilization of  $\text{CO}_2$  supply from bacterial degradation of waste organics in the influent culture medium. In such a situation both the culture pH and algal cell production will often be governed by either carbon or light limitation depending primarily on the influent BOD loading, detention time and culture depth. An example is given in which the light dependent response of a particular alga is combined with equations describing the bacterial cell and  $\text{CO}_2$  production as a function of influent BOD. The resultant calculations are used to explain why algal populations in combined algal-bacterial culture are often observed to be unstable at detention times considerably longer than theoretical minimum detention time based on laboratory culture data. The effect of increasing culture depth is shown to amplify this effect.

In spite of the obvious over-simplification of considering only light and carbon limits in describing the behavior of mass algal culture, comparisons to actual field data suggest that these two parameters will be of paramount importance in controlling net algal cell production rates.

### NOMENCLATURE

$\text{BOD}_I$  = Influent  $\text{BOD}_5$   
 $\text{BOD}_E$  = Effluent  $\text{BOD}_5$

$P_m$  = Light saturated photosynthetic rate  
 $P$  = Average photosynthetic rate

$CO_{2f}$  = Free carbon dioxide concentration  
 $[CO_2]_2$  = Effluent  $CO_{2f}$   
 $C_{T1}$  = Influent total carbon concentration  
 $C_{T2}$  = Effluent total carbon concentration  
 $[CO_2]_S$  = Atmospheric equilibrium  $CO_{2f}$  concentration  
 $C_1$  = Moles  $CO_2$  produced per mg  $BOD_5$  oxidized  
 $D$  = Dilution rate  
 $I$  = Effective light level  
 $k$  = BOD decay coefficient  
 $K_b$  = Bacterial decay coefficient  
 $K_d$  = Algal decay coefficient  
 $K$  = Overall algal productivity (from Pipes, 18)  
 $K_{La}$  =  $CO_2$  transfer coefficient  
 $K_{SCO_2}$  =  $CO_{2f}$  concentration at which  $\mu = 1/2 \mu_{max}$

$t$  = Time  
 $V$  = Reactor volume  
 $X_1$  = Influent algal cell concentration  
 $X_2$  = Effluent algal cell concentration  
 $X_A$  = Algal cell concentration  
 $X_B$  = Bacterial cell concentration  
 $Y_B$  = Bacterial yield coefficient  
 $\alpha$  = Slope of photosynthetic rate vs. light intensity curve  
 $\alpha_0$  =  $CO_{2f}$  fraction of  $C_T$   
 $\alpha_1$  =  $HCO_3^-$  fraction of  $C_T$   
 $\alpha_2$  =  $CO_3^{2-}$  fraction of  $C_T$   
 $\mu$  = Specific growth rate  
 $\mu_{max}$  = Maximum specific growth rate  
 $\theta$  = Hydraulic detention time =  $1/D$

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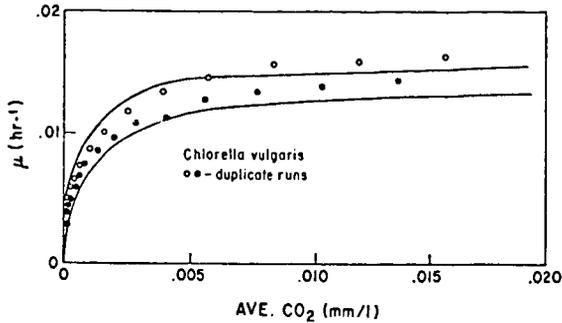


Figure 1: 95% confidence intervals around a Monod fit of  $\mu$  vs.  $CO_{2f}$  for *Chlorella vulgaris* grown at 15°C and saturated light levels.

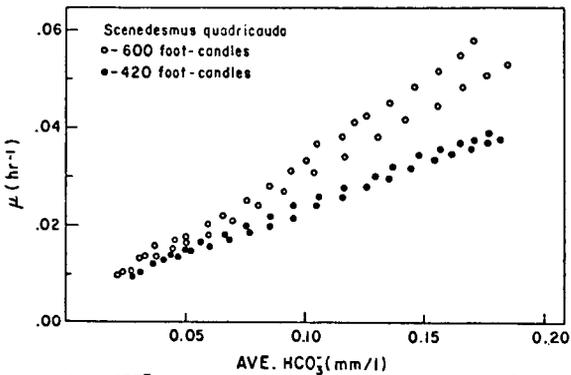


Figure 2.  $HCO_3^-$  concentration vs.  $\mu$  for batch cultures of *Scenedesmus quadricauda* grown at 27°C and two light levels.

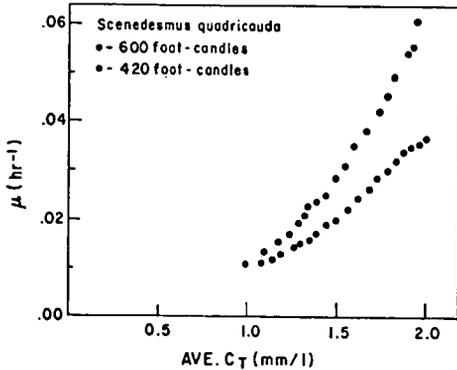


Figure 3.  $C_T$  concentration vs.  $\mu$  for batch cultures of *Scenedesmus quadricauda* grown at 27°C and two light levels.

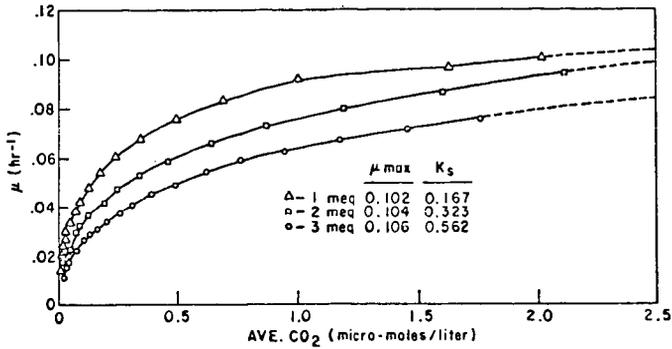


Figure 4.  $\mu$  vs.  $CO_2$  for batch cultures of *Chlorella vulgaris* grown in a medium of varying initial alkalinity.

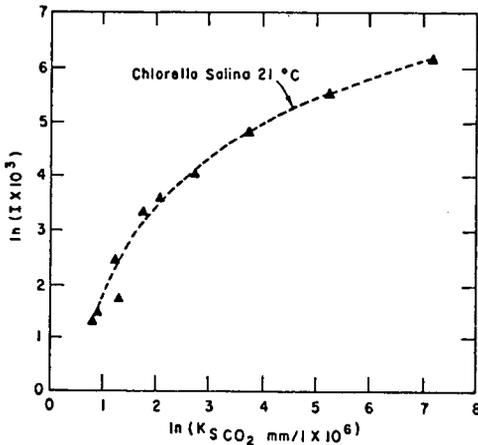


Figure 5. Observed relationship between  $K_{SCO_2}$  and the culture ionic strength for *Chlorella salina*.

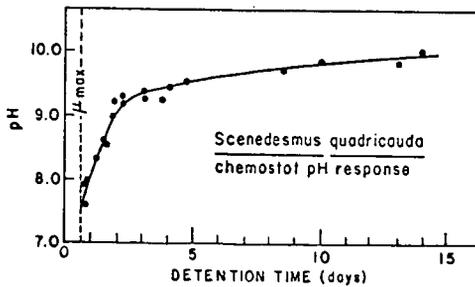


Figure 6. Continuous culture pH response of *Scenedesmus quadricauda* with influent alkalinity of 2.5 meq/liter.

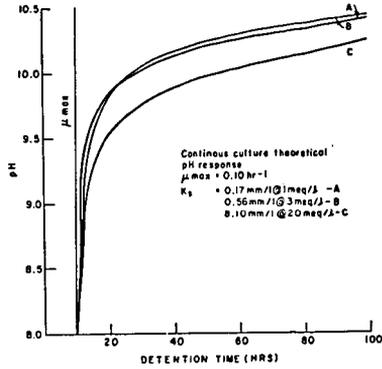


Figure 7. Theoretical pH response of continuous algal culture at varying influent alkalinity.

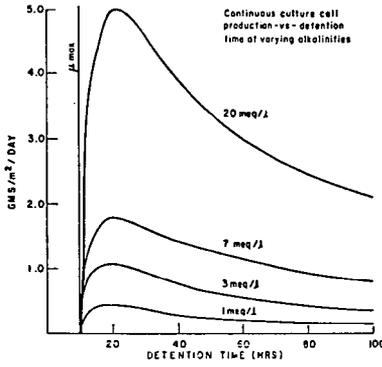


Figure 8. Theoretical production (in gms carbon/m<sup>2</sup>) from a 10 cm deep carbon limited continuous algal culture.

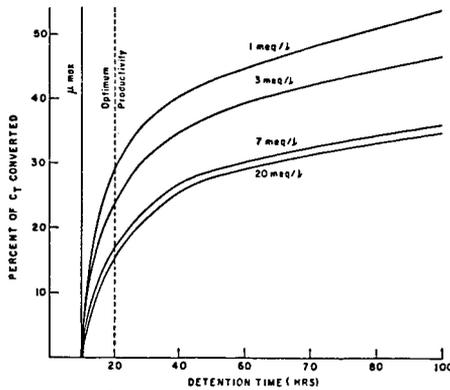


Figure 9. Percent of total carbon in influent medium converted to algal biomass in a carbon-limited continuous culture.

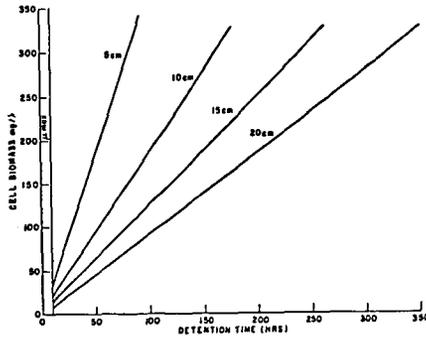


Figure 10. Theoretical algal cell biomass vs. detention time in a light limited continuous culture.

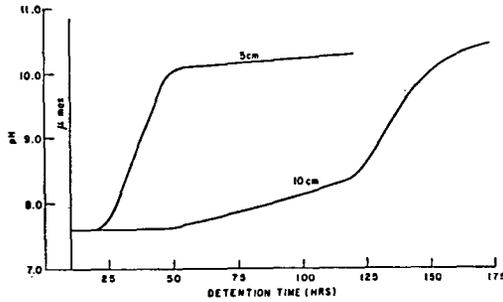


Figure 11. Prediction of culture pH based on algal response to  $CO_2f$  and bacterial  $CO_2$  production with influent  $BOD_5 = 500 \text{ mg/l}$ .

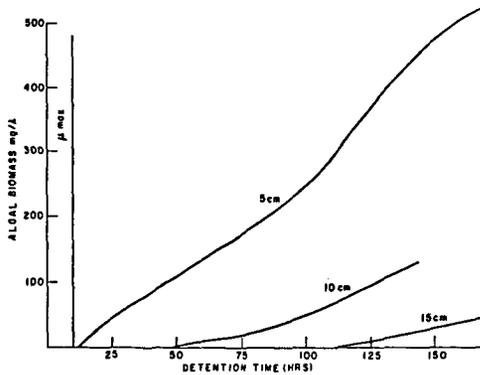


Figure 12. Effect of bacterial biomass production from BOD degradation on algal biomass density.

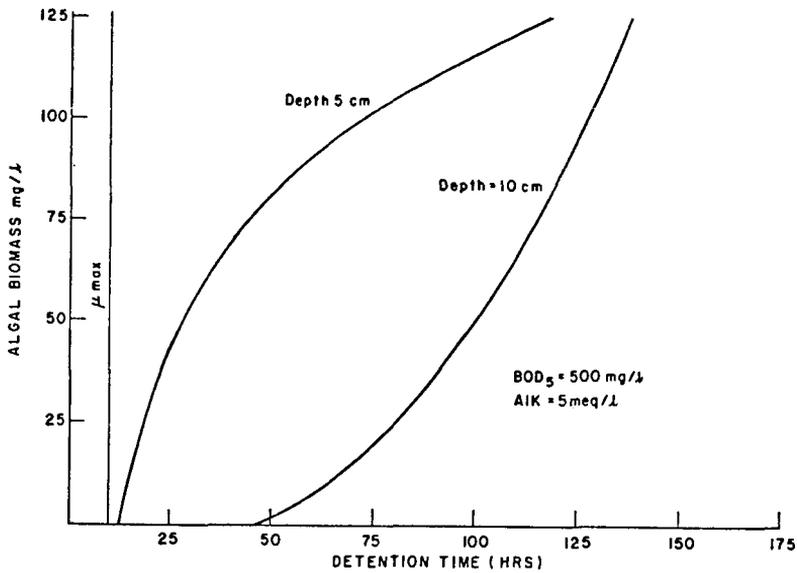


Figure 13. Combined effects of carbon limitation and bacterial biomass shading on algal biomass at different culture depths.

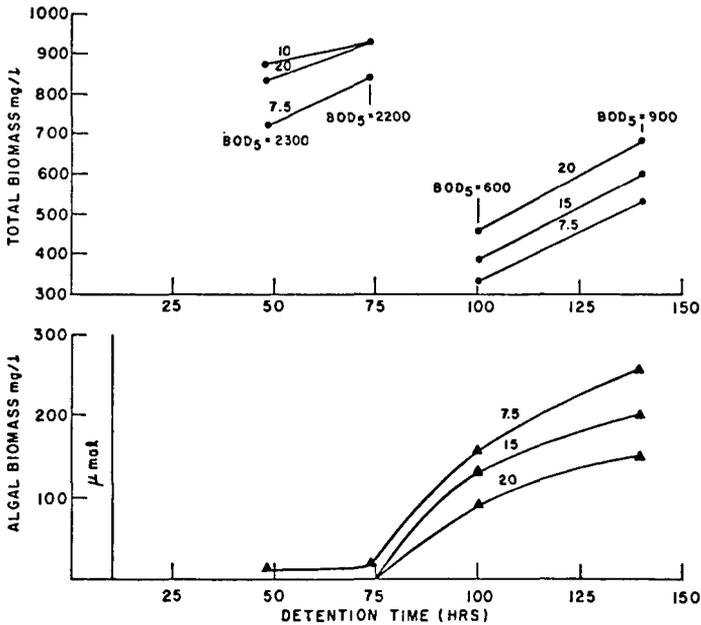


Figure 14. Data from pilot scale algal-bacterial culture (from Boersma, et al.). Total and algal biomass at culture depths of 7.5, 15 and 20 cm.

## Plants as a Source of High Energy Liquid Fuels

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The growing of green plants has received much discussion as a renewable energy source (1). Two distinct approaches are possible for energy farms. Either whole plants can be harvested as in a biomass plantation, or plants capable of producing reduced photosynthetic materials can be cultivated. In the latter case, the net product is a derivative of the total biomass, and the process would be unlike many other biomass systems where the whole plant is burned for its heat value. Conversion processes for hydrocarbon-like extracts are expected to be more efficient and less energy demanding, since the material is already in a reduced state.

A large number of plant species are capable of synthesizing isoprenoids and other hydrocarbon-like chemicals. Perhaps the best known example is the rubber tree, *Hevea brasiliensis* (family Euphorbiaceae). The family Euphorbiaceae consists of approximately 2000 species ranging from small herbs and succulents to large trees, the large majority of which produce a milky latex which is rich in reduced isoprenoids. One member of this family, *Euphorbia lathyris*, grows wild in California. To explore the feasibility of obtaining fuels or chemical feedstocks from this *Euphorbia* species, field studies were undertaken in the cultivation and harvesting of *Euphorbia lathyris*. Preliminary results with wild seed and without the benefit of optimization of fertilizer and irrigation conditions gave an annual biomass yield of 10 dry tons per acre.

Reduced photosynthetic material can be obtained from the dried plant material by hot solvent extraction. Various solvents can be used for the isolation of different plant constituents; one such extraction scheme is shown in Figure 1. The high heat value and low oxygen content of the heptane extract warranted a more detailed investigation of its chemical composition (2). This extract is a complex mixture of over 100 individual components. By various analytical methods, primarily by gas chromatography, combined gas chromatography-mass spectroscopy and high resolution mass spectroscopy, we identified approximately fifty major components. The extract is composed almost entirely of tetra- and pentacyclic triterpenoids functionalized as ketones, alcohols, or fatty acid esters. Two representative structures for a tetra- and a pentacyclic case are shown in Figure 2. Triterpenoids arise via the enzyme mediated cyclization of squalene 1,2-oxide, followed by rearrangement sequences to yield a large array of interrelated C<sub>30</sub> compounds. In *Euphorbia lathyris*, terpenoid biosynthesis is almost exclusively shunted via this pathway, since no major amount of lower terpenoids have been detected. A few of these triterpenoids have been previously identified as the major components of the latex itself (3); however, the whole plant extract yields a much greater variety of these compounds. The nature of these compounds suggests that their conversion to chemical feedstock material might be advantageous. Such conversion studies have already been carried out on vegetable oils and a *Euphorbia* latex (4).

A substantial amount of a more polar fraction can be obtained from the dried plant by methanol extraction, as shown in Figure 1. We have identified simple hexoses as major components of this fraction. These sugars are fermentable to alcohol; therefore, the possibility of obtaining this additional liquid fuel from *Euphorbia lathyris* shows promise.

Although *Euphorbia lathyris* produces reduced isoprenoids, it would be economically desirable to improve this yield. The first plant selection experiment toward this end was done using the two cultivars native to California, the

Northern and the Southern variety. In a population of one hundred individual Northern and one hundred Southern California seed source plants, we could not detect a statistically significant difference in terpenoid content between the two sets. The relatively small dispersion (8% of the mean) observed for each set is probably indicative of the limited seed source available at this time. In order to explore the feasibility of increasing terpenoid as well as biomass yields, further experiments using plant growth hormones, similar to the ones used successfully in guayule and Hevea, are in progress (5).

Since Euphorbia lathyris and other hydrocarbon producing crops are new species from the point of view of cultivation, their agronomic characteristics, requirements, and yield potentials are not yet well known. Consequently, any conceptual economic or technical evaluation will contain several uncertainties. A recent study by Stanford Research Institute on the feasibility of growing Euphorbia lathyris for energy usage identified these major uncertainties as the feedstock cost and supply (6). This conceptual process study is essentially based on solvent extraction of field dried plants at 1000 tons per day, and recovery of the sugars by water extraction. Credit is given for the sugars at 4¢ per lb. (base case) or 6¢ per lb. (optimistic case). The overall process uses the cellulose (bagasse) of the plant to generate the energy required for solvent extraction and recovery. According to this model, after recovery of the useful products, a considerable quantity of bagasse is left over. If one includes in this model an estimate of the required energy input for cultivation, the entire process still remains energy positive(7).

Based on this study, the estimated product costs are greatly dependent on the method of cultivation. In areas such as California where irrigation is required, one barrel of "oil" from Euphorbia lathyris may be produced for \$100 (optimistic case) or \$200 (base case). Cultivation of Euphorbia lathyris in a geographic region where irrigation requirements are minimal would lower the feedstock costs significantly. Consequently, one barrel of "oil" from Euphorbia lathyris grown in the Midwest is estimated to cost \$43.

Comparison of a new crop such as Euphorbia to other established ones like corn or sugar cane, which yield ethanol, indicates that in terms of energy yield of liquid fuel per acre/yr., Euphorbia lathyris is comparable. The liquid fuel yield from corn is  $16 \times 10^6$  BTU/acre/yr; from sugar cane it is  $25 \times 10^6$  BTU/acre/yr. both in the form of ethanol (8). The Euphorbia lathyris yield is  $20 \times 10^6$  BTU/acre/yr. in the form of hydrocarbons and  $13 \times 10^6$  BTU/acre/yr. in the form of alcohol. In addition a potential yield of approximately  $7 \times 10^6$  BTU/acre/yr. may yet be realized from fermentation of yet unidentified carbohydrates.

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Figure 1

EUPHORBIA LATHYRIS EXTRACTION

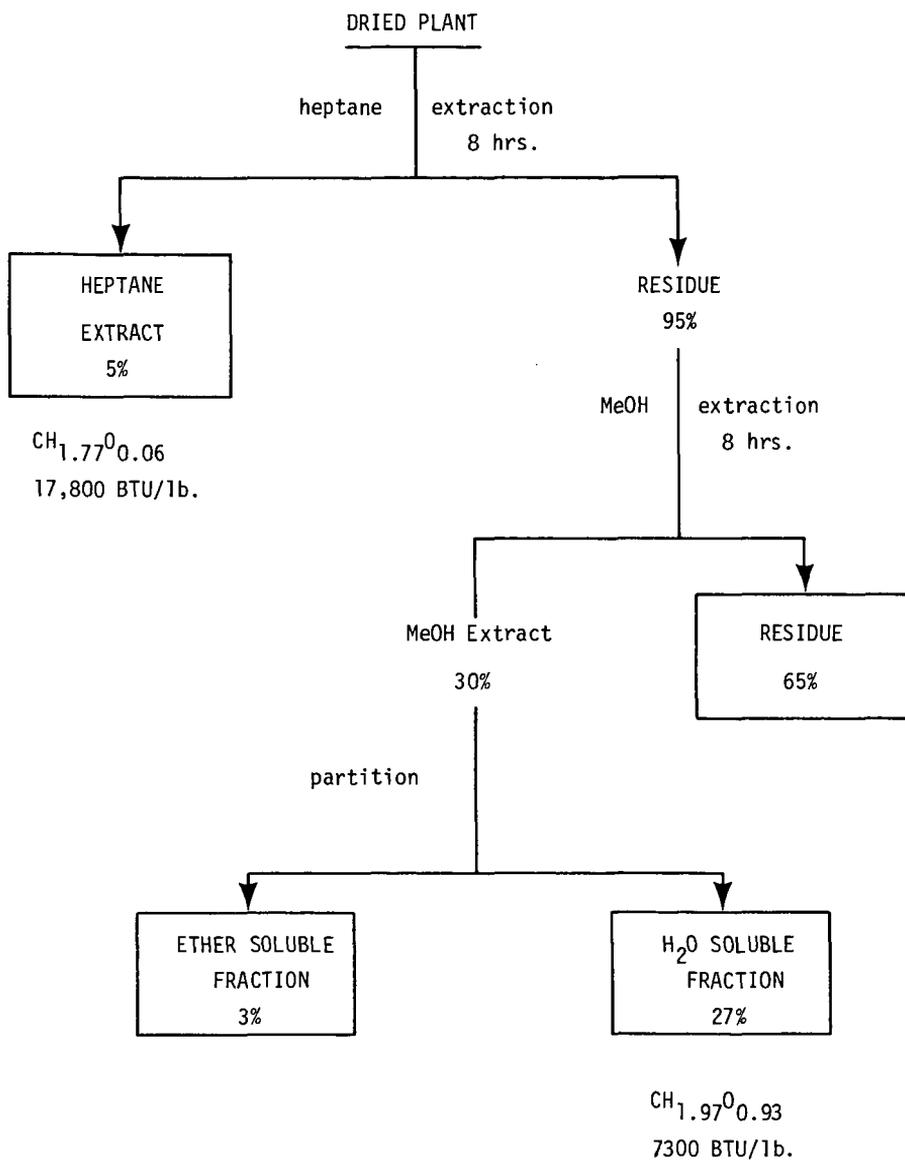
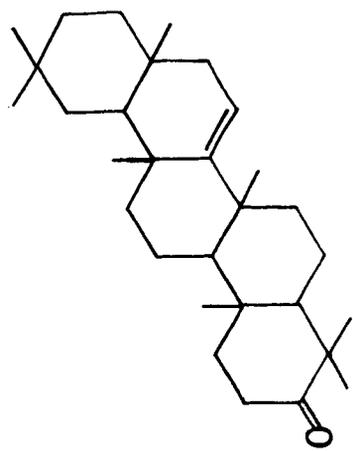
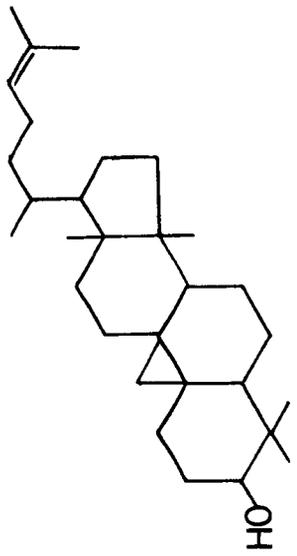


FIGURE 2.



TARAXERONE



CYCLOARTENOL

# METHANE PRODUCTION BY ANAEROBIC DIGESTION OF WATER HYACINTH (EICHHORNIA CRASSIPES)

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## INTRODUCTION

Water hyacinth (Eichhornia crassipes) is an aquatic biomass species that exhibits prolific growth in many parts of the world (1). It has been suggested as a strong candidate for production of methane because of high biomass yield potential (2). Several studies have been carried out which establish that methane can be produced from water hyacinth under anaerobic digestion conditions (3-6). Both batch and semicontinuous digestion experiments were performed. The highest apparent gas yields reported were obtained in the batch mode of operation over long detention times (4), but the yields were based on wet hyacinth containing unspecified amounts of water and ash. Some of the data in the literature on gas yield and production rate are difficult to interpret because they are experimentally observed values and are not reduced to standard conditions. The energy recovery efficiencies in the product gas are also not available because the energy contents of the feed were not determined. The work described in this paper was initiated to develop more quantitative data in terms of the physical and chemical characteristics of water hyacinth.

## MATERIALS AND METHODS

### Digesters

The digestion runs were carried out in the semicontinuous mode in cylindrical, complete-mix, 7- $\ell$  digesters (7). The culture volume for all experiments was 5  $\ell$ , and the internal diameter of the digesters was 19 cm. Continuous mixing at 130 rpm was provided with two 7.6-cm propeller-type impellers located 7.6 and 15.2 cm from the digester bottom on a central shaft.

### Analytical Techniques

Most analyses were performed in duplicate; several were performed in triplicate or higher multiples. The procedures were either ASTM, Standard Methods, special techniques as reported previously (8), or other techniques as indicated by footnotes in the tables.

### Data Reduction

Gas yield, methane yield, volatile solids reduction, and energy recovery efficiency were calculated by the methods described previously (8). All gas data reported are converted to 60°F and 30 in. of mercury on a dry basis.

### Digester Feeds

One-half to one ton samples of water hyacinth were harvested for this work.

Water hyacinth was harvested from an experimental sewage-treatment lagoon of NASA's National Space Technology Laboratory in Bay St. Louis, Mississippi. Whole adult and young plants were collected and fed directly to an agricultural chopper that provided particles about 3 in. or smaller in size. The chopped hyacinth was placed in polyethylene-lined fiber drums, frozen, shipped by refrigerated truck to IGT, stored at -10°F, ground in a laboratory grinder, mixed in a double-ribbon blender to ensure homogeneity, placed in one-half gallon cartons, and stored at about -20°F.

During one of the harvests (June 3, 1977), small samples of whole plants were also collected, in addition to the chopped plants, and shipped separately to IGT overnight in sealed

bottles without freezing for moisture, volatile matter, and ash analyses. The results are shown in Table 1 along with the corresponding analyses for the hyacinth treated as described above.

Whole water hyacinth plants were collected from a 0.25-ac freshwater pond in the Lee County Hyacinth Control District, Fort Myers, Florida. This pond is located northeast of Fort Meyers in an unincorporated area known as Buckingham and receives both surface runoff and ground water. The pond is stagnant, has no outlet, is about 3 m deep, and has a mucky bottom. The whole plants were shipped by unrefrigerated truck to IGT in polyethylene-lined fiber drums. After arrival at IGT, the water hyacinth was treated in the same manner as the Mississippi shipments.

Grinding of the water hyacinth in the laboratory was achieved with an Urschel Laboratory Grinder (Comitrol 3600) equipped with 0.030-in. cutting head. A typical particle size analysis is shown in Table 2, and the effects of storage time on the moisture, volatile matter, and ash contents are shown in Table 3.

The characteristics of the particular lots of hyacinth used to make the feed slurries for the digestion runs reported in this paper are summarized in Table 4. Feed slurries were prepared fresh daily by blending the required amounts of ground hyacinth and demineralized water. The properties of the slurries are compared in Table 5. The pH of the digester contents was maintained in the desired range by adding a predetermined amount of caustic solution to the feed slurry before dilution to the required amount with water. When added nutrient solutions were used, the compositions of which are shown in Table 6, preselected amounts were also blended with the feed slurries before dilution to the final feed volume.

#### Inoculum, Start-Up and Operation

The inoculum for the initial replicate digestion runs (Runs 1M-B and 2M-B) was developed by accumulating daily effluents from existing laboratory digesters operating on giant brown kelp and primary-activated sewage sludge as described previously (7). These digesters were then operated in the semicontinuous mode with initial mixed inoculum volumes of 2.5% and a daily feeding and wasting schedule aimed at increasing the working volume to 5% over an 8-day period, after which a transition period was incurred to change the feed to 100% hyacinth (7). The total time required from start-up to conversion to hyacinth feeds was 42 days. A second transition period was then used to adjust the operating conditions to a loading of 0.1 lb volatile solids (VS)/ft<sup>3</sup>-day and a detention time of 12 days; this required 21 days (7). Digestion was then continued at the target operating conditions with hyacinth feed only.

The experimental results obtained at steady state with Runs 1M-B, 2M-B and subsequent runs are shown in Table 7. Steady-state digestion was defined in this work as operation without significant change in gas production rate, gas composition, and effluent characteristics. Usually, operation for two or three detention times established steady-state digestion.

Mesophilic Runs 1M-4, 1M-7, 1M-8, and 1M-9 were each successively derived starting from the initial Run 1M-B. Run 1M-4 shows the effects of added nitrogen as an ammonium chloride solution. Run 1M-7 shows the effects of terminating caustic additions to maintain pH. Run 1M-8 was developed by replacing the Mississippi hyacinth in the feed slurry with Florida hyacinth. Run 1M-9 is a continuation of Run 1M-8 except caustic additions were made to control pH. Run 2M-3 was derived from Run 2M-B and was carried out with additions of the mixed nutrient solution.

Thermophilic Run 1T-5 was developed from the effluents of mesophilic Runs 1M-B and 2M-B. Successively, the effluents were collected and used as inoculum (16 days); the digester was operated at the conditions of Runs 1M-B and 2M-B to stabilize the new digester (16 days); the temperature was increased to 55°C and the digester was kept in the batch mode (14 days); the semicontinuous mode of operation was started with gradual change of the detention time from 106 days to 16.7 days and of the loading from 0.01 to 0.15 lb VS/ft<sup>3</sup>-day

(27 days); and Run 1T-5 was continued. Runs 1T-8, 1T-10, and 1T-11 were each successively derived starting from Run 1T-5. Runs 1T-8 and 1T-10 were operated at higher loading rates and lower detention times than Run 1T-5; ammonium chloride solution was added to each of these runs. Run 1T-11 is identical to Run 1T-10 except that nitrogen additions were terminated.

#### Dewatering Tests

Gravity sedimentation tests were conducted by a modification of the AEEP Method (9) in which a 400-ml sample of the effluent was examined in a 1- $\ell$  graduated cylinder giving a fluid depth of 140 mm (7). Vacuum filtration tests were conducted by a modification of the AEEP Method (10) in which a 417-ml sample of effluent was filtered through a monofilament filter cloth (7).

### DISCUSSION

#### Feed Properties

The roots of water hyacinth had higher ash and lower volatile matter contents than other parts of the plant as shown by the data in Table 1. Harvesting and storage times as well as the source of the plant seemed to have little effect on the moisture, volatile matter, and ash contents of the plants as illustrated by the data in Table 3. Samples harvested many months apart in Mississippi had essentially the same volatile matter and ash contents. The sample harvested in Florida had slightly higher volatile matter and slightly lower ash contents than the Mississippi samples, but this might be expected in view of the different growth media from which the hyacinth harvests were taken. The Mississippi hyacinth was grown in a sewage-fed lagoon, and hyacinth is known to take up heavy metals from such media (1).

The data on the chemical and physical properties of the Mississippi and Florida hyacinths used in this work (Table 4) indicate some interesting differences. The C/N and C/P weight ratios are each lower for the Mississippi hyacinth than the Florida hyacinth, but both sets of ratios appear to be somewhat high when compared with the corresponding ratios supplied by suitable feeds for anaerobic digestion such as giant brown kelp and sewage sludge (7). Although analytical data for the organic components in Florida hyacinth were not obtained, the relatively high hemicellulose content of the Mississippi hyacinth indicates potentially good digestibility (7). Interestingly, the theoretical methane yield derived from the empirical formula and stoichiometric conversion (7) of the Mississippi hyacinth has a maximum value about 14% higher than that of the Florida hyacinth.

Comparison of the feed slurries (Table 5) also reveals some interesting differences. The slurry made with the Mississippi hyacinth had a lower pH and buffering capacity than the Florida hyacinth slurry and therefore needed more caustic for pH control. However, the ammonia nitrogen concentrations in each slurry appeared too low for good digestion when compared to the beneficial range for sewage digestion (11). Concentrations of calcium, potassium, sodium, and magnesium calculated from the data in Table 4 for the feed slurries, assuming each element is totally dissolved, were either in the stimulatory range or less than the inhibitory range (11). Addition of sodium hydroxide for pH control, although increasing the sodium ion concentration several-fold, was still estimated to be insufficient to raise the sodium ion concentration to the inhibitory range. Also, addition of lime for pH control (Run 1M-9) at the level required raised the calcium ion concentration in the feed slurry but not enough to inhibit digestion based on sewage digestion and inhibition by metallic cations (11).

#### Mesophilic Digestion

Operation of replicate Runs 1M-B and 2M-B on Mississippi hyacinth without added nutrients showed good reproducibility and balanced digestion. Typical operating performance over a period of several detention times is shown in Figure 1. It was found that to maintain pH in the desired range, about 45-50 meq of sodium hydroxide per liter of feed had to be added.

To attempt to increase methane yields, pure and mixed nutrient solution additions were made in Runs 1M-4 and 2M-3, respectively, while controlling pH with added caustic. Little change was observed in digester performance; the gas production rates and yields were about the same as those observed without nutrient additions.

Elimination of both pH control and nutrient additions in Run 1M-7 resulted in small decreases in pH, methane yield, and methane concentration in the product gas, but overall performance in terms of volatile solids reduction and energy recovery efficiency as methane were about the same as those of the runs with pH control and with or without nutrient additions.

Conversion from Mississippi hyacinth to Florida hyacinth in Run 1M-8, which did not incorporate pH control or nutrient additions and which was identical to Run 1M-7 except for the feed source, showed significant reduction in most of the gas production parameters. Gas production rate and yield and methane yield decreased, but digester performance was still balanced as shown by low volatile acids in the digester effluent and the methane concentration in the product gas. From the elemental analyses and the theoretical methane yields (Table 4), the methane yield for Run 1M-8 would be expected to be about 14% less than that of Run 1M-7; it decreased by about 41%. Prolonged operation of Run 1M-8 for over six detention times did not result in any improvement; the run exhibited steady-state performance with no change in methane yield or gas production rate. Use of pH control (Run 1M-9) and continued operation reduced the methane yield even further. It was concluded from these experiments that the Florida hyacinth sample contained unknown inhibitors or that the Mississippi water hyacinth contained unknown stimulatory components. The latter possibility was considered more likely because the Mississippi hyacinth was grown in a sewage-fed lagoon, and it is well established that normal sewage has good digestion characteristics (11). Also, it is known that water hyacinth when grown in laboratory media enriched with nickel and cadmium, components often found in sewage, incorporates these metals and shows good digestion characteristics (4).

#### Thermophilic Digestion

Digestion of Mississippi water hyacinth was carried out at 55°C with and without nitrogen supplementation. Balanced digestion was achieved with all four runs, Runs 1T-5, 1T-8, 1T-10, and 1T-11. The gas production rate increased with decreases in detention time and increases in loading rate as expected. Also, as expected, the gas production rate at 55°C was higher than that at 35°C, and again there was no apparent benefit of nitrogen additions. The methane yield ranged from 1.95 to 2.63 SCF/lb VS added over the detention time range studied, 6 to 16.7 days. At the same 12-day detention times, the methane yield at 55°C, 2.42 SCF/lb VS added (Run 1T-8), was lower than those observed for all of the mesophilic runs at 35°C with Mississippi hyacinth. However, comparison of the specific methane production rates [methane production rate ÷ (loading × detention time)] in Table 7 shows that at the highest loading and shortest detention time studied in this work (Runs 1T-10 and 1T-11), the rate of methane production per pound of volatile solids added is higher at 55°C than at 35°C even though the methane yields are lower.

#### Carbon and Energy Balances

The difficulty of calculating carbon and energy balances for digestion experiments in which additions of alkali and nutrients are made has been discussed before (7). These additives contribute to ash weights. The two methods used to circumvent this problem in previous work (7) were also used in this paper. They are described in the footnotes to Table 8, which presents sample calculations by each method for Runs 1M-B, 2M-E, and 1M-9. Run 1M-9 exhibited the largest deviation from the theoretical carbon and energy balances; both balances were quite low and only accounted for 81 to 87% of the feed carbon and 86 to 92% of the feed energy. The major reason for this is probably the deviation in the experimental gas production measurements. Run 1M-9 had the largest coefficients of variation of all the runs for both gas production rate and yield (Table 7).

## Properties of Effluent and Digested Solids

A comparison of fresh feed slurries and effluents from Runs 1M-B, 1M-4, and 1M-8 is presented in Table 9. The addition of sodium hydroxide for pH control in Run 1M-B had the expected effects on total and bicarbonate alkalinities, pH, and conductivity. The effluent from Run 1M-4, which was subjected to both caustic and nitrogen additions, showed the same trends except that the ammonia nitrogen concentration also increased. Run 1M-8, which had neither caustic or nitrogen additions, showed a significant increase in alkalinities and a major reduction in volatile acids. The volatile acids present in the fresh feed slurry were expected to undergo a large decrease on balanced digestion. However, the conversion of non-ammonia nitrogen in the feed to ammonia nitrogen in the effluent is not apparent in these runs in contrast to the usual increase observed on digestion (7). Also, because of the moderate to low volatile solids reductions in these experiments, the chemical oxygen demands of the digester effluents are relatively high.

A few experiments were carried out to examine the gravity sedimentation and filtration characteristics of digester effluent from Run 1M-B. The sedimentation results for unconditioned and conditioned effluent are shown in Figure 2. The settling characteristics were poor and the conditioning treatment improved settling only slightly. A more detailed study is necessary to optimize the conditioning method. Similarly, the filtration characteristics of the conditioned and unconditioned effluent shown in Table 10 were poor.

The properties of the dry feeds and digested solids from Runs 1M-B, 2M-B, and 1M-9 are listed in Table 11. Carbon content, volatile matter, and heating value of the total digested solids decreased on digestion as expected while ash content increased. The heating value per pound of contained carbon remained reasonably constant from dry feed to dry digested solids, but there appeared to be a significant reduction in the heating value of the volatile matter in the Florida hyacinth residual solids, while the heating value of the Mississippi hyacinth residual solids remained about the same as the feed. As indicated in previous work (7), this may be due to the difference in degradabilities of different organic components.

## Thermodynamic Estimates

The maximum theoretical methane yields uncorrected for cellular biomass production for the Mississippi and Florida water hyacinth samples used for the digestion runs were estimated to be 9.36 and 8.20 SCF/lb VS reacted (Table 4). Assuming that 7% of the protein and 20% of the carbohydrate is converted to cells on one pass through the digester, the maximum theoretical yield of methane for Mississippi hyacinth is given by (7):

$$(1 \text{ lb VS added} - 0.195 \text{ lb VS to cells}) \left( 9.36 \frac{\text{SCF CH}_4}{\text{lb VS reacted}} \right) = 7.53 \frac{\text{SCF CH}_4}{\text{lb VS-pass}}$$

If the same conversion factor is assumed to be valid for the Florida hyacinth sample, the corresponding yield is 6.60 SCF CH<sub>4</sub>/lb VS-pass. The highest experimental methane yields observed for the Mississippi and Florida hyacinth samples used in this work are 3.13 and 1.66 SCF/lb VS added, or about 42% and 25% of these theoretical values.

## Comparison With Other Substrates

The methane yields, volatile solids reductions, and energy recovery efficiencies as methane in the product gas from experiments carried out under similar high-rate conditions with other substrates are summarized in Table 12 (7) along with the results from Run 2M-B. The relatively narrow span of the yields and efficiencies when considered together suggest that standard high-rate conditions in the conventional range tend to afford about the same digestion performance with degradable substrates. The basic organic components groups in these substrates are similar. Usually, the largest fraction consists of mono and polysaccharides and the smallest fraction is lignin, if present at all. The protein content is usually intermediate in concentration. Experimental data indicate that the hemicelluloses are generally more degradable than the celluloses on digestion (7), and that the celluloses and protein fraction are lower in degradability than the monosaccharides (12). Thus, feeds

high in hemicelluloses and monosaccharides should exhibit high gasification rates, but the actual concentrations of these components in the feeds might be expected to govern gas yields. Further improvements in yields and energy recovery efficiencies are therefore more likely through post- or pre-treating procedures that increase the degradabilities of the resistant organic components in biomass, or through longer residence times. For example, about 90% of the monosaccharide glucose was converted to product gas on anaerobic digestion at an overall residence time of about 4.5 days in a two-phase system (13), while long-term digestion of cellulose indicates an ultimate anaerobic biodegradability of about 75% (14). A mixed biomass-waste feed containing water hyacinth has been estimated to have an ultimate biodegradability of 66% (15).

#### CONCLUSIONS

Water hyacinth under conventional high-rate digestion conditions exhibited higher methane yields and energy recovery efficiencies when grown in sewage-fed lagoons as compared to the corresponding values obtained with water hyacinth grown in a fresh-water pond. Mesophilic digestion provided the highest feed energy recovered in the product gas as methane while thermophilic digestion, when operated at sufficiently high loading rates and reduced detention times, gave the highest specific methane production rates. Methane yields, volatile solids reduction, and energy recovery as methane for the sewage-grown water hyacinth were in the same range as those observed for other biomass substrates when digested under similar conditions.

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Table 1. MOISTURE, VOLATILE MATTER, AND ASP CONTENT OF MISSISSIPPI WATER HYACINTH PLANT PARTS Harvested 6-3-77

Plant Part	Moisture	Volatile Matter	Ash
	wt %		
Roots	91.2	63.6	36.4
Stem, Stolon	90.4	80.5	19.5
Stem, Subfloat	90.9	81.2	18.8
Stem, Float	91.1	80.5	19.5
Leaf	87.5	82.6	17.4
Average	90.2	77.7	22.3
Whole (Chopped, Frozen, Thawed, Ground) <sup>a</sup>	95.3	77.7	22.4

<sup>a</sup> After shipment to laboratory, thawing, and grinding.

Table 2. TYPICAL PARTICLE SIZE ANALYSIS OF GROUND WATER HYACINTH

<u>U. S. Sieve Size, mm</u>	<u>Retained on Sieve, wt %</u>
1.180	0
0.600	12.7
0.297	34.5
0.250	72.7
0.212	78.2
0.180	85.5
0.149	89.1
0.105	94.8
0.063	98.2

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Table 3. EFFECT OF SOURCE, HARVEST TIME, AND STORAGE ON MOISTURE, VOLATILE MATTER, AND ASH CONTENT OF WATER HYACINTH<sup>a</sup>

<u>Source</u>	<u>Harvest Date</u>	<u>Storage Time, mth</u>	<u>Moisture</u>	<u>Volatile Matter</u>	<u>Ash</u>
			<u>wt %</u>		
Bay St. Louis, Mississippi	6-3-77	2.5	95.3	77.5	22.5
		2.8	95.3	77.9	22.1
		7.8	95.0	76.9	23.1
	6-21-78	0.2	94.3	76.5	23.5
		2.2	94.3	75.2	24.8
		7-19-78	2.8	94.5	78.8
Fort Myers, Florida	3-13-78	0.5	94.7	79.9	20.1
		5.0	94.3	80.9	19.1

<sup>a</sup> All samples ground with 0.030-in. cutting head of Urschel grinder, homogenized, stored at -20°F, and thawed before analysis in triplicate.

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Table 4. PHYSICAL AND CHEMICAL CHARACTERISTICS OF WHOLE WATER HYACINTH PLANTS AFTER GRINDING

Source	Mississippi 6-3-77	Florida 3-13-78
Harvesting Date		
Ultimate Analysis, wt %		
C	41.1	40.3
H	5.79	4.60
N	1.51	1.96
S	0.41	0.49
P	0.46	0.39
Ca	2.15	5.80
Ka	1.85	0.47
K	1.46	1.00
Mg	0.35	1.40
Proximate Analysis, wt %		
Moisture	95.3	94.5
Volatile Matter <sup>a</sup>	77.7 (77.5)	80.4
Ash <sup>a</sup>	22.4 (22.5)	19.6
Organic Components, wt % of TS		
Crude Protein <sup>b</sup>	12.3	9.4
Cellulose <sup>c</sup>	16.2	—
Hemicellulose <sup>c</sup>	55.5	—
Lignin <sup>c</sup>	6.1 (5.4)	—
High Heating Value		
Btu/dry lb	6,886	6,389
Btu/lb (DMF)	8,862	7,947
Btu/lb C	16,754	15,856
C/N Weight Ratio	21.0	26.7
C/P Weight Ratio	89.3	103
Theoretical Methane Yield, SCF/lb VS reacted <sup>d</sup>	9.36	8.20
Theoretical Gas Composition, mol % CH <sub>4</sub>	56.1	51.8
mol % CO <sub>2</sub>	43.9	48.2
Theoretical Heat of Reaction, Btu/lb VS reacted	4606	4348

<sup>a</sup> USDA Agricultural Handbook methods.

<sup>b</sup> Kjeldahl N X 6.25.

<sup>c</sup> USDA Agricultural Handbook method, figure in parenthesis is by TAPPI method.

<sup>d</sup> Based on empirical formulas; yields are not corrected for cellular biomass production.

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Table 5. COMPARISON OF FEED SLURRIES<sup>a</sup>

Water Hyacinth Source	Mississippi	Florida
Density, g/ml at 25°C	1.0249	1.0170
Total Solids, wt % of slurry	2.47	2.41
Volatile Matter, wt % of slurry	1.92	1.92
Total Alkalinity, mg/l as CaCO <sub>3</sub>	425	1,463
pH	5.01	6.10
Bicarbonate Alkalinity, mg/l as CaCO <sub>3</sub>	302	556
Conductivity, umho/cm	3,500	2,100
Volatile Acids, mg/l		
Acetic	50	747
Propionic	102	323
Butyric	47	63
Valproic	9	9
Isobutyric	0	9
Isovaleric	0	11
Total as Acetic	173	1,065
Chemical Oxygen Demand, mg/l	15,860	17,479
Ammonia N, mg/l as N	28.0	9.4

<sup>a</sup> Formulated for loading of 0.1 lb VS/ft<sup>3</sup>-day, 12-day detention time, 5-l culture volume.

Table 6. COMPOSITION OF NUTRIENT SOLUTION

Component	Mixed Nutrient Formulation, g/l	Ammonium Chloride Solution, g/l
NH <sub>4</sub> Cl	30.0	170.0
NaH <sub>2</sub> PO <sub>4</sub>	20.0	—
KI	2.0	—
FeCl <sub>3</sub>	2.0	—
MgCl <sub>2</sub>	2.0	—
CoCl <sub>2</sub>	0.25	—
CaCl <sub>2</sub>	0.25	—
NaNO <sub>2</sub>	0.10	—
CuCl <sub>2</sub>	0.10	—
MnCl <sub>2</sub>	0.10	—
N Concentration, mg/ml	7.85	31.42
P Concentration, mg/ml	0.26	—

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Table 7. SUMMARY OF SELECTED STEADY-STATE DIGESTION DATA

Run	1M-B	2M-B	1M-4	2M-3	1M-7	1M-8	1M-9	1T-5	1T-8	1T-10	1T-11
Feed Source	Miss.	Miss.	Miss.	Miss.	Miss.	Fla.	Fla.	Miss.	Miss.	Miss.	Miss.
<u>Operating Condition</u>											
Temperature, °C	35	35	35	35	35	35	35	55	55	55	55
pH <sup>b</sup>	7.05	7.05	7.02	6.99	6.72	6.57	6.87	7.08	7.00	6.82	6.80
Caustic <sup>a</sup> Dosage, meq/l feed	49	45	47	50	0	0	31	21	17	4	5
Loading Rate, lb VS/ft <sup>3</sup> -day	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.15	0.21	0.30	0.30
Detention Time, day	12	12	12	12	12	12	12	16.7	12	6	6
Total Solids in Feed Slurry, wt %	2.47	2.47	2.47	2.47	2.47	2.41	2.41	3.70	5.19	7.41	7.41
Volatile Solids in Feed Slurry, wt %	1.92	1.92	1.92	1.92	1.92	1.92	1.92	2.87	4.03	5.76	5.76
Nutrients Added <sup>b</sup>	0	0	N	MN	0	0	0	0	N	N	0
C/N Ratio in Feed Slurry	21.0	21.0	8.2	8.2	21.0	26.7	26.7	21.0	11.8	15.1	21.0
C/P Ratio in Feed Slurry	89.3	89.3	89.3	73.2	89.3	103	103	89.3	89.3	89.3	89.3
Detention Times Operated	5.1	5.1	2.8	2.8	2.7	6.6	3.5	1.0	1.4	3.0	1.0 <sup>c</sup>
<u>Gas Production<sup>c</sup></u>											
Gas Production Rate, vol/vol-day	0.480(13)	0.497(10)	0.477(6)	0.483(7)	0.488(15)	0.268(13)	0.179(21)	0.688(10)	0.865(11)	1.062(6)	1.026(6)
Gas Yield, SCF/lb VS added	4.81(13)	4.98(10)	4.76(6)	4.82(8)	4.88(15)	2.69(12)	1.79(21)	4.58(8)	4.11(10)	3.55(5)	3.41(8)
Methane Concentration, mol %	64.0	62.8	62.3	60.6	57.4	61.8	66.2	57.5	58.7	57.9	57.3
Methane Yield, SCF/lb VS added	3.08	3.13	2.97	2.92	2.80	1.66	1.19	2.63	2.42	2.06	1.95
Specific Methane Production Rate, SCF/lb VS added-day	0.26	0.26	0.25	0.24	0.23	0.14	0.10	0.16	0.20	0.34	0.33
<u>Efficiencies</u>											
Volatile Solids Reduction, %	28.8	29.8	28.5	28.9	29.2	17.0	11.3	27.4	24.6	21.3	20.4
Feed Energy Recovered as Methane, %	35.2	35.7	33.9	33.3	32.0	21.1	15.2	30.0	27.6	23.5	22.3
Effluent Volatile Acids, mg/l as HOAc	27	26	26	51	9	5	63	7	10	21	16

<sup>a</sup> pH maintained as indicated by addition of sodium hydroxide solution, except for Run 1M-9 where lime was used. No caustic additions were made for Runs 1M-7 and 1M-8.

<sup>b</sup> "0" denotes no nutrients added to feed slurry. "MN" denotes mixed nutrient solution added to feed slurry. "N" denotes ammonium chloride solution added to feed slurry.

<sup>c</sup> Mean values; the values in parentheses are coefficients of variation.

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Table 8. SUMMARY OF CARBON AND ENERGY BALANCES

	Accounted For			
	Feed Carbon %		Feed Energy, %	
Run 1M-B	99.5, <sup>a</sup>	102 <sup>b</sup>	105, <sup>a</sup>	107 <sup>b</sup>
Run 2M-B	98.3, <sup>a</sup>	100 <sup>b</sup>	104, <sup>a</sup>	106 <sup>b</sup>
Run 1M-9	80.8, <sup>a</sup>	87.0 <sup>b</sup>	85.7, <sup>a</sup>	91.9 <sup>b</sup>

<sup>a</sup> Calculated from experimental determinations for moisture, volatile solids, ash, carbon, and heating values of feed and digested solids, and yield and composition of product gas. Volatile solids in digested solids calculated from percent volatile solids reduction.

<sup>b</sup> Calculated from parameters in footnote "a" except that ash in digested solids estimated by assuming original ash in feed is in digested solids, that NaOH used for pH control is converted to NaHCO<sub>3</sub> on ashing at 550°C and remains in ash, and that NH<sub>4</sub>Cl, if added, is volatilized on ashing.

Table 9. COMPARISON OF FEED AND DIGESTER EFFLUENT SLURRIES

Reactor	Mississippi Hyacinth Slurry	Run 1M-B	Run 1M-4	Florida Hyacinth Slurry	Run 1M-8
Total Alkalinity, mg/l as CaCO <sub>3</sub>	425	3,400	3,460	1,443	2,300
pH	5.01	7.05	7.02	6.10	6.57
Bicarbonate Alkalinity, mg/l as CaCO <sub>3</sub>	302	3,390	3,430	556	2,290
Conductivity, $\mu$ mho/cm	3,500	5,620	9,870	2,100	2,680
Volatile Acids, mg/l as HOAc	173	27	26	1,065	5
Chemical Oxygen Demand, mg/l	15,860	12,020	--	17,479	14,630
Ammonia N, mg/l as N	28	27	640	9	2

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Table 10. VACUUM FILTRATION CHARACTERISTICS OF DIGESTION EFFLUENT  
(Run 1M-B)

Effluent		Cake		Yield <sup>a</sup>		Conditioned <sup>b</sup>
TS, wt %	VS, wt % of TS	TS, wt %	VS, wt % of TS	Dry Cake, lb/ft <sup>2</sup> -hr	Filtrate, lb/lb dry cake	
1.63	60.7	11.5	82.1	1.75	136	No
1.60	61.3	14.4	73.5	0.445	420	Yes

<sup>a</sup> 30 sec cycle time, 6 sec form time, 12 sec drying time, 12 sec removal time, 20 in. Hg.

<sup>b</sup> Flocculent doses were FeCl<sub>3</sub>, 5 wt % TS; Ca(OH)<sub>2</sub>, 10 wt % TS.

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Table 11. COMPARISON OF DRY FEED AND DIGESTED SOLIDS

	Mississippi Hyacinth	Run 1M-B	Run 2M-B	Florida Hyacinth	Run 1M-9
Ultimate Analysis, wt %					
C	41.1	31.7	31.3	40.3	27.3
H	5.29	3.82	3.78	4.60	3.30
N	1.96	1.98	1.98	1.51	--
Proximate Analysis, wt %					
Moisture	95.3	--	--	94.5	--
Volatile Matter	77.7	60.7	60.7	80.4	69.4
Ash	22.4	39.3	39.3	19.6	30.6
Heating Value					
Btu/dry lb	6,886	5,280	5,249	6,389	4,391
Btu/lb (MAP)	8,862	8,698	8,647	7,947	6,327
Btu/lb C	16,754	16,656	16,770	15,854	16,084

<sup>a</sup> The dry digested solids were prepared by evaporation of the total effluent to dryness on a steam bath, pulverization, and drying in an evacuated desiccator to a constant weight.

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Table 12. COMPARISON OF STEADY-STATE METHANE YIELDS AND EFFICIENCIES UNDER STANDARD HIGH-RATE CONDITIONS<sup>a</sup>

	Coastal Bermuda Grass <sup>b</sup>	Kentucky Bluegrass	Giant Brown Kelp	Mississippi Water Hyacinth <sup>c</sup>	Primary Sludge
Methane Yield, SCF/lb VS added	3.51	2.54	3.87	3.13	5.3
Volatile Solids Reduction, %	37.5	25.1	43.7	29.8	41.5
Energy Recovered as Methane, %	41.2	27.6	49.1	35.7	46.2

<sup>a</sup> Loadings of about 0.1 lb VS/ft<sup>3</sup>-day, detention time of 12 days, 35°C.

<sup>b</sup> Supplemented with added nitrogen.

<sup>c</sup> Run 2M-B.

A80030700

# GASIFICATION OF FEEDLOT MANURE IN A FLUIDIZED BED

## The Effects of Superficial Gas Velocity and Feed Size Fraction

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### INTRODUCTION

The dwindling supplies of oil and impending shortages of natural gas have made it worthwhile to consider recovering energy from solid wastes. Agricultural wastes such as feedlot manure, are one class of materials that are being investigated for possible utilization. Feedlot manure is a low sulfur material that is renewable and available in significant amounts in certain areas. Manure can be converted into useful products by anaerobic digestion, atmospheric pressure gasification or liquefaction. Of these, atmospheric pressure gasification appears to be the most economically attractive [Engler et al., (1)]. Contacting devices, such as the fixed bed, the moving bed, the entrained bed and the fluidized bed can be used for gasifying manure. From the standpoint of gas production, fluidized beds are highly desirable because of their high heat transfer characteristics and their capabilities for maintaining isothermal conditions.

A survey of the literature on the gasification of manure indicates that the available experimental data are somewhat limited. Most investigators have only examined the influence of temperature. Burton (2) carried out two experimental runs with dried cow manure in a fluidized bed reactor. The reactor used was 0.38 m (15") in diameter and employed inert matrix of sand as the bed material. Hot fluidizing gas for the reactor was generated by combusting methane or propane. The reactor operating temperatures used for the two runs reported were 1041 K and 1022 K. Smith et al., (3) published partial oxidation data obtained in a moving bed reactor using manure as the feed material. The experiments were conducted in a 0.05 m (2") diameter reactor and used recycled product gas and air as the gas medium. Data were obtained for a temperature range of 894 K to 950 K.

Bench scale operating data were obtained by Halligan et al., (4) in a 0.05 m (2") diameter reactor, which was operated in a partial combustion mode using steam and air. The reactor was externally heated with electrical heaters and the data were obtained between 977 K and 1069 K. Mikesell et al., (5) reported limited data on the flash pyrolysis of steer manure in a multiple hearth reactor. The operating temperatures for these experiments were between 873 K and 1023 K. Recently, Beck et al., (6) presented partial oxidation data on manure obtained in a pilot plant reactor. Steam and air were used as the fluidizing medium in the 450 kg/day pilot plant. The reactor used was 0.15 m (6") in diameter and had an axial temperature variation of about 500 K. The data were presented for an average temperature of about 870 K in the reactor. Howard et al., (7) have recently completed a comparative study on the gasification of a variety of biomass materials (including manure) in a 0.5 m ID fluid bed pilot plant. They examined the influence of fluidization velocity and reactor loading and gasifier performance.

To properly design a system for the gasification of manure or other biomass, it is necessary to develop systematic data base which includes the effect of operating temperature, feed size, superficial gas velocity and perhaps other variables on the gasification characteristics. These would be most useful if obtained on a pilot plant scale. The objectives of the present work were to conduct gasification experiments

with manure in a fluidized bed reactor and to assess the influence of the feed size fraction and superficial gas velocity on the following: 1) produced gas composition; 2) higher heating value of the produced gas; and 3) produced gas yield. The operating temperature was also varied in the experiments.

## EXPERIMENTAL

### Facilities

The pilot plant facility used for the gasification of manure is shown schematically in Figure 1. The pilot plant consisted of the following seven components: 1) the reactor, 2) a screwfeeder, 3) a cyclone separator, 4) a Venturi scrubber, 5) an afterburner, 6) a control and instrumentation panel and 7) a gas sampling train.

The reactor was constructed from heat resistant stainless steel 316 alloy. The reactor proper had an I.D. of 0.23 m (9") with an expanded freeboard of 0.41 m (16") I.D. A burner with a duty of 47.5 MJ/hr (45,000 BTU/hr) located at the bottom of the reactor (plenum) generated the gas for fluidization by the combustion of propane under starving air conditions. Water was also injected into the plenum section as necessary to maintain the temperature below 1250 K and to supply additional gas for fluidization. A sampling port was provided at the plenum section to permit monitoring of the composition of the fluidizing gas. Supplemental heat (as needed) for operation was transferred across the walls of a radiant jacket surrounding the reactor. A burner with a duty of 105.5 MJ/hr (100,000 BTU/hr) supplied heat to the jacket using natural gas as the fuel. The distributor plate for the reactor was made from a 3 mm thick 316 stainless steel plate and had 844 holes of 1.5 mm diameter. The reactor was well insulated with a minimum of 0.1 m of Kao Wool and had adequate temperature and pressure measuring elements located at various strategic points. An inert matrix composed primarily of silica sand was used as the bed material. Approximately 45 kg of sand with a mean particle size of 0.55 mm was used to give a static bed height of 0.6 m (24"). An overflow pipe for withdrawing solid samples from the bed was provided on the reactor as shown in Figure 1.

The solids to be gasified were fed into the bed through a feed pipe of 0.075 m (3") diameter, which discharged the feed just above the expanded bed surface. The feed material was delivered to the feed pipe from a sealed hopper with a variable speed screw feeder. A purge stream of about 0.36 cubic meter/hr of helium was used to maintain a positive pressure on the feed hopper as well as the feed pipe so as to prevent the backflow of off-gas into the feeder and subsequent condensation in the feeder. The off-gas from the reactor was withdrawn from the top and passed through a cyclone separator for removing the entrained solid particles which were collected in a receiver located below the cyclone. The cyclone could remove particles up to a diameter of 5 micrometers. A gas sampling point was provided at the inlet of the cyclone for monitoring the composition of the reactor off-gas. The solids free gas from the cyclone was then sent into a Venturi scrubber, which served to quench the off-gas and remove condensibles. The scrubber waste water was discharged to the sewer and the scrubbed gases were sent to an afterburner. The afterburner served as a flare stack which permitted the gas to discharge to the atmosphere after incineration.

All the temperature and flow measuring instruments and the temperature recorder for the pilot plant were mounted on a control panel. Control loops with alarms were provided to ensure safe operation. A twelve point strip chart recorder was used to monitor the temperatures at several locations, including the plenum section, the radiant section, the portion just above the distributor, the middle portion of the reactor, and the freeboard section.

A sampling train was constructed to collect samples of the plenum gas as well as the reactor off-gas. The sample stream was passed through a series of glass condensers and condensate receivers permitting the separation of condensibles from the

stream. The cooled sample gas was passed through a wet test-meter, and then through a sample bottle, and subsequently incinerated.

#### Feed Material Preparation

The manure used was collected from paved feedlots at Kansas State University's Beef Research Center. The manure had a moisture content of about 80% and was subsequently flash dried to reduce the moisture content to about 8%. The dry manure was sieved to obtain three size fractions, namely; -2 + 8 mesh (0.45 cm), -8 + 14 mesh (0.19 cm) and -14 + 40 mesh (0.09 cm). The ultimate analyses of the three sizes of manure are presented in Table 1.

#### Procedure

The reactor was initially heated to the desired operating temperature using both the plenum and radiant burners. The temperatures in various parts of the reactor were monitored to establish a stable starting condition. The propane used in the plenum burner was burnt under starving air conditions to ensure an oxygen deficient atmosphere in the reactor. Gas samples (2 or 3) were taken from the plenum section for analysis before a run was initiated. Over the course of the sampling period, condensate was collected for a measured volume of the burner gas (saturated at the metering conditions) to determine the water content of the fluidizing gas.

Manure was introduced into the reactor at a continuous prespecified rate, and the temperature profile of the reactor was closely monitored. Samples of the reactor off-gas were taken with the simultaneous collection of condensate. Run durations were 30 minutes to one hour. Feeding was then terminated and the char collected in the cyclone was weighed. Samples of the cyclone char were reserved for analysis. After the completion of each run, the char retained in the reactor was burnt with excess air and the ash produced was elutriated from the bed and collected in the cyclone. A sample of the ash generated was also reserved for analysis.

The flow rates of the propane, air and injection water were noted during each run. The solid feed rate was determined by the difference in weights of solids in the hopper before and after the experiment. For each of the runs, the gas samples were drawn after flushing the sample bottles for about five minutes. The volumetric flow of gas through the wet test meter and the pressure and the temperature of the wet test meter were noted. The condensates collected were measured volumetrically.

#### Chemical Analysis

Gas analysis was accomplished using a Packard Model 417 Becker Gas Chromatograph equipped with thermal conductivity detectors. The gas components of interest included H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, H<sub>2</sub>S, N<sub>2</sub> and O<sub>2</sub>. Column packings used were a 5A molecular sieve for the separation of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, and CH<sub>4</sub>, while the remaining components were separated using a column of Porapak Q with a short lead section of Porapak R to shift the retention of water. The chromatograph was operated isothermally at 80°C with helium as a carrier gas. The instrument was calibrated with purchased calibration mixtures. Solid materials were analyzed with respect to their elemental composition (C, H, N, O) using a Perkin-Model 240 Elemental Analyzer. The ash analysis was performed according to the standard ASTM procedure in a muffle furnace and the moisture content was determined by drying the samples in an oven for 3 hours at 373 K. The compositions of the solids and gases given in this study represent the average of at least two determinations.

#### Operating Conditions

Gasification experiments were conducted by varying the operating temperature, the feed size fraction and the gas superficial velocity. The arithmetic average

between the bed temperature and the freeboard temperature was taken as the operating temperature of the reactor. In all the experiments, the freeboard temperature was less than the bed temperature. The maximum temperature difference observed in this study was 120 K and the average temperature difference was 80 K. A summary of the operating conditions is presented in Table 2.

#### Data Analysis

Mass balance calculations were first performed on the plenum burner using the analysis of the dry plenum gas, the condensate collected and the flow rates of propane, air and injection water. The flow rate of the dry burner gas entering the reactor was computed by performing a nitrogen balance around the burner. An overall nitrogen balance on the reactor was then used to evaluate the dry off-gas flow rate with the aid of the off-gas analysis. For computing the amount of gas produced from the manure, it was assumed that the burner gas did not significantly take part in the reactions. The yield and the composition of the dry produced gas were computed as the difference between the dry off-gas and the dry burner gas.

From the condensate collected for a unit volume of the burner gas, the total water content of the burner gas was computed using the volumetric flow rate of the dry burner gas. Similarly, the condensate associated with the dry off-gas was computed from the volumetric flow rate of the dry off-gas and the condensate data obtained for a unit volume of the dry off-gas. The liquid produced during gasification was computed as the difference between the two after making appropriate corrections for the water of saturation of the metered gases.

To complete the overall material balance around the reactor, it was necessary to know the total amount of char produced. Since a portion of the char was retained in the bed, it was necessary to establish a procedure for evaluation of the total char generated. Attempts were made to estimate the char in the bed by performing an inert balance on the ash produced during combustion and the char. This method was not very satisfactory since substantial amounts of the ash were carried past the cyclone to the scrubber and drain. From experimental observations, it was found that for any run, the elemental analysis of the cyclone char and the char retained in the reactor agreed with each other closely. Hence, the char retained in the bed was assumed to have the same composition as that of the cyclone char. The total char produced was estimated using the ultimate analysis of char and feed coupled with an ash balance on the reactor. This procedure was subsequently checked with a pelletized feed material, whose char could be separated out from the inert solids in the bed. The check indicated that the inert balance was a satisfactory approach.

#### RESULTS AND DISCUSSION

Approximately 100 experiments were conducted, 45 each for the -8 + 14 mesh and -14 + 40 mesh fractions and the remainder for the -2 + 8 mesh fraction. For each run, material balance calculations were performed to evaluate the quantity and the composition of the produced gas. Material balance closure ranged from 80-115% with most runs closing to better than 90%. The higher heating value of the produced gas was calculated from its composition and the heating values of the individual components. The effects of superficial gas velocity and the feed size fraction were assessed from the results obtained.

#### Product Gas Composition

To examine the influence of gas superficial velocity on the concentrations of the individual components of the produced gas, data obtained at different superficial velocities were plotted against the operating temperature for a given

feed size fraction. These plots, presented in Figures 2 and 3 (for the -8 + 14 mesh and the -14 + 40 mesh sizes) showed a minimal scatter ( $\pm 1\%$ ) indicating that for the range investigated, the gas superficial velocity did not have a discernible influence on the produced gas composition. In these two plots as well as in the subsequent ones, the actual data points are not shown for the sake of simplicity.

The effect of the size fraction used on the composition of the produced gas can be assessed by comparing Figures 2 and 3. For a given operating temperature, comparison shows that the concentrations of  $C_2H_6$  and  $C_3H_8$  are very close to each other for the two feed size fractions. The concentrations of  $CH_4$ ,  $C_2H_4$  and  $CO_2$  show similar trends in both cases. Their numerical values are in good agreement with each other up to an operating temperature of about 950 K. Beyond this temperature, the differences are more pronounced. The concentrations of  $H_2$  and  $CO$  complement each other in the two plots. A higher value of  $H_2$  concentration is offset by a lower value of  $CO$  concentration and vice versa. It can also be seen that the concentration of  $CO_2$  goes through a minimum in the two figures with the numerical values for the two size fractions being distinctly different.

Figure 2 shows that for the -8 + 14 mesh size fraction, the concentration of  $H_2$  in the produced gas varied between 19% and 35% and that of  $CO$  varied between 20% and 25%. In Figure 3 it can be seen that for the -14 + 40 mesh size fraction, the concentration of  $H_2$  varied between 15% and 50% and that of  $CO$  between 25% and 15%. These two figures suggest that there is a distinct difference in the concentrations of  $CO$ ,  $H_2$  and  $CO_2$  from the two size fractions. Limited data for the -2 + 8 mesh size fraction did not show an appreciable difference from the results for the -8 + 14 mesh fraction.

#### Heating Value

In Figure 4 the higher heating value of the gas produced at different gas superficial velocities is plotted against the operating temperature. It can be seen that the heating values go through definite maxima and then diminish. As in the case of the produced gas composition, for a given feed size fraction, the gas superficial velocity did not have a significant influence on the heating values. The deviation observed was  $\pm 0.8 \text{ MJ/Nm}^3$  (+ 25 BTU/SCF).

By comparing the two curves in Figure 4, the effect of the size fraction on the heating value of the produced gas can be assessed. For the size fraction of -8 + 14 mesh, the heating value increases from  $10.43 \text{ MJ/Nm}^3$  (280 BTU/SCF) to  $19.75 \text{ MJ/Nm}^3$  (530 BTU/SCF) and then diminishes to  $13.41 \text{ MJ/Nm}^3$  (360 BTU/SCF) over the temperature range studied. In the case of -14 + 40 mesh fraction, the heating value increases from  $13.04 \text{ MJ/Nm}^3$  (350 BTU/SCF) to  $18.26 \text{ MJ/Nm}^3$  (490 BTU/SCF) and then decreases to  $12.3 \text{ MJ/Nm}^3$  (330 BTU/SCF). These data indicate that the feed size fraction may have a marginal influence on the heating value of the produced gas. This trend was confirmed when the data were compared with a limited number of data obtained for a -2 + 8 mesh fraction of manure as shown in Figure 4. A comparison of the heating value curves for the three size fractions indicates that the smaller the size, the lower the heating value of the produced gas at temperatures above 900 K. The peak of the heating value curve shows a shift to the right as the size fraction becomes larger. Also, as size increases, the peaks become narrower.

#### Produced Gas Yield

Figure 5 presents plots of the yield of dry produced gas (on a dry ash free basis) versus temperature for the different size fractions. The data points for a given size fraction showed a fair amount of scatter. The scatter was such that bands of  $\pm 0.25 \text{ Nm}^3/\text{kg}$  about the lines shown in Figure 5 were needed to contain the data for

a given size fraction. There were no discernible trends in the data to suggest that superficial velocity variations were responsible for the scatter observed. The average yield of dry produced gas ranges from 0.13 Nm<sup>3</sup>/kg (2.1 SCF/lb) at 820 K to 0.86 Nm<sup>3</sup>/kg (13.8 SCF/lb) at 1020 K for the -14 + 40 mesh fraction. For the -8 + 14 fraction the average yield ranges from 0.04 Nm<sup>3</sup>/kg (0.6 SCF/lb) at 820 K to 0.72 Nm<sup>3</sup>/kg (11.5 SCF/lb) at 1020 K. A limited amount of data for the -2 + 8 size fraction are also presented in Figure 5. The comparison shows a definite tendency for higher gas yields with smaller feed size fraction.

A simple conceptual model for the gasification of manure can be envisioned to consist of the following steps: 1) Devolatilization of the solid to form char and volatile matter; 2) Thermal cracking of heavy volatiles to produce light components and char (carbon deposition) and gas phase water-gas and steam-hydrocarbon reactions. The yield of total volatiles in the first step will dictate the level of gas yield that can be obtained from the solid feed. The extent of thermal cracking and other gas phase reactions of the volatiles is determined by their time-temperature history. These reactions will establish the final ratio of gas to liquid and the gas composition.

Thermogravimetric studies on manure have indicated that the devolatilization step starts around 420 K and is complete around 770 K [Howell, (8)]. Statistical analysis of additional data taken in this laboratory indicate that the heating rate employed (40 K/min to 160 K/min) has no effect on the devolatilization characteristics. Antal's work (10) on manure indicates a slight dependence on heating rate (5 K/min to 140 K/min) but this was not examined to determine if it was statistically significant. Anthony and Howard (9), in their work with coal, have argued that high heating rates (10,000 K/sec) give a greater extent of devolatilization than can be obtained with normal TGA heating rates.

Since the rate of heat transfer is very high in the fluid bed (1000 K/sec) and normal operating temperatures are well above those for completion of devolatilization, it can be assumed that the devolatilization step takes place instantaneously. Further more, for the range of temperature employed, it is anticipated that the variation in operating temperature has little effect on the extent of devolatilization. In this work comparisons are made at a given operating temperature and even if a temperature dependence of the devolatilization did exist, the phenomenon would not be a variable that influenced the comparison. Consequently the devolatilization phenomenon can be ruled out as a cause for the observed variations in gas yield for a given feed size.

Antal (10) conducted studies of the vapor phase cracking reactions with volatiles produced from cellulose under conditions where the devolatilization phenoma was held constant. He found that at a given temperature, the amount of each component in the produced gas was affected by the residence time. His results indicated that for residence times up to about 5 seconds, the yield of the components such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> increased dramatically and beyond five seconds the effect was much less pronounced. He also found that the amount of each component increased with temperature and in the case of both C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>6</sub> the amounts of each passed through maxima as temperature increased.

In the present work, the residence time of the gas in the reactor was calculated to be approximately six seconds. The variation in this value over the experimental range was about  $\pm 1$  second. Since this value is more than five seconds and the variation observed is not extensive, it can be expected that the gas residence time does not have a significant effect on the data. This is corroborated by the experimental observation that the superficial velocity of the gas, which is related to the residence time, did not have a significant influence on the gas composition and heating value for a given feed size fraction and a given gasification temperature. However, the yields obtained with a given feed size fraction and temperature showed a significant scatter

which is far beyond the bounds of variations that can be expected on the basis of the variations in the time-temperature history that the produced gases experience.

One plausible explanation for the observed behavior might lie in possible variations in the feed make-up as a consequence of segregation effects between batches. This is supported by the observation made during the test program that the gas yield data for a given batch of manure were consistent but varied from batch to batch for a given feed size and operating temperature. An examination of the elemental analysis of the different feed batches did not indicate significant variations in elemental composition. Since manure consisted of a mixture of stalks, hulls and other plant materials, it was next decided to examine possible variations in the cellulose content of these components. Whistler and Smart (11) indicate that a considerable variation in cellulose content exists for different parts of a plant as well as between different types of vegetation. For example, leaves contain 10-20% cellulose, stalks, 40-50%, hulls, 35% and cobs, 40% cellulose. Consequently segregation phenomena between batches could give rise to feeds with different cellulose content.

The influence of cellulose content on the devolatilization characteristics of biomass materials was then examined. Howard et al. (7) reported on the maximum oil yield obtainable from different biomass materials. The maximum oil yield can be related to the extent of devolatilization that will take place for a given material. In their work with paper, sawdust and mixtures of the two, it was observed that the maximum oil yield increased in the order sawdust, mixture, paper. The cellulose content increases in the same order. Their study does not relate this observation to the gas yield, unfortunately.

In order to examine this dependence further, limited data on the cellulose content, TGA analysis and gas yields for cellulose, paper hardwood, softwood, manure and coal were compared. Table 3 presents the summary of the TGA results obtained by Antal (10) for cellulose, paper and wood and by Howell (8) for manure and coal. The cellulose content as well as the relative gas yield for some of these materials are also presented for comparison. The relative gas yield is for 970 K with the result for cellulose from Antal (10) and the remaining values from this laboratory. As these limited data indicate, it appears that the TGA results, gas yields and cellulose content show the same trends implying that increasing cellulose content may correlate with increasing devolatilization. This possible correlation needs to be examined further.

It is quite possible in this work, that between batches, the cellulose content of the manure feed could have been different due to segregation. This difference could very well be responsible for the scatter observed in the produced gas yield for a given feed size fraction. In view of this, caution should be exercised in interpreting the influence of particle size on the gasification characteristics of biomass.

For the different feed size fractions, variations in the material make-up were evident. The -2 + 8 mesh size fraction consisted of hulls and undigested grain. The -8 + 14 mesh size fraction was spherical in shape and had a small amount of undigested grain, whereas the size fraction of -14 + 40 mesh was comprised of fine strands of stalks.

The differences in heating value and yield observed for different size fractions could well be due to variations in material make-up alone but it cannot be ruled out that particle size may also have some influence. Maa and Bailey (12) in their study on cellulosic materials, theorized that for particle sizes less than 0.2 cm in diameter, pyrolysis is reaction controlled and the particle size has no influence. In the present study the size fraction -14 + 40 mesh (0.09 cm) falls below this value, the size fraction -8 + 14 mesh (0.19 cm) is marginally below, while the size fraction -2 + 8 mesh (0.45 cm) is above the 0.2 cm size stipulated by Maa and Bailey.

Consequently for this study size effects should not be important for the smallest size fraction but may be intruding for the other two sizes, especially the largest size.

#### CONCLUSIONS

Gasification studies were conducted with different size fractions of manure particles in a fluidized bed reactor. The effects of gas superficial velocity and feed size fraction on the gasification were studied at different operating temperatures. Superficial gas velocity did not appear to have a significant influence on the composition and heating value of the produced gas. The feed size fraction did have a definite influence on the composition, heating value and yield of the produced gas. The observations indicate that the yield increases and the heating value decreases as the size fraction becomes smaller. In the conduct of the experiments considerable scatter was observed in the gas yield obtained with different batches of feed for a given operating condition. A possible explanation for this behavior is offered which suggests that segregation phenomenon between batches of feed and subsequent variations in the cellulose content of the batch may be primary factors influencing the observed scatter. The apparent correlation between the cellulose content and the gas yield needs further examination.

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This is Contribution No. , Department of Chemical Engineering, Kansas Agricultural Experiment Station, Kansas State University, Manhattan, Kansas 66506.

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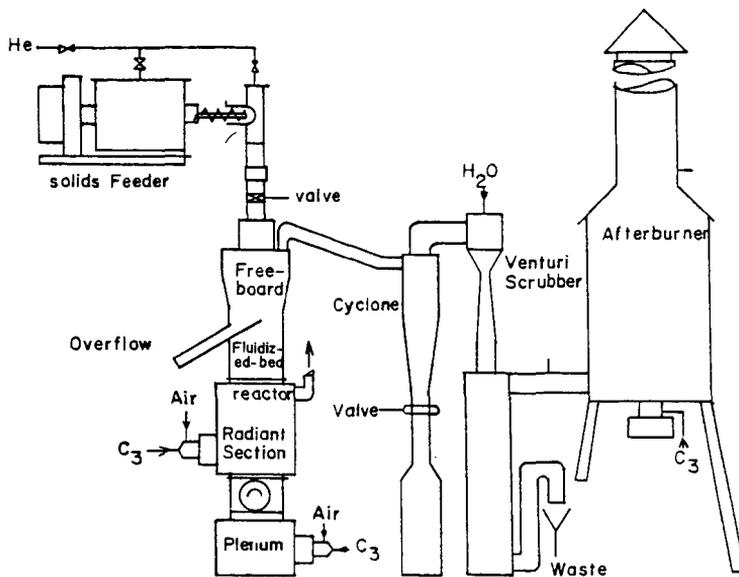


Figure 1. Flow scheme of the Pilot plant.

Table 1. Elemental Analyses of the Feed

	-2 + 8 mesh (wt %)	-8 + 14 mesh (wt %)	-14 + 40 mesh (wt %)
C	43.1	38.9	41.1
H	5.8	5.4	5.2
N	3.0	3.1	3.3
O (by difference)	26.5	30.4	30.0
Moisture	4.8	9.4	6.6
Ash	16.8	12.8	13.8

Table 2. Summary of Operating Conditions

Feed Size Fraction	-2 + 8 Mesh	-8 + 14 Mesh	-14 + 40 Mesh
Feed Rate (kg/hr)	11.0 to 17.2	11.9 to 30.2	5.1 to 31.8
Reactor Temperature (K)	900 to 980	800 to 1040	800 to 1040
Superficial Gas Velocity (m/sec)	0.31 to 0.37	0.33 to 0.45	0.33 to 0.45
Injection Water Rate (kg/hr)	2.0 to 2.5	2.0 to 3.5	2.0 to 3.5

Table 3. Devolatilization Characteristics of Different Materials

Materials	Total Devolatilization (weight %)	Relative gas yield	Cellulose content (weight %)
Cellulose	90	11	100
Paper	85	-	
Cherry (Hardwood)	80	-	
Pine (Softwood)	70	-	58
Cane (Sorghum)	-	7	35-50
Manure	55-60	5	
Coal	30	3	0

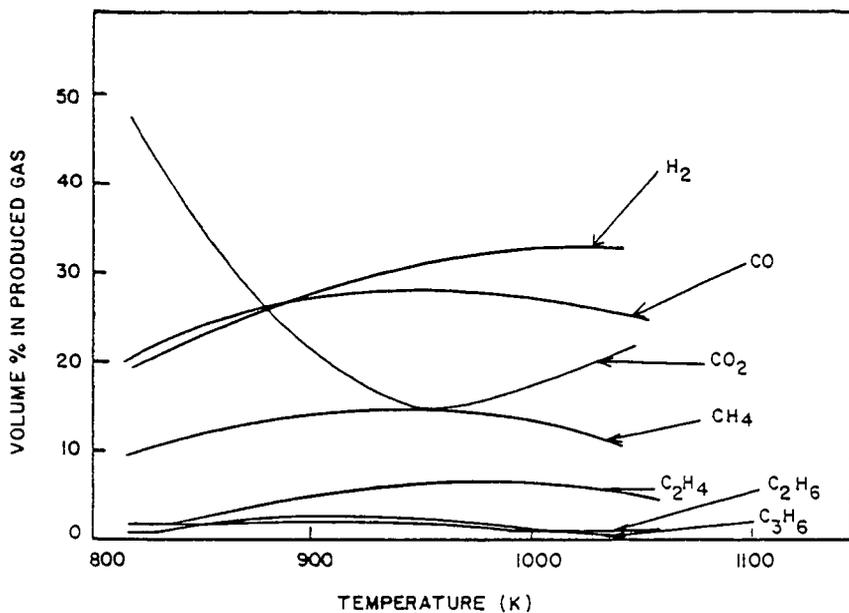


Figure 2. Produced gas composition versus temperature for -8 + 14 mesh size.

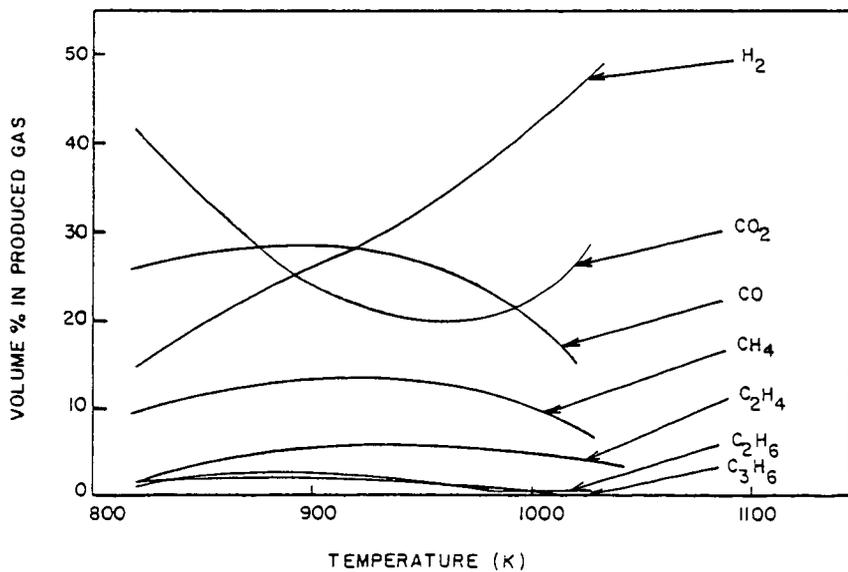


Figure 3. Produced gas composition versus temperature for -14 + 40 mesh size.

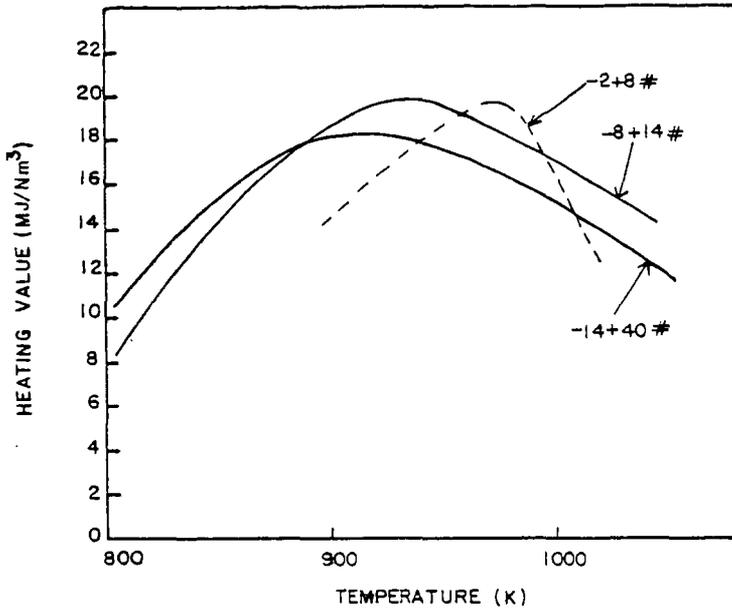


Figure 4. Gas higher heating value versus temperature.

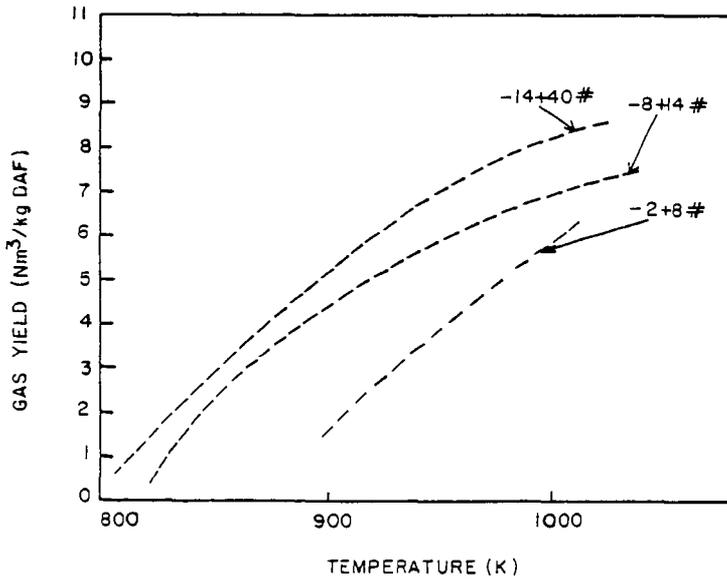


Figure 5. Gas yield versus temperature.

## LANDFILL GAS RECOVERY AT THE ASCON DISPOSAL SITE

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### INTRODUCTION

The rapid rise in the cost of energy has prompted increased interest in the recovery and utilization of landfill gas (LFG) at locations throughout the United States. The U.S. Department of Energy (DOE) has estimated that the nation's solid waste landfills generate 200 billion cubic feet of methane gas annually. Except for a few locations, this potential resource is being lost to the atmosphere. Further, approximately 0.5 million tons of solid waste are added daily to active sanitary landfills in the United States.

The generation of methane gas during the anaerobic decomposition of landfilled solid waste is a well-known phenomenon. Landfill gas typically contains 50-60 percent methane. The balance is composed of carbon dioxide and trace quantities of many other gases. The rate of gas generation will generally be highest during the first few years after solid waste burial and will tend to decrease with time. The exact details of this time variation are not well known for full size landfills. Small scale experiments do not appear to simulate what is found in the field. For lack of a better understanding, it is often assumed that the long term gas generation rate, after the first few years, can be described by an exponential decay and associated half-life.

Theoretically, the maximum amount of methane which can be produced during the life of a gas-generating landfill is about 4.5 cu ft of methane per lb of refuse. This amount would not, however, be generated in a reasonable time. Moreover, actual recovery will be less than 100 percent. A maximum recovery of 1 to 2 cu ft of methane per lb. of refuse is considered reasonable at this time.

Initial efforts at LFG recovery occurred in Los Angeles County at the Palos Verdes Landfill operated by the Los Angeles County Sanitation Districts in the mid-1960s. From this modest beginning, LFG recovery technology has been successfully applied at five other landfills and is under active consideration at another 17 locations nationally.

### ASCON SITE DESCRIPTION

The Ascon disposal site is located in the Wilmington area of Los Angeles, California. The site was a former borrow pit and occupies an area of approximately 38 acres. Household and commercial rubbish, tank bottoms from refining operations, and oil field drilling muds have been disposed at the site since 1960 to an average depth of about 60 feet. Soil is scarce at the site, and auto shredder waste is used as daily cover material for the compacted wastes.

A portion of the site was formerly used as a storage area for petroleum coke. Large quantities of water were added to these storage piles and resulted in perched water and high moisture conditions within the landfill. Filling operations are scheduled to cease in 1980.

## FEASIBILITY STUDY

A field test program was conducted during 1976 at the Ascon site by SCS Engineers under contract to the site owner, Watson Energy Systems, Inc. This test program was designed to determine if methane gas could be technically and economically recovered from the site. Three test wells were installed and pumping tests performed over a 3-4 month period to determine:

- Gas composition as a function of withdrawal rates from the test wells.
- Gas flow rates as a function of pressure drop.
- Influence area of withdrawal wells.

During the field test program, preliminary negotiations were being conducted with an adjacent Shell Oil refinery for gas sales. Requirements for gas processing and delivery specifications were identified.

Results of the feasibility study indicated that up to 1170 cu ft per minute of LFG containing 500 to 550 Btu/cu ft could be recovered from the site. This withdrawal rate was estimated to be sustainable for at least 6 years. User requirements for the LFG were also found to be acceptable - compression to 70 psi and moisture removal at 40°F.

System design and installation proceeded and was completed in mid-1978. The LFG extraction system as originally installed was comprised of 24 vertical wells drilled to an average depth of 50 ft with associated header pipe collection system. PVC piping was used throughout the collection system. Wells were perforated for the lower 15 to 20 ft and sealed from the surface with concrete and bentonite clay.

The LFG compressor and cooling equipment utilized rebuilt equipment. A schematic of the gas withdrawal and processing system is shown in Figure 1.

During the placement of extraction wells, a number of unanticipated conditions were encountered. First, landfilled wastes were more compact and had a higher moisture content than indicated by the feasibility testing. Secondly, as a result of high moisture levels, wells would partially fill with water after drilling. Standing water levels were as high as 30 ft deep in some wells. This water could be pumped out, however replacement by seepage occurred with time. Injector pumps were installed in the deeper wells to remove excess moisture.

System start-up occurred in August 1978. Great variation existed in gas production rates of wells. Some wells were free-flowing and produced large quantities of LFG, while others were without positive pressure and yielded little or no gas, (even when considerable vacuum was applied). During the ensuing months, additional wells (averaging 35-40 ft deep) were installed to tap more productive areas of the site. Several none-producing wells were abandoned. A total of 60 wells are now located on the site.

The system has been operating essentially continuously since early 1979 and is currently capable of delivering up to 1050 scfm to the user. Deliveries are averaging about 800 scfm (1.2 mmcf/day). No

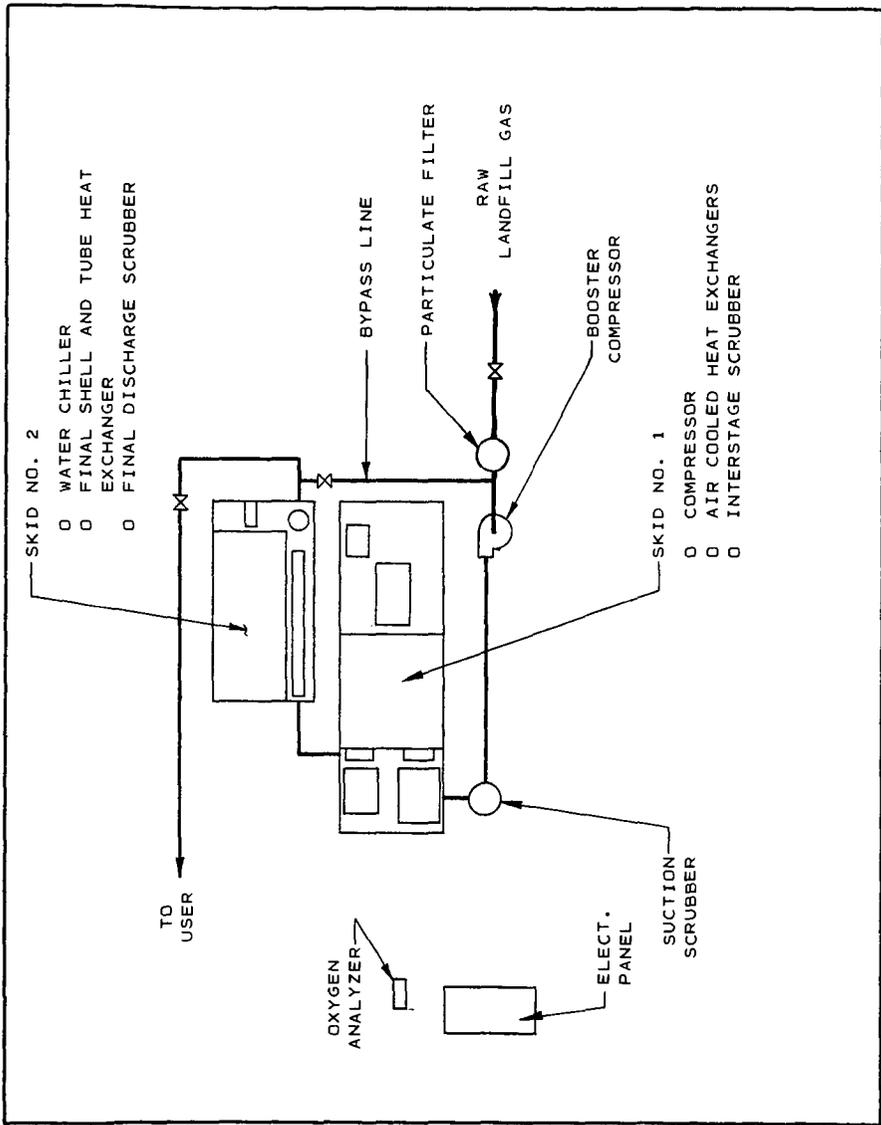


FIGURE 1. Schematic of Gas Withdrawal and Processing System

major operating difficulties or maintenance problems have arisen. However, supervision (8 hr/day) was found to be necessary for system adjustments. The system is also monitored by computer and equipped with an alarm system which shuts the system down if problems occur.

### ECONOMICS

Tables 1 and 2 summarize the capital and operating costs associated with the installed system, respectively. Annual operating costs, including amortization of capital, average 45 percent of total installed cost.

Table 3 presents the estimated annual income from the system. As can be seen, a favorable economic return exists. The sales agreement between Watson Energy Systems, Inc., and Shell Oil pegs the value of the LFG to 70 percent of the value of #6 fuel oil on an equivalent Btu basis. Entitlements are earned by Watson Energy Systems, Inc., under the applicable DOE program.

### GAS QUALITY

Gas quality at the Ascon landfill has been consistent with methane concentrations averaging in excess of 50 percent. Gas obtained from the Ascon landfill is routinely analyzed (bi-monthly) by an independent laboratory. A typical result is shown in Table 4.

Extensive analyses of gas obtained from one Los Angeles area landfill has identified more than 65 trace constituents in LFG. Trace components of the gas obtained from Ascon have been identified also. A sample analyses is contained in Table 5.

### FUTURE FOR LFG RECOVERY

Increases in energy costs have given LFG recovery a needed "shot in the arm". An additional impetus is on its way from the U.S. Environmental Protection Agency (EPA). The Resource Conservation and Recovery Act (RCRA) requirements for controlling migration of LFG as dictated by EPA's sanitary landfill criteria require methane gas concentrations at the disposal site property line to not exceed 5 percent by volume. Methane gas concentrations in facility structures cannot exceed 1-1/2 percent by volume. These requirements will necessitate installation of LFG control systems at most sites. The installed LFG control system may include some of the same facilities (extraction wells, pumps, etc.) required for an LFG recovery system. If the LFG must be removed, many enterprising site owners will actively seek a profitable market for the gas.

Finally, DOE has become increasingly interested in LFG recovery. DOE is supporting a number of projects aimed at improving LFG recovery technology. A number of new projects are likely to be supported under provisions of P.L. 96-126. Legislation supporting LFG recovery has also been introduced at the Federal level.

Thus, we can expect more LFG recovery projects in future years. Hopefully, the beneficial effects associated with LFG recovery can dispell some of the negative public reaction to landfilling of our solid wastes, while contributing to our national fuel supply inventory.

TABLE 1.  
SYSTEM CAPITAL COSTS (1978)

Compressor/Gas Chiller	\$103,000
Wells/Header	376,000
Discharge pipeline	35,000
Site work	10,000
Instrumentation/Controls	100,000
Electrical service	20,000
Engineering	65,000
	<hr style="width: 100%;"/>
Total Capital	\$709,000

TABLE 2.  
ESTIMATED ANNUAL OPERATING COSTS (1979)

Electrical Power (150,000 KW/mo. @ 5¢)	\$ 90,000
Compressor Maintenance (5% of capital cost)	5,200
Maintenance Labor (8 hr/day @ \$15)	43,800
Admin. & Testing (\$2500/mo)	30,000
Amortization (7 yr. @ 12%)	155,400
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Total Operating	\$324,400

TABLE 3.  
ESTIMATED INCOME FROM GAS SALES (1979)

Direct Sales*:	\$517,000
Entitlements <sup>+</sup> :	137,000
	<hr style="width: 100%;"/>
	\$654,000

\*1.2 mmcf/day @ 535 Btu/cf @ \$2.45 mm Btu @ 90% availability.

<sup>+</sup>Estimated based on 65¢/mm Btu

TABLE 4.  
MAJOR CONSTITUENTS - ASCON LANDFILL GAS

<u>Constituent</u>	<u>% (Volume)*</u>
Methane	55
Carbon Dioxide	42
Hydrogen	0.5
Oxygen	0.2
Nitrogen	1.2

---

\*Average of several samples

TABLE 5.  
TRACE CONSTITUENTS - ASCON LANDFILL GAS

<u>Constituent</u>	<u>Parts per Million*</u>
Acetone	32.5
Ethyl mercaptan	21.1
2-methyl furan	6.9
Methyl ethyl ketone	5.2
Benzene	5.5
Toluene	20.4
Terpene	12.4
Ethyl benzene	21.4
Xylene	14.9
Butyl alcohol	5.2
Alpha terpinene	11.1
Limonene	26.2
C <sub>3</sub> substituted benzenes	9.8
C <sub>4</sub> substituted benzenes	7.6
Dichlorobenzene	4.1
2-ethyl-1-hexanol	6.2
C <sub>4</sub> - C <sub>14</sub> hydrocarbons	114.2

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\*Sample date: May 15, 1979

## USE OF CORN COBS FOR SEED DRYING THROUGH GASIFICATION

Stanley L. Bozdech

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Coupled with discoveries of the earliest uses of corn in the western hemisphere are indications that very early the cob was in general use as fuel for cooking, and firing pottery and brick kilns. Later the early farmers of the United States, especially those in the Plains where wood was scarce, found that cobs could cook their meals and heat their homes. The petroleum age came, harvest systems changed, the cob was left to rot in the field. Today I would like to talk about that old fuel which the seed industry is attempting to mate to an old technology. The seed industry generates enough by-products (cobs) to satisfy these needs for fuel for drying seed. Gasification promises to be the technology to efficiently convert cobs to clean, controllable, heat for that purpose.

I have been introduced. But let me introduce, very briefly, one company which creates the favorable environment and provides the support for a gasifier project, and many other developing technologies.

In 1936, with the marketing of DEKALB's first hybrid corn seed, came the winged-ear trademark, touting this new product as the mortgage lifter for the corn farmers. Genetic research is the soul of the business; the production and marketing of hybrids, its physical manifestation. Today the hybrids are not only corn, but sorghum, wheat, sunflower, chickens, hogs; - all of which are distributed world wide.

In later years DEKALB has diversified into the manufacture of irrigation equipment and electronics, into petroleum production, copper mining, commodity brokerage; but DEKALB has always kept close to its central theme of "Food and Energy."

The hybrid seed corn industry is unique. It's objectives, and therefore the seed conditioning procedures, are in no way similar to the grain handling industry.

Nowhere is this more apparent than in the harvesting and drying operations. Seed corn is harvested early and with high moisture content. It is also dried on the cob, in large batch bins. Temperature of the drying air must be maintained below 110 degrees Fahrenheit to preserve the vitality of the germ.

As early as 1972 DEKALB recognized cobs as a natural fuel for its seed drying operations. It took a therm to dry a bushel of seed, but the cobs from that bushel contained about 1.3 therms. Cobs are good fuel, and have been conditioned with the seed. The market value of the cobs, at that time, at the plant site, was about 72 cents a million Btu's. This since has gone down to about 34 cents. Natural gas costs are ten times that amount; propane twenty times. That spread would provide the capital for a conversion system for cobs, although driers are used only five weeks a year, each consuming 7,000 mcf of natural gas during that time. Readily available, good, cheap fuel is definitely an advantage. But the short season with low annual fuel consumption puts constraints on capital costs.

Marginal fuel supply dictated an equipment development plan which would make use of tempered combustion gases as the drying medium. Without heat exchangers, which are wasteful, the drying stream had to be relatively free of particulate matter and toxic gases. The batch drying system itself is a good filter for particulate, and it is soon apparent how clean a system is.

In 1973 because of the high price of fuel oil in Europe, DEKALB's French associate, RAGT, invested in an incineration system for cobs, and piped the combustion gases

to the driers. Today it is still used but with tubular heat exchangers which must be cleaned weekly. Its high particulate output without the heat exchanger is shown in Table 2.

DEKALB, in the U.S., felt that since the French had done so well with everything but particulate, surely some American technique could readily solve that problem. Two direct combustion units were installed in seed plants in 1976: - one a sophisticated incinerator with after-burners, which performed poorly; the other a torroidal unit for burning fine material in suspension, which in addition to high grinding costs, threw particulate as fast as the other units. Additionally, both units slagged badly. Both were complex, expensive, difficult to operate.

The advantage of the nadir is that the only way out is up. It was time to re-evaluate our needs.

In addition to the financial incentive, fuel interruption, therefore drying interruption, would expose a seed crop to frost and wipe it out completely. The machinations of bureaucracy in releasing emergency stocks are no match to the speed of the weather. We had to go ahead.

For some time, we had been following the work of Sweden with wood gasifiers. The elemental and physical similarity between wood and cobs to us became more apparent. During the spring of 1977 I made a quick tour of Europe, including Sweden, visited with all of the gasifier people available, including several people who had been practitioners of the art during the Second World War. Additionally DEKALB researched, heavily, technical libraries in the United States.

TYPICAL ELEMENTAL ANALYSIS

	Cobs	Oak
Carbon	44.96%	50.49%
Hydrogen	6.10%	6.59%
Nitrogen	2.42%	--
Oxygen	44.77%	42.77%
Chlorine	0.29%	--
Ash	1.46%	0.15%
Moisture	0.55%	Dry
Btu/lb.	7,215	8,810

Table 1

The result is a system specifically designed to dry grain with cobs, as seen in figures 1 and 2. It meets the criteria we had established at the outset. Although it requires more management than methane or oil fired equipment, the technology is attractive enough to be widely acceptable:

- Continuous operation
- Automated output control
- Five to one turn down ratio
- Simple and direct operating techniques
- Safe operation
- Clean, efficient, heat output

It also meets economic tests:

- Low capital costs
- Reasonable operating costs
- Serviceability
- Complete heat release
- Complete utilization of the heat
- No fuel preparation costs
- Favorable fuel prices

DEKALB's gasifier system is an atmospheric, up-draft, negative-pressured, system, powered by a single fan which discharges regulated, heated, gases to a seed drier. Starting at the right, a valve at the discharge of the fan modulates the complete system starting with the production of the gas in the gasifier.

Dry cobs, as they come from the sheller, whole or in bits and pieces, are fed, on demand, into the system through alternating slide grates which keep the system sealed. At the reactive zone, with the reduction in cob size, channeling has a tendency to occur. The agitator, in an adjustable cycle, keeps the bed packed. The grates are perforated stainless steel, and in operation are generally protected

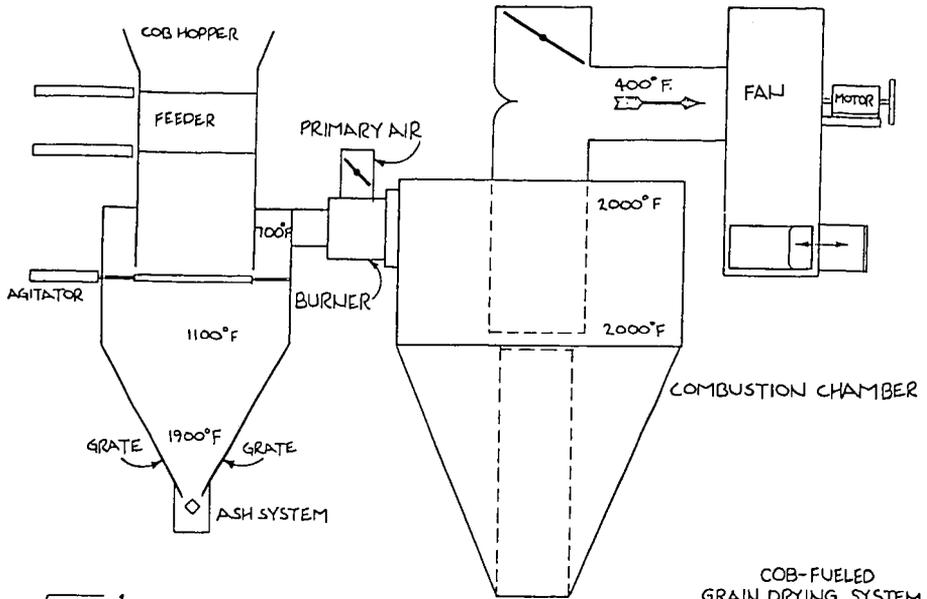
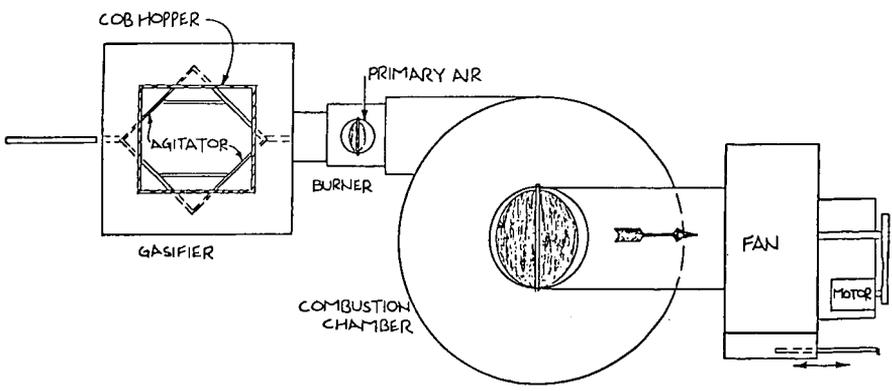


Fig. 1

COB-FUELED  
GRAIN DRYING SYSTEM  
DEKALB AGRESEARCH INC.  
DEKALB IL. 3-28-80



PLAN VIEW

Fig. 2.

COB-FUELED  
GRAIN DRYING SYSTEM  
DEKALB AGRESEARCH INC.  
DEKALB ILL 3-28-80

by layer of ash. At 1,900 degrees there is usually some indication of slagging which appears as soft clumps of ash and carbon. While slagging is not completely eliminated, the horizontal, rotary, powered, ash removal system breaks up and removes most slagged materials.

Producer gas leaves the system at 700 degrees, carrying, as a vapor, tars that often cause serious problems in updraft units. In some earlier tests, tars going through the burner as droplets were not totally consumed and left a sticky coating on fans and drying equipment. The tars are in the gas stream; - the challenge is to burn them.

On extremely cold days, primary air at the burner has a tendency to condense the tars in the burner head. This can be overcome by feed back from the combustion chamber to heat the ambient. The primary air adjustment is manual. Once set, it responds with the pressure variations in the system and maintains a constant ratio.

The design of the combustion chamber offers the gas dwell time in high temperature environment to promote complete combustion. We are striving for stoichiometric conditions. Additionally the combustion enclosure offers the first chance to blend ambient air with combustion gases. Final tempering to 400 degrees is accomplished by a modulating valve controlled by a sensor at the fan inlet.

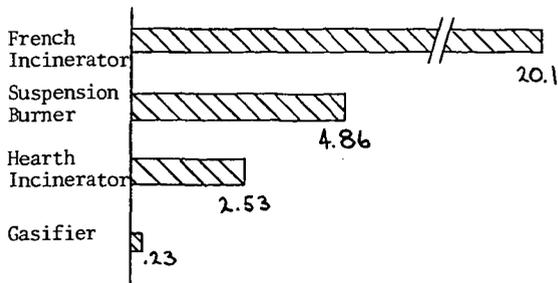
This fan discharges to a mixing chamber at the intake of the fan that supplies drying air to the corn bins. A thermostat in this final air stream controls the damper in the discharge of the fan, in the sketch, to provide a constant, correct, amount of heat.

After one thousand hours running time on a 1.6 mm Btu pilot unit and many hours on a full size 6 mm Btu unit, we have enough answers for a strong positive program.

The particulate emissions are now controllable without a heat exchanger. That expense is eliminated. The cobs produced from the dried seed will now satisfy fuel needs for drying the seed.

Gas quality is good and burns well. Gas samples are taken just ahead of the burner. Analyses of the gases from two typical runs show some variations, but Btu content stays within a range of 122 to 143, which provides satisfactory ignition and combustion.

Although the system satisfies, in many aspects, the definition of attractive technology, it is not a push button unit. One man can operate two units, if close together. Fuel is bulky and cannot



PARTICULATE EMISSIONS IN POUNDS/TON OF FUEL CONSUMED

Table 2

PRODUCTION GAS COMPOSITION  
PERCENTAGE BY VOLUME

	Tests	
	1	2
N2	56+	54+
O2	1.61	0.66
CO2	8.00	7.40
H2	7.50	8.00
CO	24.72	27.10
CH4	1.99	2.80
Cob		
Moisture	11%	
Btu's/SCF	122	to 143

Table 3

be piped from a tank. Special handling equipment is necessary.

The system does utilize all the thermal potential of the cob; sensible heat from the gasifying process, which in some systems can escape to the atmosphere, is captured by placing the unit in the inlet air stream to the drying fan. Mechanically, the gasifier is simple. Most of the annual maintenance problems will probably come from deterioration of refractory during the 47 weeks of down time.

The fuel, as it comes from the seed dryer, requires no further drying, nor does it need classification by size, or grinding. We expect cob prices to stay low since demand for cob products has been severely depressed by substitutes with lower collection and processing costs. Electrical power consumption is low.

The final table is an indication of comparative costs of the gasifier system over a petroleum-fueled system already installed. Cob handling equipment is included in capital outlay.

SEED DRYING COSTS PER BUSHEL-ANNUAL BASIS

	Methane	Propane	Gasifier
Capital			141,000
Depreciation charge			11,280
Operating days	34	35	35
Operating labor	960	960	3,200
Operation electrical	116	116	1,920
Cobs (\$0.34/mm Btu's)			2,500
Propane (\$5.45/mm Btu's)		38,150	
Methane (\$3.50/mm Btu's)	24,500		
Maintenance	400	400	1,100
Bushels dried	70,000	70,000	70,000
\$/Bushel	\$0.371	\$0.566	\$0.286
	29.7%	97.9%	

Table 4

The additional cost of using petroleum fuels is high and will probably advance at a fast pace. On new installations, where the capital cost for propane storage and firing equipment, or for methane transportation and firing equipment, must be considered, the figures are much more favorable.

Finally, gasifiers for cobs protect the seed industry from sudden interruptions of drying fuel supplies. These interruptions, if they occur at certain times, could wipe out a complete year's work.

DEKALB intends to start equipping its seed corn plants with gasifiers. Our system is not perfect, but in actual use, development will come faster.

This gasifier system is particularly adapted to retro-fitting grain driers. Purdue is developing a cob separator for a combine which may solve the mechanical problems, but the economics of collection and transportation of cobs must be tested. In the Midwest, on-farm drying of grain uses 20 gallons of propane per acre to dry the 140 bushels of corn from that acre.

If cobs are an available fuel, the gasifier concept can be used to provide fuel for internal combustion engines. Gas clean-up and efficiency become a problem. Energy lost in tars must somehow be recaptured. There is a need for this energy. The average irrigation pump in this country uses the equivalent of 50 gallons of diesel per year per acre.

In addition, with the right fuel, the gasifier is an excellent biomass combustion

system for heat exchangers. Properly designed, emissions stay below EPA levels; cost is competitive with other systems; couplings are simple.

We are excited about gasifiers. It will help DEKALB and its customers control rising costs. It may provide, under the right conditions, energy conversion hardware to the agricultural community. Above all, conservation and the divorce from the dependency of petroleum must start at the energy consumer. By the wise use of biomass in agriculture, substantial amounts of petroleum fuels and their transportation costs can be dislocated for other uses.

## PROCESS DEVELOPMENT FOR BIOMASS LIQUEFACTION

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### INTRODUCTION

The U.S. Department of Energy's Biomass Liquefaction Experimental Facility at Albany, Oregon, was constructed for the purpose of developing biomass to oil conversion processes. Facility equipment was sized to process 1-3 tons per day of wood chip equivalent. Process development work has been underway at Albany since the summer of 1977. A multitude of reactant and product handling difficulties have resulted in numerous facility and process modifications. Presently, there are two main versions of the CO-Steam process being tested at Albany. The original process, called the Bureau of Mines Process (BOM) because it was developed by researchers at the former Bureau of Mines facility near Pittsburgh, involves dried and ground wood chips slurried in a heavy oil medium. The newer process is called the LBL process, since it was developed by staff members of the Lawrence Berkeley Laboratory. In the LBL process wood chips are broken down into a pumpable water slurry by acid hydrolysis. In either process the slurry is then pumped into a high temperature, high pressure reactor wherein the biomass oil is formed through the action of carbon monoxide and steam under the influence of a sodium carbonate catalyst. The role of the Pacific Northwest Laboratory (PNL) in the process development effort has been twofold, 1) provide bench scale process development experimental support and 2) provide analytical support as needed. The bench scale work has involved for the most part batch autoclave tests and this work has been reported elsewhere.<sup>(1,2,3)</sup> This paper provides the details of the latest analytical work completed on the biomass derived oil.

### PROCESS DESCRIPTIONS

#### BOM Process -

The Albany facility was originally constructed to develop the process of biomass conversion to fuel oil in a recycling oil slurry mode. As shown diagrammatically in Figure 1. Wood chips are dried, ground and mixed with oil at 20-30% solids to provide a pumpable slurry. Anthracene oil, a coal tar distillate is used as the start-up slurry oil. This slurry along with carbon monoxide and aqueous sodium carbonate are pumped at high pressure 2000-4000 psig through a scraped-surface preheater and into a stirred tank reactor. The average residence time in the reactor can be varied from 20 to 90 minutes at temperatures ranging from 300°C to 370°C. After leaving the reactor the product is cooled and the pressure is let down into a flash tank where fixed gases and most of the water is removed. A major change in the original process flow is the replacement of the centrifuge in the product cleanup stage with a vacuum still. After pressure let down the product is reheated and flashed in the still where a light product oil is drawn off; a middle fraction is recovered and a portion is recycled for slurry makeup; and heavy product, solids and catalyst residue are removed from the still bottom. This is the extent of the unit operations at Albany, however, the total process plan would have the still bottoms pumped to a gasifier for production of CO/H<sub>2</sub> gas feed for the liquefaction process. Sodium could be leached from the gasifier ash and could be recycled to the process probably after reaction with carbon dioxide from the offgas and gasifier product gas.

## LBL Process -

There are several basic differences between this process and that for which the Albany facility was designed. However, through plumbing modifications the plant was made to operate in this mode, and, in fact, the first large scale wood oil production was by this process. By the LBL process (Figure 2) the wood chips are reduced directly to a pumpable aqueous slurry through an acid hydrolysis step without preliminary drying and grinding. By this hydrolysis step the wood to water ratio can be maintained at a level equivalent to the wood to oil ratio used in the BOM process. The aqueous slurry must then be made basic by sodium carbonate addition and then passes through the plant in the same manner as in the BOM process. After pressure letdown a gravity separation is made of oil from water and the product can then be distilled as a clean-up step. No recycle oil is used in the LBL process as it is essentially a once through process for the biomass. The aqueous stream will likely have to be recycled to recover the catalyst residues and other soluble organics.

## PRODUCT ANALYSIS

After approximately 15 months of operation of the Albany facility in various configurations by the BOM process, no pure (or nearly pure) wood derived oil had yet been produced. This was due to various mechanical difficulties. The major difficulty was the inability to remove residual solids from the product stream because the product clean-up centrifuge would not operate effectively in this process. The build-up of residual materials in the system led to increases in viscosity over time and the eventual plugging and shut down of the test run before the start-up oil could be effectively purged from the system. The initiation of LBL process tests at Albany in the spring of 1979 led to the first production of nearly pure wood oil in May and the first large scale production of catalytically converted wood oil in September of 1979. This oil is the basis for the analytical work reported here. Due to the differences in the processes, primarily the acid hydrolysis step, it is likely that there will be some differences between the LBL process oil described here and that produced by the BOM process. It has been suggested, based on the amount of degradation of the wood, that the major effect of the hydrolysis is to break down the hemicellulose with minor effect on the cellulose and little or no effect on the lignin portion of the wood.

## Vacuum Distillation Procedure -

A vacuum fractional distillation of wood oil was performed by the use of an ASTM-D1160 distillation apparatus with a modified receiver which allows fraction collection while continuing the distillation under vacuum. The fractions collected are described in Table 1. Fraction #1 includes both the water which was dissolved or emulsified in the wood oil as well as a light oil fraction which was immiscible with water and distilled in the same temperature range. The codistillation could be the result of similar boiling points or may also be the result of a steam distillation phenomenon. The atmospheric true boiling points were calculated based on the instructions included in the D1160 procedure. The distillation was discontinued at the point that decomposition of the product in the still pot became evident. The decomposition point is approximately 100°F below that experienced for petroleum crude oils.

## Analysis of Distillate Fractions -

A summary of the analytical data derived from the wood oil and its distillate fractions is presented in Table 2. The elemental analyses show a trend of increasing carbon content from the lighter to heavier fraction and a stronger reverse trend in hydrogen content. The hydrogen to carbon atomic ratio as a result shows a trend from nearly 2 in the lightest fraction to less than 1 in the still bottoms.

TABLE 1. Vacuum Fractional Distillation of Wood Oil  
ASTM-D1160 For Sample TR7-136

Fraction	Actual Amount	Relative Amount	Color	TBP atm	TBP Torr
#1	8 ml Light Oil 23 ml Water	3% 8%	Clear	To 280°F	To 50°F
#2	45 ml	18%	Clear To Yellow	280-510°F	50-270°F
#3	35 ml	14%	Green To Orange	510-600°F	270-330°F
#4	40 ml	16%	Orange	600-720°F	330-470°F
#5	20 g	8%	Orange To Brown	720-810°F	470-510°F
Residue	86.6 g	32%	Dark Brown	Above 810°F	Above 510°F (Pot at 630°F Decomposition)

TABLE 2. Analytical Data for Distillation Fractions

Fraction	C	H	N	O	Atomic H/C	Hc	C <sup>13</sup> NMR Ali/Aro C	H <sup>1</sup> NMR Ali/Aro H
#1 (Oil Layer)	78.8	12.0	0.0	9.7	1.31	16,000	12	30
#2	77.2	9.9	0.0	13.3	1.52	15,200	1.1	10.0
#3	77.1	8.9	0.0	13.4	1.37	15,100	1.0	7.3
#4	79.2	8.9	0.5	12.1	1.33	15,800	1.2	6.6
#5	79.4	7.9	0.2	12.3	1.19	15,100	1.0	5.3
Residue	82.3	6.5	0.0	10.4	0.94	14,900	---	---
TR7-136 (Including 8% Water)	72.3	8.6	0.2	17.6	1.41	14,500	0.53	---

The oxygen content is less patterned in that it is lowest in the light distillate, maintains a higher nearly constant level through most of the distillate range then drops to a lower level in the still bottoms. This data is mirrored in the heats of combustion results for the various oils. It is interesting to note that the nitrogen appears for the most part in two of the heavier distillate fractions but not in the still bottoms. Elemental sulfur analysis puts the content at 0.006% for the total wood oil; (4) similar analyses for the distillate fractions were not performed.

The use of proton and C<sup>13</sup> nuclear magnetic resonance spectrometry (NMR) and infrared spectrophotometry has provided some insights into the chemical structure of the wood oil components. The C<sup>13</sup> NMR data shows a fairly even balance between saturated and unsaturated carbon in the distillate oils. However, proton NMR shows a much larger amount of aliphatic hydrogen in proportion to aromatic hydrogen. There is essentially no olefinic hydrogen. Aromatic compounds, as a result of molecular bonding and structure have a lower hydrogen to carbon ratio than aliphatics, (one

or less for aromatic, greater than 2 for aliphatic). The disproportionately large amount of aliphatic hydrogen is an indication of the large amount of aliphatic substitution on the aromatic ring structures. This data is an average of dozens of chemical compounds and as such shows a trend of decreasing amounts of aliphatic compounds and of aliphatic substitution on the aromatic rings through the distillation range. The proton NMR data also show the presence of other functional groups such as furans in fraction #2 and naphthalenic and aromatic acid and ester compounds in fractions #4 and #5. The methoxy aromatic structure is very prominent in fraction #2 but is also evident in the heavier fractions. Long chain oxygen containing alkyl groups disappear from prominence after fraction #2, however, the ethyl ether functional group remains prominent throughout. The infrared spectra of these fractions do not provide nearly so definitive results as the NMR spectra, however, they generally confirm the above-stated conclusions.

We have thus far been able to identify a significant number of the actual components of the distillate fractions of the wood oil through the use of Gas Chromatography Mass Spectrometry (GCMS). The components in Table 3 were identified by analysis of computer matched data. Those compounds listed with a question mark could not be matched due to the limitations of the computer search library, but were determined by analysis of the mass spectra. In addition, the acid functional groups shown in fraction 4 and fraction 5 were identified in derivatized (trimethylsilylation) samples of the wood oil fractions. Work continues in this area as those compounds identified are not nearly all the compounds present, and no quantification of this analysis has yet been done.

TABLE 3. Chemical Components of Wood Oil Fractions by GCMS

<u>Fraction #1</u>	<u>Fraction #2</u>	<u>Fraction #3</u>
C <sub>6</sub> Diene	Methyl Pentenal	Propyl Guaiacol
Methyl Cyclopentene (Two Isomers)	Formyl Dihydropyran	Dimethyl Methoxy Phenol?
Methyl Hexadiene (Two Isomers)	Dimethyl Furan	Trimethyl Methoxy Phenol?
2-Pentanone	(Two Isomers)	C <sub>4</sub> Methoxy Phenol?
Dimethyl Hexadiene	Trimethyl Furan	C <sub>7</sub> Phenol?
2-Methyl Cyclopentanone	Guaiacol	C <sub>8</sub> Phenol?
Methyl Cyclopentadiene	Furfural	Dimethyl Naphthol
Ethyl Benzene	Ethylstyrene	Trimethyl Naphthol
Cyclo Octane	Para Cresol	
Dimethyl Heptene	4-Methoxy Phenol	<u>Fraction #4</u>
C <sub>3</sub> Benzene	Methyl Indan	Methyl Naphthol
Indan	Dimethyl Phenol	(Two Isomers)
Guaiacol	Ethyl Phenol	Dimethyl Naphthol
Furfural	Dimethyl Indan	(Seven Isomers)
Methyl Indan	Methyl Ethyl Phenol	Trimethyl Naphthol
(Three Isomers)	(Two Isomers)	Alkylated Hydroxy Phenyl Acids?
Dimethyl Indan	Trimethyl Phenol	(MW 133-206)
(Five Isomers)	Dimethyl Ethyl Phenol	
Ethyl Styrene	Dihydroxy Acetophenone	<u>Fraction #5</u>
	Sec Butyl Phenol	Alkylated Hydroxy Phenyl Acids?
	Propyl Guaiacol	(MW 132-224)

Additional analytical results from petroleum crude oil test methods have also been produced for the wood oil.<sup>(4)</sup> These tests, performed at Southern Petroleum Laboratories, Inc., are indicative of the difference between LBL process wood-derived oil and crude petroleum. The numbers in Table 4 show that the wood oil is a heavy non-aliphatic oil. The high solids and salt content will likely be reduced to nearly zero by the vacuum distillation step of product clean-up. Neutralization numbers for the distillable fractions of the oil ranged from 17.7 to 5.3 when expressed in units

of mg KOH/gr. The existant gum ranged from 621 to 827 mg/100 ml sample of the same distillable fractions.

TABLE 4. Analysis of LBL Process Wood-derived Oil

API Gravity	@ 60°F	-4.93
Specific Gravity	@ 60°F	1.12
Density	@ 60°F      lbs/gal	9.31
Pentane Soluble, Volume Percent		3.25
Salt, lbs/1000 bbls		79.4
Total Solids, BS&M		8.0

From Reference 4

ECONOMIC ANALYSIS

An economic evaluation of the two processes under study at Albany was performed and the results presented earlier this year.<sup>(5)</sup> This study was undertaken with very little continuous pilot scale data available and as such provides only a rough estimate of the projected economics. It does indicate that with the present technology the product oil will be expensive. Table 5 is a summary of the relevant data.

TABLE 5. Cost Data for Wood-derived Oil

	<u>LBL Process</u>	<u>BOM Process</u>
Capital Cost		
2000 Green ton/day	\$39.5 million	\$56.1 Million
Product Cost		
\$/Million BTU	\$ 7.98	\$ 8.56
100% equity		
\$/Million BTU	\$ 6.59	\$ 6.82
65/35 debt/equity		
\$/barrel	\$45.7	\$42.7
100% equity		
\$/barrel	\$37.8	\$34.0
65/35 debt/equity		
Mid 1979 constant dollars		
15% DCF ROR on equity		
Debt interest rate	9% long term, 10% short term	
Wood cost at 1.25/million BTU (\$11/green ton)		

From Reference 5

These calculations are for a commercial sized plant including many unit operations which have not yet been demonstrated at the Albany scale of operation and as such are based to a significant degree on engineering judgment. The conclusion from the economic analysis was that the processes appear to be viable technically and that significant cost reductions may be possible through process improvement and optimization. There are many remaining questions relative to the Albany processes. Process development work at DOE's Experimental Facility should provide answers to these questions. These answers will likely have a significant effect on process costs, however, it is not entirely clear whether the costs will increase or decrease. An additional area which will require analysis will be the use of the wood oil as a petroleum substitute in chemical production. The separation and use of various chemical fractions of the wood oil is presently under study at PNL.

## CONCLUSIONS

When considered for use as a substitute fuel oil, wood oil as produced at Albany by the LBL process appears qualitatively to fall somewhere between petroleum derived #6 Fuel Oil and the synthetic oil derived from the Occidental Flash Pyrolysis process as shown in Table 6. Wood oil falls nearly half way between the other two oils in nearly all categories except that wood oil is very low in sulfur content.

TABLE 6. Comparison of Some Fuel Oils

	<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>	<u>S</u>	<u>Ash</u>	<u>Moisture</u>	<u>H<sub>c</sub></u> <u>BTU/lb</u>	<u>Density</u> <u>g/ml</u>
Wood Oil	72.3	8.6	0.2	17.6	0.006	.078	3.5	14500	1.19
Dry Wood Oil (by calculation)	80.2	8.5	0.2	11.1	0.006	.085	0.0	15800	--
#6 Fuel Oil	85.7	10.5	2.0	0-3.5	0-3.5*	0.05	0.20	13200	1.02
Pyrolytic Oil	57.0	7.7	1.1	33.2	0.2	0.5	14	10600	1.39

\* Legal sulfur limit determined by use site, e.g., 0.35% maximum in Los Angeles County

This comparison is valid on a chemical basis, however, as stated earlier the use of wood oil purely as a substitute fuel is not currently economically attractive. Despite the large amount of resources already expended on research of this process, it remains in a developmental stage and new technology could have a significant impact on the process economics. The alternate use of wood oil as a chemical feed-stock is also being studied.

## ACKNOWLEDGEMENTS

I wish to acknowledge the support provided by other staff members at PNL, but particularly J. A. Franz who operated the NMR and R. E. Schirmer who operated the GCMS. Also, I wish to thank those staff members at the Department of Energy's Biomass Energy Systems Division who have provided the financial support for this work.

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FIGURE 1

BOM PROCESS DIAGRAM

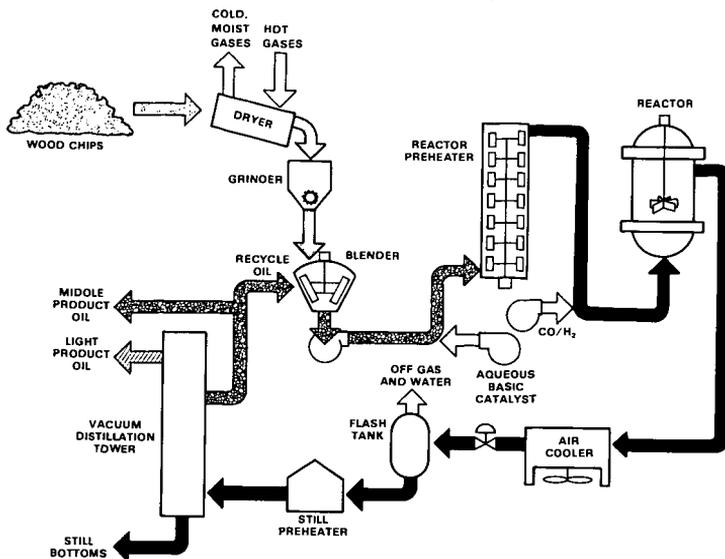
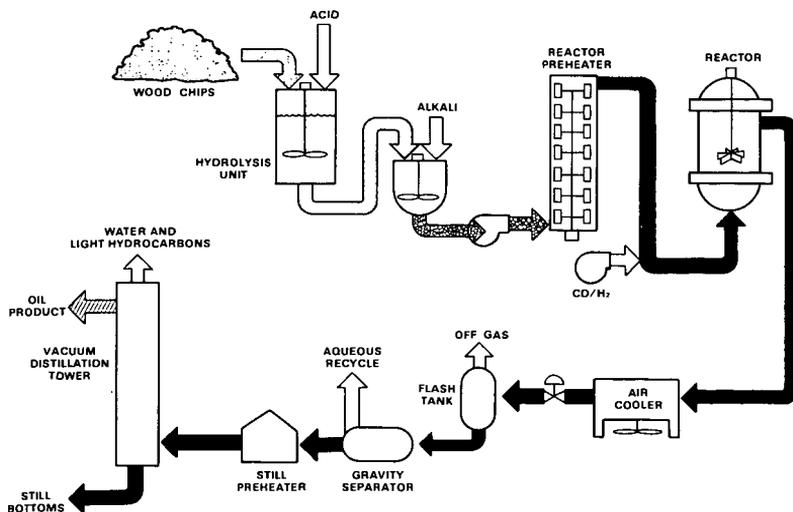


FIGURE 2

LBL PROCESS DIAGRAM



## Starch Hydrolysis for Ethanol Production

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Ethanol and ethanol-gasoline mixtures have been considered for use as fuel since the early days of the automobile. The abundant and less expensive petroleum supply precluded extensive use of ethanol as fuel and only in the last few years has the general public become aware of and concerned about the dwindling and increasingly expensive petroleum supplies. Interest in extending gasoline supplies with ethanol-gasoline mixtures has increased greatly.

Mankind since early recorded history has produced ethanol from simple sugars by anaerobic yeast fermentation. I will discuss the enzymatic production of the simple sugar, glucose from starch for conversion by yeast into ethanol and the contribution of enzyme cost in producing ethanol.

Referring to Figure 1, starch is a polymer of glucose. The glucose units are joined in hemiacetal bonds between carbon one and carbon four for nearly all the bonds and between carbon one and carbon six for a small number of bonds which are branch points in amylopectin, one of the two types of starch polymers. The hemiacetal bonds are all alpha configuration, that is, in the Haworth structure shown the carbon one bond to another glucose unit is below the plane of the molecule. Cereal grain starch is normally a mixture of two types of polymers: amylose, a linear glucose polymer, and amylopectin, a branched polymer.

The process steps in converting starch to dextrose are gelatinization, liquefaction and saccharification. Starch is found in nature as insoluble, non-dispersible granules resistant to enzymic breakdown. Starch-bearing grains such as corn, wheat, rye and sorghum must be ground to a fine meal, at least 12-16 mesh, to expose the starch granules to the slurring water. Gelatinization is the swelling of the starch granule in the presence of heat and water. The starch loses its crystallinity and becomes an amorphous gel that can be attacked by enzymes. At this point, the starch or ground grain slurry thickens considerably and would be difficult to process if an alpha-amylase were not added to partially hydrolyze the starch to dextrans. The dextrin solution is much more fluid; thus, we say the starch gel is liquefied. The alpha-amylase serves to reduce the viscosity of the solution and also to produce a lower molecular size substrate. This smaller substrate molecule is needed for the efficient action of glucoamylase which hydrolyzes the dextrans to glucose.

As described above, the hydrolysis of starch to glucose requires two types of enzymes. The alpha-amylase is a bacterial thermostable endo-amylase. It hydrolyzes  $\alpha$ -1,4 bonds at random points in the starch molecule to rapidly reduce the viscosity of gelatinized starch solutions. This enzyme is a metal ion-containing protein and requires a small amount of calcium ion during use for maximum activity and stability. The action of alpha-amylase on amylopectin is illustrated in Figure 2; the action on amylose is identical. The enzyme cannot hydrolyze  $\alpha$ -1,6 bonds but can by-pass these branch points in amylopectin. The product of the reaction is dextrans - short glucose chains, and small amounts of glucose and maltose.

Glucoamylase, produced by fungi, is an exo-amylase. It hydrolyzes the maltose and dextrans from the non-reducing end of the molecule. Glucoamylase hydrolyzes both  $\alpha$ -1,4 and  $\alpha$ -1,6 bonds to completely degrade the dextrans to glucose. The enzyme is optimally active at pH 3.5-4.5 so pH adjustment after

saccharification is not needed for the yeast fermentation. The yeast fermentation takes place at pH 3.7 - 4.

The most plentiful and most commonly used cereal grain as source of starch is corn. The composition of the corn kernel is given in Table 1; the moisture content can vary considerably. With 16% w/w moisture the starch is typically 61% w/w of the corn kernel. On a dry basis the starch constitutes 72% w/w of the corn composition. There are three cooking procedures used for starch gelatinization and liquefaction: atmospheric batch, pressure batch and continuous liquefaction. The mash concentration to use depends on the substrate, processing conditions and equipment. This step requires high temperature and solids concentration should be as high as can be handled to minimize the energy cost. Typical mash concentrations are 20-30% w/w dry solids for ground whole corn and 25-35% w/w dry solids for corn starch as substrate.

TABLE 1  
Approximate Composition of the Corn Kernel

	<u>Percent, As-Is</u>	<u>Percent, DSB</u>
Moisture	16	
Starch	61	72
Protein	9	11
Oil (Fat)	3.8	5
Fiber	2	2
Pentosans	5.3	6
Sugars	1.6	2
Minerals (Ash)	1.3	2

The substrate slurry, under continuous agitation, is adjusted to pH 6-6.5 with lime slurry and 0.02% - 0.15% w/w Taka-Therm® on dry starch basis (DSB) is added to the slurry depending on the cooking process as indicated in Table 2. A 60°C hold period is recommended for ground whole corn to ensure thorough hydration. Starch gelation begins at 66°C and maximum viscosity is reached at 72°C. In the atmospheric and pressure batch processes the temperature rise may need to be slowed or, if necessary, the temperature held to allow the enzyme time to attack the starch and reduce the viscosity for efficient stirring. In the atmospheric batch process (ABL) the substrate is held at 90°C-95°C until liquefaction is complete. This typically requires 30-90 minutes. The substrate should have a dextrose equivalent (DE) of at least 10-14 and should not give a starch-iodine blue color. The substrate in the pressure batch process (PBL) is held at 140°C-163°C for 15 minutes and then flash cooled to 90°C-95°C. An additional 0.1% w/w, DSB, enzyme is added and liquefaction completed as with the atmospheric batch process. In the continuous cooking process (CL) the substrate slurry is jet-cooked to 140°C-163°C, held for five minutes at this temperature and flash cooled to 90°C-95°C. At at point 0.13% w/w, DSB, enzyme is added and liquefaction completed as for the atmospheric batch process.

TABLE 2  
Starch Liquefaction

<u>ABL</u>	<u>PBL</u>	<u>CL</u>
Taka-Therm®:	Taka-Therm®:	Taka-Therm®:
0.15% w/w, DSB	0.05% w/w, DSB	0.02% w/w, DSB
Heat to 90°-95°C	Heat to 140°-163°C	Jet cook to 140°-163°C

Flash cool to 90°-95°C,  
add 0.1% w/w, DSB  
Taka-Therm®

Flash cool to 90°-95°C,  
add 0.13% w/w, DSB  
Taka-Therm®

Hold at 90°-95°C,  
30-90 minutes

Hold at 90°-95°C,  
30-90 minutes

Hold at 90°-95°C.  
30-90 minutes

There are advantages and disadvantages for the three processes. The atmospheric batch process does not require pressure equipment and high pressure steam which are cost advantages. On the other hand, complete gelatinization and solubilization of high corn starch concentrations is difficult to accomplish in a short processing time at the lower atmospheric batch process temperature. Incomplete liquefaction gives a lower ethanol yield per unit mass of substrate or will require a longer yeast fermentation time, which are cost disadvantages.

Diazyme® L-100, a glucoamylase, is used to hydrolyze the dextrins to dextrose for the yeast fermentation. The saccharification can be completed before the yeast fermentation or a continuous saccharification during the yeast fermentation can be used (Table 3). The first method is essentially that used in dextrose production. The liquefied starch is cooled to 60°C, titrated to pH 4-4.5 and glucoamylase added at 0.22% v/w, DSB. The enzyme level used is 100 Diazyme® units per pound of dry starch. The mixture is held at 60°C until a reducing sugar level of 95 DE or greater is reached; this takes 36-72 hours. Insoluble materials such as protein, fiber and fat can be removed at this stage if desired by centrifugation or filtration. The syrup is diluted to 19% w/w solids with water and cooled to 30°C. Yeast is added for the fermentation.

TABLE 3  
Saccharification and Fermentation

Liquefied Starch:	60°C pH 4-4.5 0.22% v/w, DSB, Diazyme® L-100
<u>Complete</u>	<u>Continuous</u>
Hold to 95 + DE (36-72 hours)	Dilute to 19% w/w solids, Hold 1-2 hours
Dilute to 19% w/w solids	
Cool to 30°C and ferment	Cool to 30°C and ferment

In the concurrent or continuous saccharification process the liquefied starch is cooled, titrated to pH 4-4.5 and enzyme added as in the complete saccharification process. The mixture is diluted and held at 60°C for only one to two hours to produce enough dextrose for the start of the fermentation. Dextrin hydrolysis to 40 DE is sufficient to give the yeast an initial rapid fermentation rate. The syrup is cooled to 30°C and yeast is added for the ethanol fermentation. The glucoamylase action is considerably slower at 30°C but the enzyme activity is great enough to keep the yeast supplied with dextrose. Diazyme® L-100 also contains an alpha-amylase which aids in hydrolyzing the dextrins and starch which may have survived the liquefaction step.

To calculate the efficiency of the fermentation we need to calculate the theoretical ethanol yield from starch. Referring to Table 4, in the hydrolysis of starch a water molecule is added across each glycosidic bond so one gram starch completely hydrolyzed would give 1.11 g glucose. From Gay-Lussac's equation the 1.11 g glucose would theoretically yield 0.567 g ethanol. Using

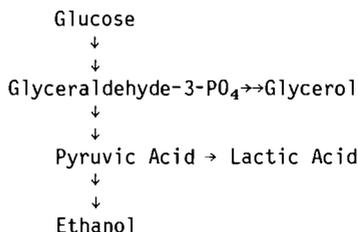
the density of ethanol we calculate the production of one gallon 100% ethanol from 11.59 pounds starch. In terms of corn as substrate and taking the weight of a bushel of corn to be 56 pounds containing 61% w/w starch, a bushel of corn would yield 2.95 gallons of ethanol.

TABLE 4  
Theoretical Ethanol Yield

1.0 g starch + H <sub>2</sub> O	→	1.11 g glucose
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	→	2 C <sub>2</sub> H <sub>5</sub> OH + 2 CO <sub>2</sub>
1.11 g		0.567 g
Bushel corn	→	2.95 gallons
61% w/w starch		Ethanol

This theoretical yield does not take into account ethanol loss due to carbohydrate used for yeast growth and to carbohydrate used in the formation of small amounts of non-ethanol products by the yeast. A simplified biosynthetic pathway from glucose to ethanol is shown in Table 5. This is the Embden-Meyerhof-Parnas scheme for glycolysis. Glycerol and lactic acid are formed in small amounts compared to ethanol synthesis but contribute to give a yield less than stoichiometric formation of ethanol from glucose. Allowing for the growth of yeast cells and the formation of fermentation by-products the maximum fermentation efficiency is about 95% of stoichiometric yield.

TABLE 5  
Ethanol Biosynthesis



A fermentation will typically yield 2.5 gallons ethanol per bushel corn, an 85% fermentation efficiency. In calculating the enzyme cost in producing a gallon of ethanol, I used the prices for standard packages of our enzyme products, a 55 gallon drum for Taka-Therm® and a 200 liter drum for Diazyme® L-100. (Table 6) Theoretical ethanol yield is one gallon from 11.59 pounds starch. The recommended enzyme use levels are 0.15% w/w, DSB for the α-amylase and 100 Diazyme® units or one milliliter Diazyme® L-100 per pound dry starch. The cost for the theoretical yield is 5.4 cents per gallon. For a yield at 85% fermentation efficiency the enzyme cost is 6.4 cents per gallon. The enzyme cost can be reduced by using lesser amounts of enzyme. One must take into consideration that an α-amylase level that is too low will give incomplete starch solubilization and concomitant loss of ethanol yield. A glucoamylase level that is too low will extend the fermentation time for the concurrent saccharification-fermentation process because dextrose is not produced as rapidly as the yeast can convert it to ethanol.

TABLE 6  
Enzyme Cost

	<u>Standard Pkg.</u>	<u>Price</u>
Taka-Therm®	500 lb. drum	\$1.35/lb.
Diazyme® L-100	200 liter drum	\$2.625/liter
One gallon ethanol from 11.59 lb. starch.		
Taka-Therm®:		
11.59 lb. x 0.15% x \$1.35/lb. enzyme		\$0.0235
Diazyme® L-100:		
11.59 lb. x 10 <sup>-3</sup> l/lb x \$2.625/l, enzyme		<u>0.0304</u>
	Total	<u>\$0.054</u>
Fermentation at 85% efficiency		\$0.064

FIGURE 1  
STRUCTURE OF STARCH

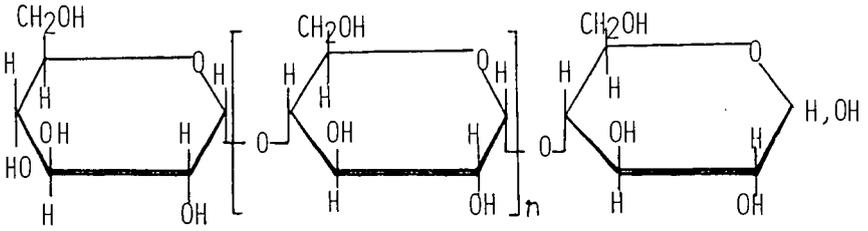
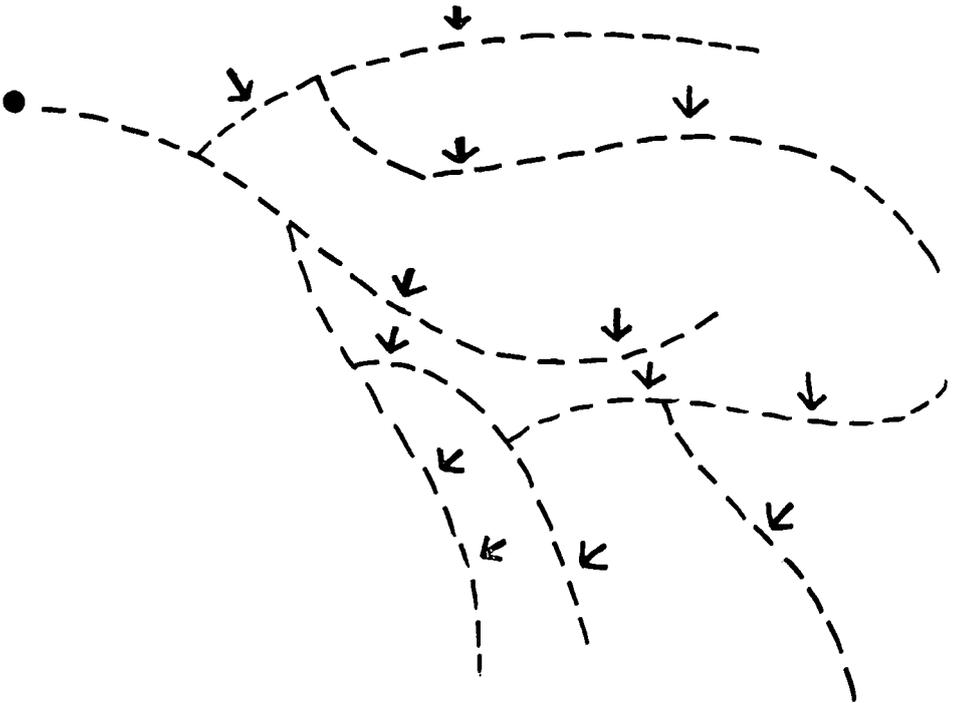


FIGURE 2  
ALPHA-AMYLASE ACTIVITY ON AMYLOPECTIN WITH  
THE FORMATION OF DEXTRINS



The NYU Continuous Acid Hydrolysis Process - Hemicellulose Utilization  
Preliminary Data and Comparative Economics for Ethanol Production

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### INTRODUCTION

There has been a recent increased interest in the possible commercial utilization of waste biomass for both material and energy recovery due to the steadily rising price of fossil fuels. Currently employed methods for dealing with these solid residues are inadequate for the cost effective utilization of their latent energy values; waste cellulose conversion via acid hydrolysis to xylose and glucose followed by fermentation to ethanol offers an attractive alternative. Additionally, as is shown in Figures 1 and 2, the xylose and glucose from cellulosic wastes could be used as the basic raw material for the manufacture of many "petrochemicals", or more precisely volume chemicals which are presently obtained from petrochemical feedstocks.

Ethanol production from biomass sources is proposed to increase due to various government incentives to meet projected "Gasahol" production levels by 1985. A reliable, high yield, energy efficient process based on waste cellulose would have many advantages as compared to the more conventional grain processing technology now being utilized. The economic viability of ethanol from cellulose does not exclusively depend on by-product values, as does ethanol from grain, but would be most sensitive to the cost of the waste cellulose feedstock.

The NYU continuous acid hydrolysis process has been utilized in the past primarily for the conversion of crystalline  $\alpha$ -cellulose to glucose. Under the rather severe conditions of high temperature required for this process, the amorphous hemicellulose fraction primarily composed of pentosans in hardwoods is converted beyond the sugars to furfural. It has been the objective of our recent experiments to show the feasibility of performing a continuous two stage hydrolysis which would allow for a more complete utilization of carbohydrate content. Conceptually, the process is shown in Figure 3. By using a mild prehydrolysis and extraction, it is possible to reclaim a major portion of the hemicellulose fraction as xylose. Subsequently it is proposed to hydrolyze continuously the remaining hexosan fraction to glucose by the usual process.

### HISTORICAL REVIEW

Acid hydrolysis of cellulose has been extensively studied for the better part of a century, particularly in connection with the manufacture of ethanol from wood wastes. (1,2,3) Attempts to commercialize this technology in Europe and the U.S. occurred only at war-time when petroleum was cut off. A significant effort has been ongoing in the USSR.

Cellulose derived from forestry, agricultural or municipal residues has three main components; crystalline  $\alpha$ -cellulose, amorphous hemicellulose and lignin. The cellulose fractions in these residues react differently when exposed to acid hydrolysis conditions because of their relative degree of molecular order or accessibility. The amorphous hemicellulose reacts to form sugars at conditions much less severe than those required for the crystalline  $\alpha$ -cellulose conversion to glucose.(4) Therefore, in order to extract the maximum carbohydrate value from cellulose residues, studies to accomplish a two stage hydrolysis in which the hemicellulose fraction is prehydrolyzed and extracted prior to a concentrated sulfuric acid  $\alpha$ -cellulose hydrolysis have been reported by Dunning et. al. and by Sitton et. al. (5,6)

There exist, both economic and technical factors which favor dilute acid hydrolysis of  $\alpha$ -cellulose to glucose to be conducted at high temperatures for short times so as to maximize the glucose yield. Numerous kinetic studies, initially by Saeman and later Porteous, Fagan, Converse and Grethlein have been useful in the characterization of heterogeneous hydrolysis of various cellulose feedstocks. Porteous predicted a maximum sugar yield of 55% with 0.4% acid at 230°C, the yields being based on percentage conversion of available  $\alpha$ -cellulose to glucose. The Fagan experiments were carried out with rather small samples (0.5 gms) of ball mill Kraft paper and verified the Porteous predictions. Such kinetic studies are of considerable value for the development of improved process designs and economic data of waste cellulose and/or ethyl alcohol production facilities (2,7,8,9, 10).

Grethlein has recently proposed and built a plug flow pipe reactor in which nearly isothermal conditions can be maintained. Verification of previously developed data based on a batch reactor is currently underway. The kinetic model indicates that high temperature, short time dilute acid hydrolysis reactions favor the production of glucose versus its degradation. Yields of 80-90% of the available glucose may theoretically be obtained under ideal conditions. (11,12)

Experimental investigations on the dilute acid hydrolysis of waste cellulose to glucose have been carried out at the Department of Applied Science of New York University over the past five years. The waste cellulose feedstock employed in the initial studies was newspaper pulp. This experimental work involved an evaluation of the cost effectiveness of various pretreatments for enhancing the accessibility of the cellulose and the determination of the optimum reaction conditions for maximizing the sugar yields.

The hydrolysis experiments were initially carried out batchwise with two differently sized stirred stainless steel autoclave reactors. The optimum reaction conditions were determined to be temperatures around 220°C-230°C and reaction times of less than 30 seconds with about 1 wt% of sulfuric acid. (13) These results agree quite well with the results of the kinetic rate studies which were previously reported by Porteous and Fagan. (9)

More recently, over the past three years, studies at NYU have resulted in the design, costing and construction of a continuous waste cellulose to glucose pilot plant with a nominal 1-2 ton/day capacity. This pilot plant is based on the concept of employing an intensive screw mixer/conveyor for continuously reacting waste cellulose at suitably elevated temperatures in the presence of acid.

The key to successful operation of a continuous acid hydrolysis process is the design of the hydrolysis reactor. This reactor must be capable of feeding, conveying and discharging hydrolyzable cellulosic materials continuously while maintaining appropriate temperatures and associated pressures in a reaction zone. Because this hydrolysis requires exposure of the reactor components to dilute acids at high temperatures and pressures, all materials of construction have to be resistant to corrosion especially in the reaction zone.

A Werner & Pfleiderer ZDSK53 (53mm) twin screw extruder (Werner & Pfleiderer Corporation, Ramsey, N. J.) was selected on account of its capacity for conveying, mixing and extruding the required amounts of cellulosic feedstock. This machine allows accurate control of temperature, pressure, residence time, etc., within the previously established acid hydrolysis operating conditions while continuously feeding and discharging material.

This equipment was obtained and installed at the Antonio Ferri Laboratories of New York University (Westbury, Long Island, N.Y.) and considerable progress has been achieved in the development and characterization of reaction conditions. Conversions of 50-60% yield based on available  $\alpha$ -cellulose have been reported. (14) Experiments have been run with diverse feedstocks such as paper pulp (10% solids) and hardwood sawdust (95% solids). It is anticipated that significant increases in yield will result with improved process control.

#### CONTINUOUS ACID HYDROLYSIS STUDIES-HEMICELLULOSE UTILIZATION

In the course of recent experiments to improve the level of carbohydrate utilization for the continuous acid hydrolysis process, the feedstock used was a mixed hardwood sawdust; A representative analysis of this is shown in Table 1.

Table 1: Analysis of Mixed Hardwood Sawdust. (4)

$\alpha$ -cellulose (crystalline)	45	
hemicellulosic glucan	3	}
glucomannan (acetate)	5	
arabogalactan	1	
4-O-methyl-glucurono (arabino) xylan (acetate)	25	
lignin	21	
Total	100	

Analytical procedures for this complex system are being developed using high pressure liquid chromatography (HPLC). Initial determinations of sugar yields from hemicellulose, however, utilized a dual-wavelength spectrophotometric technique with orcinol reagent (15); this and similar early methods are unfortunately, subject to significant interferences.

Initial prehydrolysis experiments for the hardwood sawdust were directed toward the determination of reaction conditions (acid concentration, temperature and residence time) for satisfactory utilization of the hemicellulose fraction. Preliminary findings are presented in Figure 4. Subsequently, it is proposed to hydrolyze the residual  $\alpha$ -cellulose fraction by previously described methods (13, 14)

#### YIELD ANALYSIS - SUGARS AND ETHANOL

For the purpose of a preliminary analysis to determine the impact on ethanol yield of hemicellulose prehydrolysis, the chemical composition for hardwood sawdust is given in Table 1. The data given in Table II assumes 80% conversion of the hemicellulose to sugar (glucose, mannose, or xylose) and 60% conversion of the  $\alpha$ -cellulose to glucose. A 45% conversion of all sugars is assumed to ethanol. Based on these assumptions, one could expect a yield of 72.2 gallons of anhydrous alcohol per ton of dry hardwood sawdust.

PRELIMINARY ECONOMIC ANALYSIS

A preliminary cost analysis of a plant processing 2000 tons/day of sawdust producing 48MM gallons of fuel grade ethanol is presented in Figure 5. The total plant investment cost was estimated at \$75MM in 1980. The plant scheme assumes the energy saving advantages of continuous fermentation and energy efficient distillation. The ligno-cellulosic residue is

TABLE II: YIELD ANALYSIS; BASIS 100 LB HARDWOOD SAWDUST

Hemicellulose fraction (assume 80% conversion to sugars)

$$3 \text{ lb glucan} \times (180/162)^a \times .8 = \underline{2.26 \text{ lb glucose}}$$

5 lb glucomannan (Ratio of glucose/mannose = 1/4)

$$1 \text{ lb glucan} \times (180/162)^a \times .8 = \underline{0.89 \text{ glucose}}$$

$$4 \text{ lb mannan} \times (180/162)^a \times .8 = \underline{3.55 \text{ lb mannose}}$$

25 lb 4-O-methyl-glucurono (arabino) xylan (acetate)  
(approximately 70% of weight due to xylan)

$$25 \text{ lb} \times .7 \times (150/132)^b \times .8 = \underline{15.96 \text{ lb xylose}}$$

$\alpha$ - cellulose fraction (assume 60% conversion to glucose)

$$45 \text{ lb} \times (180/162)^a \times .6 = \underline{30 \text{ lb glucose}}$$

Hydrolysis Summary

$$\left. \begin{array}{l} \text{Glucose} = 33.55 \text{ lb} \\ \text{Mannose} = 3.55 \text{ lb} \\ \text{Xylose} = 15.96 \text{ lb} \end{array} \right\} \text{ total sugars} = 53.06 \text{ lb}$$

Fermentation Yield (assume 45% conversion of sugars to ethanol)

$$53.06 \text{ lb} \times .45 = \underline{23.88 \text{ lb ethanol/100 lb sawdust}}$$

or  $23.88/6.61 = \underline{3.61 \text{ gallon ethanol/100 lb sawdust}}$

or  $3.61 \times 20 = \underline{72.2 \text{ gallons ethanol/ton sawdust}}$

a) ratio of molecular weight of glucose/glucan = mannose/mannan

b) ratio of molecular weight of xylose/xylan

utilized to generate high pressure steam for continuous acid hydrolysis while the total plant is assumed to operate at a 91% capacity factor. The results of the analysis are quite promising assuming a \$30/ton feedstock sawdust cost; at the current market price of \$1.77/gal for anhydrous ethanol the plant would earn \$40.8MM the first year. IF an 80/20 debt/equity ratio is assumed, a conservative payback for the plant would be 1.84 years.

#### CONCLUSION AND FUTURE WORK

The development of the NYU continuous acid hydrolysis process has been most favorable. The characterization of preferred reaction conditions for both hemicellulose prehydrolysis and extraction followed by  $\alpha$ -cellulose hydrolysis is continuing. Potential alcohol yield with hemicellulose utilization is estimated to increase 70% beyond that without prehydrolysis.

A data base for the utilization of various waste cellulose feedstocks is being developed. Preliminary studies on the fermentation of waste cellulose acid hydrolyzates is underway.

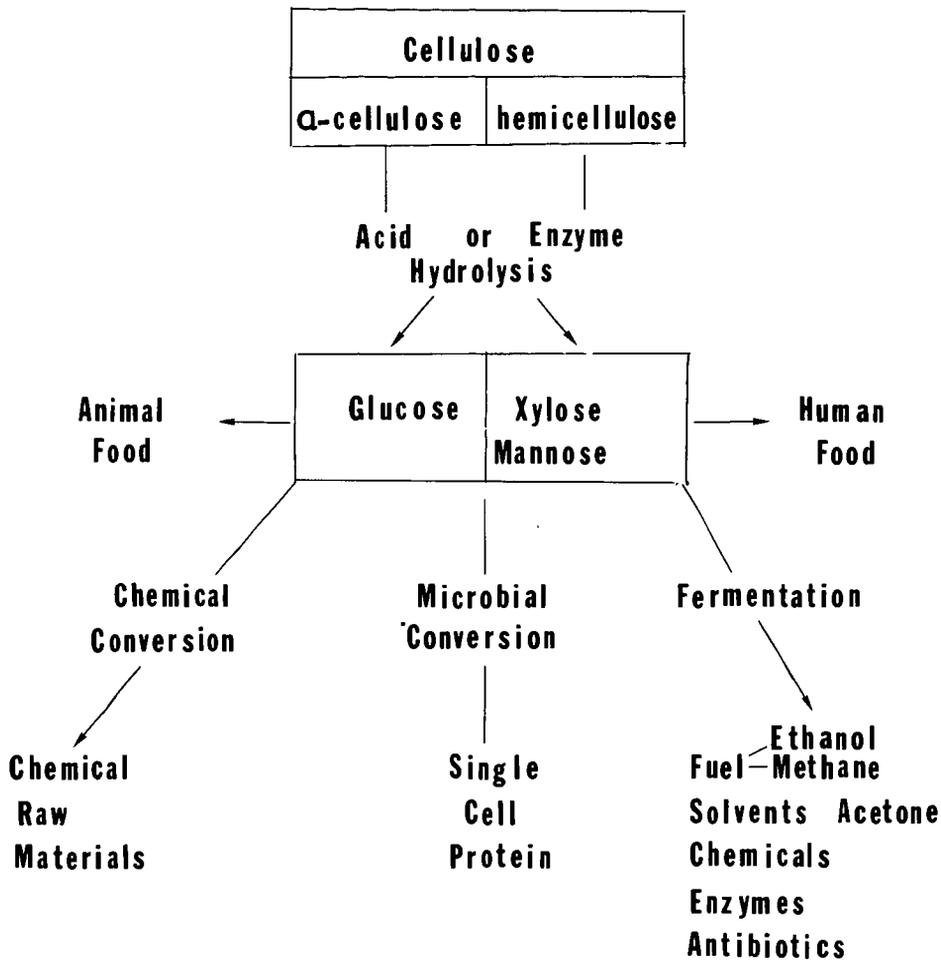
#### ACKNOWLEDGEMENT

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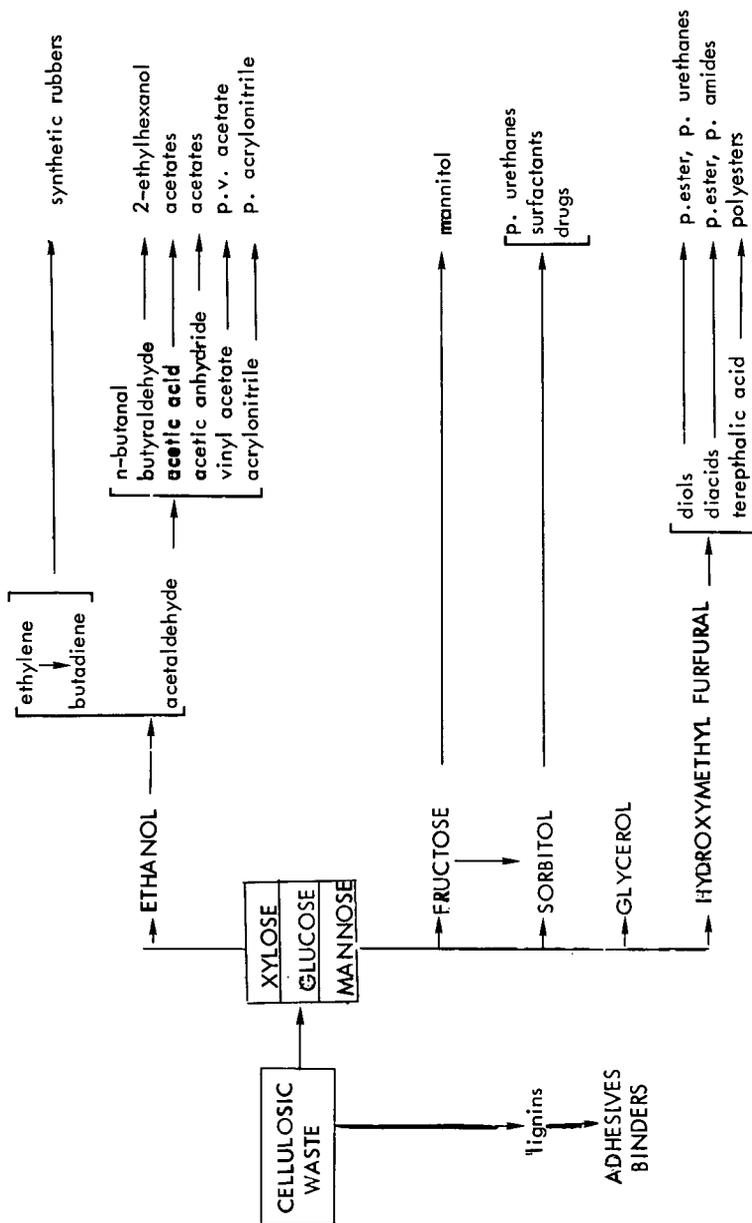
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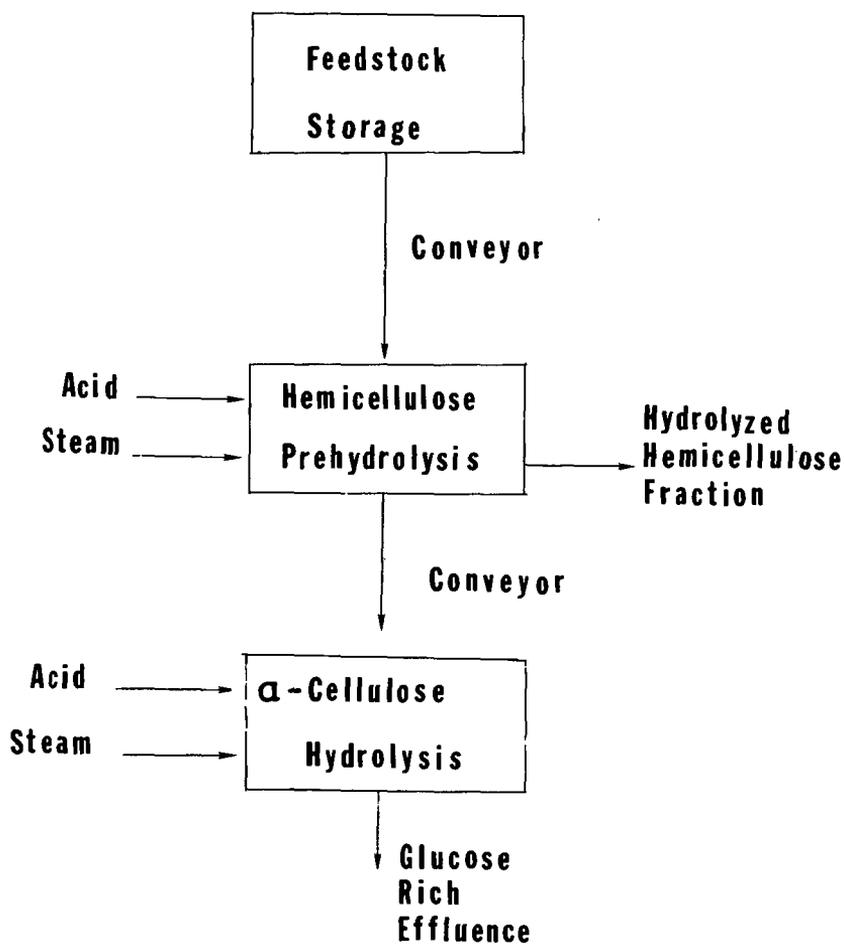
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**Fig. 1: Waste Cellulose Utilization Routes**



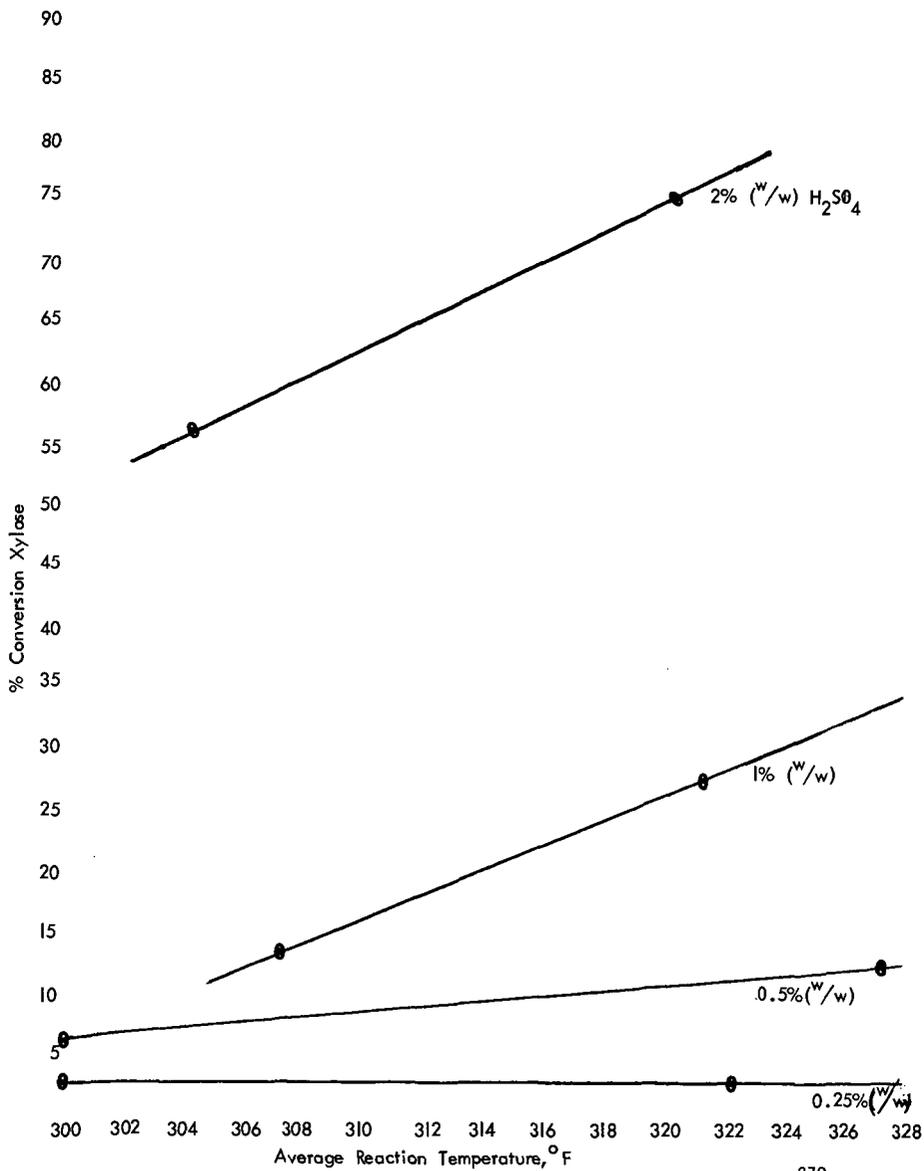
**Fig. 2: Possible routes to petrochemicals from cellulosic wastes**

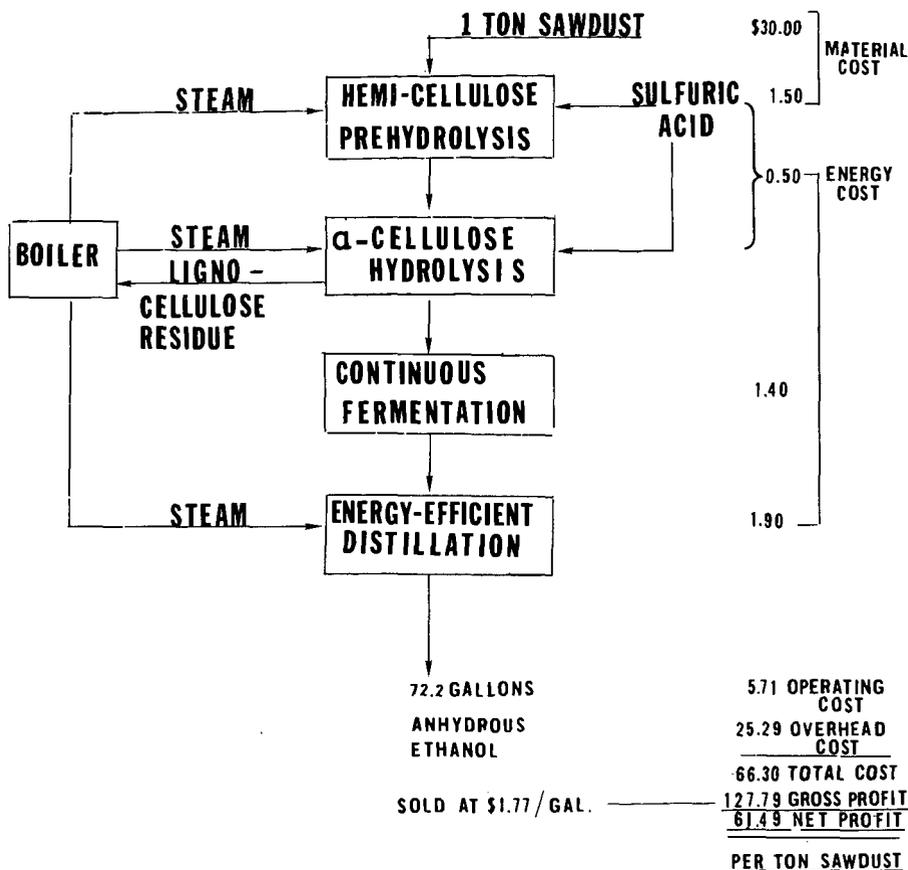


**Fig. 3: Schematic of continuous acid hydrolysis with hemicellulose utilization**

PRELIMINARY DATA ON THE EFFECTS OF ACID CONCENTRATION AND TEMPERATURE  
ON THE CONVERSION OF HEMICELLULOSE TO XYOSE IN HARDWOOD SAWDUST

Fig. 4





**2,000 TON PER DAY PLANT**

Total plant cost (1980):	\$75 million
Conversion of hemi-cellulose to xylose:	80%
Conversion of α-cellulose to glucose:	60%
Conversion of sugars to ethanol:	45%

NET PROFIT: \$122,980 per day, \$40.8 million per year @ 91% capacity factor

PRODUCTION: 48 million gallons anhydrous ethanol per year from 666,000 tons sawdust

**FIG. 5: PRELIMINARY ECONOMICS OF CONTINUOUS PREHYDROLYSIS ACID HYDROLYSIS, FERMENTATION AND DISTILLATION**

# Fuel Alcohol Production from Whey and Grain Mixtures

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In the United States, because of recent increases in cheese production to nearly 4 billion pounds yearly, more than 38 billion pounds of fluid whey are generated each year. Although considerable advances have been made recently in developing novel approaches for the utilization of surplus whey, more than half of the whey produced is thrown away or dumped into the sewer. For example, in Nebraska only 140 million of the 700 million pounds of whey produced annually are used, while 560 million pounds are wasted.

Liquid whey contains approximately 5% lactose, 1% protein and 1% fat and salts. As such, dumping huge quantities of whey down the drain constitutes a significant loss of a potential energy source as well as imposing a large biochemical oxygen demand on our waste water treatment facilities. Fermentation of the lactose to ethanol for use in gasohol (10% alcohol/90% gasoline fuel blend) is an attractive alternative in light of today's current petroleum shortages and ever increasing costs.

Preliminary studies revealed that lactose in sweet as well as acid whey can be fermented into alcohol. Whey obtained from the manufacture of Cheddar, Mozzarella, Swiss and other hard cheeses is sweet whey, whereas the Cottage cheese whey is called acid whey because of its high acid content. To optimize the economics of the process, the highly nutritious and relatively expensive whey proteins were recovered by ultrafiltration and the resulting permeate used for alcohol production. One hundred milliliter aliquots of permeate were inoculated with a trained lactose fermenting *Kluyveromyces* yeast or a combination of *K. fragilis* and the classical alcohol producer *Saccharomyces cerevisiae*. As shown in Table 1, there were no differences in the utilization of lactose or the production of ethanol when either the *K. fragilis* or the mixed culture was used.

Table 1. Fermentation efficiency of selected organisms in sweet whey permeate<sup>a</sup>

Culture	% Residual lactose		% Ethanol
	12h	24h	24h
<i>K. fragilis</i>	0.21	0.10	2.0
<i>K. fragilis</i> + <i>S. cerevisiae</i>	0.25	0.12	2.0

<sup>a</sup>The whey permeate contained 5.1% lactose initially.

Theoretically, 180 grams of lactose would be expected to yield 92 grams of ethanol and 88 grams of carbon dioxide. The 5.1% lactose in whey would yield approximately 2.5% ethanol assuming 100% efficiency. A more realistic estimate of 70-75% efficiency would result in the production of 70 million gallons of ethanol from the 23 billion pound annual whey surplus in the U.S. According to our estimates (Table 2)

the cost would be \$1.02 to \$1.07 per gallon of ethanol. These figures, however, are based on dry whey powder and do not take into account the unfeasibility of distilling a dilute ferment of 2% alcohol. Low energy concentration would be required in order to make fermentation of liquid whey economically feasible.

Table 2. Costs for producing ethanol from dried whey powder

Whey costs <sup>a</sup>	\$110
By-product credit	- 85
	\$ 25
Direct costs	
Conversion	\$ 40
Loan interest	13
Indirect costs <sup>b</sup>	
Depreciation	13
Taxes	8
20% return	8
	\$ 1.07

<sup>a</sup>Based on 20 lbs of dried whey @ \$5.50/cwt.

<sup>b</sup>Figures adapted from Scheller (1).

Additionally, another process involving fermentation of whey:grain mixtures has also been developed in our laboratory. As shown in Fig. 1, the whey permeate replaces the water required in the preparation of the grain mash. The amount of corn which is otherwise required is reduced proportionately to the amount of whey sugar in the process and the residual whey solids are part of the distiller's dried grain. This process requires no equipment modification other than the addition of a whey handling facility at the alcohol plant.

Figure 3 shows the course of fermentation by K. fragilis when mash was prepared with sweet whey permeate and 20% less corn than normal. There appeared to be adequate sugar for fermentation by the K. fragilis as indicated by the production of approximately 12% alcohol in 60 hours. Substitution of whole sweet whey or whole acid whey for the water also appeared to have no adverse effect on the fermentation. As shown in Table 3, the production was slightly higher in the early stages when whole whey rather than permeate was used. By 60 hours, however, the sweet whey permeate, sweet whey and acid whey all produced 12% ethanol.

At the present time studies are underway to compare the fermentation efficiency of the K. fragilis and a mixed culture of K. fragilis and S. cerevisiae on whey:grain mixtures with reduced grain and, for comparison, on standard water mashes. Preliminary results indicate that up to 24% of the grain requirement can be replaced with the whey with no apparent loss in fermentation efficiency.

A feasibility study is currently underway to utilize the whey: grain fermentation process for a 21,000,000 gallon alcohol plant in Wisconsin. Such a plant would require about 7.5 million bushels of corn and 96 million gallons of whey based on a 15% reduction in the

Table 3. Ethanol production by *K. fragilis* with various types of whey in a 20% reduced grain system

Substrate	% Ethanol				
	12h	24h	36h	48h	60h
Sweet whey permeate <sup>a</sup>	4.4	6.7	10.9	11.8	12.2
Sweet whey <sup>b</sup>	7.4	10.7	11.5	11.7	12.1
Acid whey <sup>b</sup>	7.6	10.3	11.8	12.2	12.0

<sup>a</sup>Data are an average of four separate trials with duplicate samples taken at each time interval.

<sup>b</sup>Data are an average of three separate trials with duplicate samples taken at each time interval.

corn requirement. The substitution of whey would amount to a savings of more than a million bushels of corn per year amounting to a total of nearly 3 million dollars or 14 cents per gallon of alcohol.

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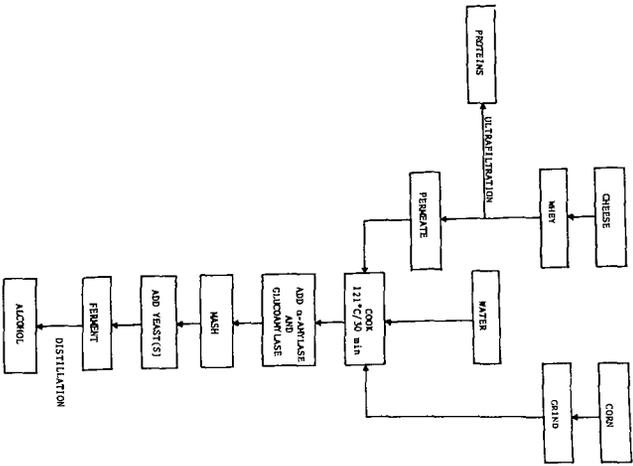


Fig. 1. Schematic of combining whey and grain to produce industrial alcohol.

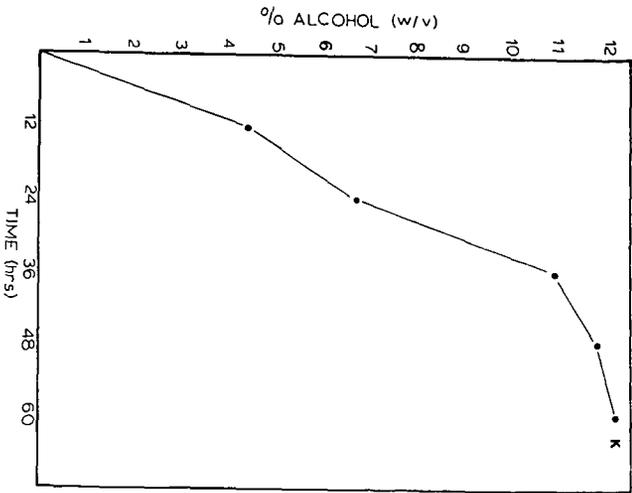


Fig. 2. Alcohol production in a medium in which the water is replaced by undiluted sweet whey permeate and the concentration of grain is 20% less than normally used.

## ECONOMIC OUTLOOK FOR THE PRODUCTION OF ETHANOL FROM FORAGE PLANT MATERIALS

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### SUMMARY

Lignocellulose is an immense potential resource for the production of ethanol and other fermentation chemicals and fuels. The recalcitrant nature, however, of this material due to the high cellulose crystallinity and the lignin barrier has tended to make the process economics unattractive. As an alternative to woody biomass, vegetative forage crops may be good substrates for ethanol fermentation due to their low lignin content.

In this research project, we have tested vegetative alfalfa, vegetative sudan grass and vegetative, mature and ensiled sorghum species as possible feedstocks for ethanol production. Results are presented here for the yield of sugars via cellulose hydrolysis of these materials and for the projected alcohol production costs for a  $25 \times 10^6$  gallon/year plant. These costs ranged from \$1.68/gallon for vegetative sudan grass to \$2.58/gallon for vegetative alfalfa. Substrate costs comprised the major fraction of the total cost. This leads to the conclusion that a viable process economics depends on options such as the following: use of unconventional crops; stillage protein credit; co-hydrolysis of starch in immature grain component and sharing of feedstock production cost with mature grain harvest.

### INTRODUCTION

Diminishing fossil fuel reserves and recent dramatic increases in crude oil prices have prompted the United States and other oil-importing nations to develop renewable sources of energy.

Solar energy could well contribute a significant portion of the United States energy consumption within the next decade. The potential in developing solar biotechnology is immense (1), not only for liquid fuels, but also for the range of petrochemical substitutes which can be produced fermentatively.

Ethanol has received considerable attention because it can be used as a clean-burning gasoline extender and octane-number improver. Moreover, since it can be converted to other chemicals, it is likely to become a key chemical feedstock for a renewable resources chemicals industry.

In the near term, since fermentation technology based on easily fermentable substrates (such as sugar and starch) is established, these materials are being used to produce ethanol for gasohol. But the feedstock cost represents a large fraction (more than

50%) of the cost of producing ethanol. If grain prices were to rise dramatically, the final product cost of ethanol would soar.

An alternative and relatively cheap substrate is lignocellulose. The processing technology, however is not fully developed as yet. Lignocellulose is not readily converted because of the crystallinity in cellulose structure and also since lignin shields cellulose and hemicellulose from attack by enzymes.

The only biological process which has been operated successfully at greater than the bench scale is based on municipal solid waste. In the Emert process (2) ethanol (190 proof) has been produced at 75 gallons/day from about 1 metric ton/day of waste.

The development of alternative processing technology using thermophilic anaerobes, for converting lignocellulose directly to ethanol is being pursued (3,4 for example). Most cost analyses predict an ethanol production cost well above \$1.40/gallon (5,6).

In herbaceous plant materials, cell walls are composed of cellulose, lignin, hemicellulose and minor amounts of gums, pectins and other compounds. The major barrier to efficient hydrolysis of cellulose, either by acid or with enzymes, are complexes of lignin and hemicellulose with cellulose. While covalent bonds between these components have been demonstrated (7), limitation of hydrolysis is thought to be primarily due to sheathing of cellulose microfibrils with the lignin hemicellulose matrix (8). Access of the hydrolysis catalyst and reactants to the glucosyl linkages is retarded until lignin is removed. Because of the high cost of reducing lignocellulosic complexes to hydrolyzable form, it would seem reasonable to utilize sources of cellulose with minimal lignin content. During the growth and development of plant cells, lignification occurs at a stage after cellulose biosynthesis (9). This fact suggests that vegetative parts of plants may be a source of low lignin cellulose.

The possibility of using sorghum fiber for biomass and for papermaking pulp has already prompted numerous agronomic and chemical studies (10,11,12). Sweet sorghum is attracting interest in this respect in all agriculturally productive regions of the United States; high sucrose hybrids suitable even for the northern states are now available. Potential for utilizing the sucrose invert sugar, and starch contents as substrates for ethanolic fermentation and for utilizing the fiber as a source of fuel energy or, alternatively, of synthetic gas is promising but is hampered by the relatively poor storability of harvested cane (13).

The practice of ensiling forage materials has interesting potential as a means of storage of the fiber feedstock for alcohol production schemes. During ensiling the organic acids produced from soluble sugars by the *Lactobacillus* and *Streptococcus* bacteria may cause hemicellulose-lignin sheathing to break down. As a result the accessibility of water to cellulose for hydration and of enzymes for hydrolysis is reportedly improved (14).

In the present work experimental results were obtained for the enzymatic hydrolysis of low-lignin forage materials (alfalfa, sudan grass and several species of sorghum) and a preliminary economic assessment for the alcohol fermentation of such hydrolyzates was made.

#### METHODOLOGY

The experimental basis for this study was conducted to determine whether biomass at an early vegetative stage of development was more readily hydrolyzed by cellulolytic enzymes than at the mature stage of development, which is characterized by extensive lignification. Representative samples of forage crop materials, including alfalfa, sudan grass and sorghum in vegetative and mature growth were assessed by the extent of enzymatic hydrolysis of lignocellulose to glucose as a function of cellulose and

lignin content. Experimental materials and methods used to obtain quantitative information about forage composition and enzymatic hydrolysis have been detailed earlier (15).

Ethanol production costs were obtained for a process flow sheet similar to the Natick process (6). A simplified diagram of the processing operations is shown in Figure 1. The process consists of mechanical grinding of the biomass, cellulase production, enzymatic hydrolysis of the lignocellulosic materials, filtration of the undigested solids, and production of 95% ethanol using conventional yeast fermentation and distillation technology. Enzyme hydrolysis is assumed to occur over a 48-hour period at an enzyme load of 10 IU/gram of substrate and without enzyme recycle.

While the laboratory hydrolysis data reported in this paper was obtained at an enzyme load of 86.7 IU/gram of substrate, it was found that hydrolysis performed at an enzyme load of 8.7 IU/gram of substrate over a period of 48 hours gave 95% of the original values. It is thus felt that the hydrolysis conditions used for the plant design will be representative of the laboratory data.

Forage biomass culturing and harvesting costs were charged according to Saterson *et al.* (16) at the following levels:

Alfalfa	----	\$26.78/MT
Sudan Grass	----	\$17.75/MT
Sorghum (any species)	----	\$22.71/MT

where the sudan grass cost was estimated assuming an average forage yield of 22.15 MT/ha (16) and the same harvesting costs as for sorghum.

A preliminary economic evaluation ( $\pm 25\%$ ) was then performed using the Natick information (6). Since the sole experimental data available was the 24-hour sugar yield from the enzymatic hydrolysis of the forage material it was felt that a complete plant design would be unreliable and somewhat premature at this time. The evaluation was then based on the assumption that the cost of producing 1 gallon of 95% ethanol (without charge for the cellulosic substrate) would be a constant and independent of the substrate. This assumption essentially means that, as long as the sugars are in the soluble form, the cost of producing ethanol is the same no matter what the sugar source is.

The cost of ethanol production was \$1.32/gallon according to the Natick report (6), at 1978 prices and with no substrate cost included. In order to generate the ethanol production costs for our analysis, the Marshall & Stevens index was used to update the equipment costs to the third quarter of 1979. An index of 545.3 for 1978 and of 606.4 for the third quarter of 1979 was used (17). Labor costs were increased at a rate of 7%/year over the Natick data. The remaining items were calculated on the same basis as in the Natick analysis:

- depreciation - 10%/year of total fixed investment
- plant on-stream factor - 330 days/year
- plant overhead - 80% of total labor cost
- taxes and insurance - 2%/year of total fixed investment

This analysis generated an ethanol production cost of \$1.11/gallon. This cost does not reflect any pretreatment charges since there is no need for pretreatment steps when using vegetative forage crop materials. To obtain the total production cost a substrate charge was added to this cost. This substrate charge was calculated according to the following formula:

$$\text{Substrate charge } (\$/\text{gallon } 95\% \text{ EtOH}) = \frac{(\text{Forage crop cost } \$/\text{MT})}{\left(\frac{\text{Glucose yield}}{\text{kg/MT}}\right) \left(\frac{\text{EtOH conversion}}{\text{kg/kg}}\right) \left(\frac{1 \text{ l EtOH}}{0.789 \text{ kg}}\right) \left(\frac{1 \text{ gallon}}{3.783 \text{ l}}\right)}$$

The main limitation of this economic analysis lies in the fact that a 10% glucose syrup after hydrolysis as assumed in the Natick study may not be possible for all the forage materials included in this work using an enzyme load of 10 IU/gram of substrate. This would make a concentration step necessary in some cases; however, since no data was available on the maximum substrate charge possible on the hydrolyzer, no calculations were made in this study for this purpose.

## RESULTS AND DISCUSSION

### (Experimental)

Lignin content is related directly to plant maturity. The conversion of the cellulose component of forage crops to glucose by enzymatic hydrolysis is related inversely to the lignin content. Generally, hydrolysis of cellulose from young plant tissues is superior to that from mature tissues. In Tables 1 and 2 and in the following paragraphs are presented examples of these findings from studies on alfalfa, sudan grass, sorghum silage, and brown-midrib sorghum mutants.

Mature alfalfa tissue contains proportionally more lignin than does younger tissue. The percent conversion of cellulose proportionally varies from 41 percent for the most mature tissue to 84 percent for the youngest parts of the plant. Fermentable sugar yields from the most easily hydrolyzed top segment of the plants are however, less than those from the mature bottom segment because of the higher cellulose content of the bottom fraction.

Studies on whole plant samples of half-grown and mature sorghum supported the stated relationships between maturity, lignin content and cellulose hydrolysis. As an example, mature sorghum with 6.5 percent lignin gave 31 percent of theoretical conversion of cellulose while vegetative material with 3.1 percent lignin gave 47 percent conversion. Mature sorghum, but not vegetative sorghum, contains considerable fermentable sugars which are extractable from leaves and stalks. The differences were compensating and resulted in similar glucose yields after cellulolytic hydrolysis of mature and of vegetative sorghums.

Ensiling would provide a means of storage of vegetative feedstock and a biological process to improve the conversion of constituent cellulose. The hydrolysis of the silage of the same sorghum variety described above resulted in 71 percent theoretical cellulose conversion as compared to that from the mature sorghum equal to 31 percent. Since the lignin content of the silage was equal to that of the mature material, changes in the fiber structure resulting from ensiling apparently improve accessibility of enzymes to the fibers. Hydrolysis of the cellulose in silage may be enhanced by the action of organic acids (pH 4) on the lignocellulosic structures over time. During enzymatic hydrolysis, the loss of the glucose product to the acid-forming *Lactobacillus* and *Streptococcus* bacteria was prevented by addition of 0.01% (w/v) of agricultural grade tetracycline hydrochloride. This level of antibiotic did not inhibit the fermentation of the hydrolyzed sugars by *Saccharomyces cerevisiae*.

Unlike sorghum, sudan grass in vegetative growth contained considerable amounts of sugars which were extractable from leaves and stalks. Cellulolytic hydrolysis added to the extractable 6.4 percent glucose and yielded a total of 20.4 percent fermentable sugar on a dry weight basis. This material contained 3.1 percent lignin, and the cellulose was converted to 56 percent of theoretical

Conversions of cellulose averaging 75 percent of theoretical were obtained from brown mid-rib sorghum mutant lines. The average lignin content of these materials was 2.6 percent. The literature described mature bmr-mutants as having lignin content 61 percent lower than isogenic lines (19). These mutants in vegetative growth contained 7.4 percent extractable glucose and upon hydrolysis yielded a total of

23.7 percent glucose on a dry weight basis.

*(Economics)*

The results obtained by a detailed analysis of the bioconversion process of the various forage materials are shown in Tables 3 through 8. Observation of Table 3 shows that the total fixed investment for a 25 x 10<sup>6</sup> gallons/year ethanol plant is estimated at about 57 million dollars, or about \$2/gallon of installed capacity which is considered a reasonable figure by most of the researchers working in this area. Start-up and working capital estimates bring the total capital investment to about 71 million dollars.

Table 4 presents a breakdown of the ethanol production costs from the forage crops, without a substrate charge. No pretreatment costs were included in this table since these materials do not require such pretreatment. As a consequence, the processing costs are estimated at \$1.11/gallon, well below the \$1.30-\$1.75/gallon range reported by other researchers (5,6). Enzyme production is the major factor in the ethanol cost (53% of the total), followed by fermentation and distillation (30%) and hydrolysis (17%). This finding stresses once more the need for strong research efforts in the area of cellulase production.

Estimates for the ethanol yield from the forage crops included in this study are shown in Table 5. These estimates are based on a 45% ethanol yield from glucose during anaerobic fermentation. As expected, sudan grass and the brown midrib mutants of sorghum show the highest potential with respectively 276 and 250 gallons of EtOH/acre-year. The ensiled sorghum materials show the second best possibility with an ethanol yield close to 200 gallons/acre-year. Vegetative Frontier 214 sorghum and vegetative alfalfa rank at the bottom with respectively 109 and 97 gal/acre-year.

The estimated total production costs are shown in Table 6. These costs show that vegetative sudan grass and brown midrib mutants of sorghum are the most promising substrates with the ensiled sorghum crops being the second best. Total ethanol production costs are now at least \$1.68/gallon, with alfalfa and Frontier 214 sorghum reaching \$2.58/gallon of 95% EtOH.

A breakdown of the total production costs presented in Table 6 can be seen in Table 7. It can be observed that substrate costs represent the major fraction of the total cost, ranging from a minimum of 34% to a maximum of 57%. Enzyme costs rank second, ranging from 23 to 35%, followed by fermentation and distillation costs which vary from 13 to 20% of the total. Hydrolysis costs represent the minor fraction, varying from 7 to 11% of the total production costs.

Table 8 shows the estimated total ethanol production costs for a fermentation yield of 50% (weight of ethanol/weight of glucose). As expected, a decrease in the production costs relative to those in Table 6 is observed, reflecting the smaller quantity of forage raw materials required for the same ethanol production rate. The decrease averages about 10¢/gallon and reflects the high cost of the raw materials and the need for an efficient substrate conversion at all stages of the process.

#### CONCLUSIONS

The production of ethanol by fermentation of the glucose obtained via enzymatic hydrolysis of the vegetative forage crops considered in this study requires further research and development before economic feasibility can be attained. The total production costs ranged from \$1.68/gallon for vegetative sudan grass to \$2.58/gal. for vegetative alfalfa. These high costs are not totally unexpected since the forage crops considered here have a high cash value. It should be noted that the costs obtained in this study do not account for the use of reducing sugars other than

glucose and do not include any byproducts credit; if proper account of these credits were observed, the costs reported in this study could be lowered by as much as 54¢/gallon. Since no pretreatment is required for the vegetative forage materials, processing costs are about 30% lower than other published processing costs (6). This represents a considerable advantage of vegetative forage crops over other lignocellulosic materials.

Substrate costs constituted, in most instances, the major fraction of the total production costs, varying from 34% to 57%. In view of this, an efficient substrate conversion must be obtained at all stages of the process. Enzyme production costs were also very important, ranging from 23 to 35% of the total cost; this indicates the need for continued research on cellulase production technology.

The total capital investment for a 25 million gallons/year ethanol plant was found to be about 71 million dollars. This represents a fixed capital investment of about \$2/gallon EtOH capacity.

In order to reduce substrate costs, one might either look for less expensive means of culturing and harvesting the crops or to coupling to other operations whereby the lignocellulosics obtain a discounted value. Examples could be coupling alfalfa hydrolysis to a soluble protein extraction operation or harvesting sorghum grain and stalks simultaneously but separately. Alternatively, one may obtain other substrates whose culture is indigenous to a growing area. Such unconventional plants may have the same processing costs, yet may be obtained for zero to ten cents/gallon of ethanol product.

These studies were definitive in showing how hydrolysis and endogenous sugar levels influence the yield of fermentable sugar. This yield is also proportional to the biomass yield. Saterson et al. (16) in work supported under a D.O.E. contract to A.D. Little Corporation and Jackson (20) at Battelle Columbus Laboratories screened herbaceous plants for potential biomass production in ten regions of the contiguous United States. Many were plants whose culture was indigenous to a growing area. Some were unconventional as food and forage crops, but were good candidates in terms of their projected biomass production potential. Crops appropriate for the Great Plains included 14 species of grasses and legumes and 9 species of unconventional crops and/or weeds. The comparative analysis of Heichel of cultural energy requirements placed such crops high with respect to total energy yield (21). Sweet sorghum rated highest in that study, but in terms of practical energy recovery, cane storage, and juice expression present major difficulties at present (22).

Future crops for alcohol fermentation may include other traditional food crops, certain weeds, syrup sorghum, Jerusalem artichoke, and the forage grasses. The latter are adapted to a wider range of growing conditions than other crops and are the more productive under adverse conditions. Since they are grown primarily for plant material they are more likely to produce significant yields of biomass than other crops. They possess the more efficient photosynthesis route, permit multiple cuttings which maintain the plant at a high rate of photosynthesis for a large part of the growing season, have low water requirements, and their culture requires less energy than other crops. The use of such crops as raw materials may bring the cost of fermentation ethanol down to the economically viable range.

The high cost of feedstock is a major barrier to the conversion of biomass to alcohol fuels (4). In order to reduce substrate costs, one must optimize the efficiency of either production or conversion. Production costs are reduced when yields are increased, when means of culturing and harvesting are the most energy efficient in terms of cultivation, irrigation and fertilization, and when the harvesting costs can be discounted, as with the simultaneous collection of grain and straw. Conversion costs are relatively reduced when the biomass requires no pretreatment in order to obtain high percentage of cellulose hydrolysis, when a significant proportion of

the plant dry matter is soluble fermentable sugar, and when the fermentation system can utilize both cellulose and hemicellulose hydrolysis products.

For these reasons, it is important to study simultaneously the agronomic and biochemical aspects of a potential biological conversion feedstock as a production-conversion system (1). An advantage gained by the production of great quantities per unit area of biomass is offset if the cellulose is resistant to hydrolysis. On the other hand, materials containing relatively little lignin can be hydrolyzed very efficiently and would be very attractive as feedstock if biomass yields were reasonable. The balance between the potential for production and conversion must be known in a controlled comparative experimental setting.

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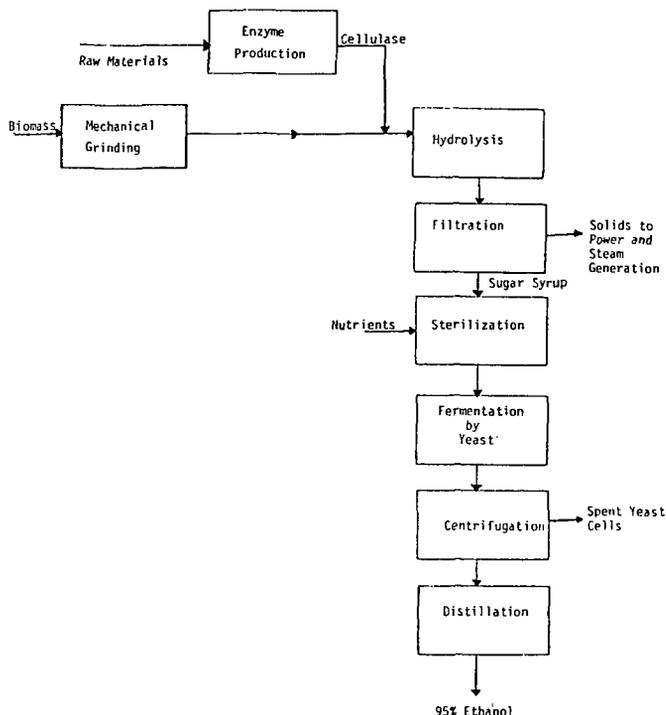


Figure 1. Simplified process flow diagram for ethanol production from vegetative forage crops.

Table 1. Enzymatic hydrolysis products and theoretical conversion of cellulose to glucose from forage crops at various stages of maturity.

	total glucose	extractable glucose	net hydrolysis <sup>a</sup>	cellulose conversion <sup>b</sup>	percent
	mg	mg/gm dry substrate	- day		
Dekalb FS-25A+ Sorghum					
vegetative	155	0	155	47	
mature	151	57	94	31	
silage	188	0	188	71	
Frontier 214 Sorghum					
vegetative	103	0	103	34	
silage	175	0	175	68	
Sudan Grass					
vegetative	204	64	140	56	
Brown Midrib Mutants of Sorghum					
vegetative, fieldgrown					
bmr 6	215	61	154	75	
bmr 12	251	80	171	77	
bmr 16	236	84	152	68	
bmr 17	257	74	183	89	
bmr 18	288	69	159	70	
Alfalfa (1st cutting, vegetative)					
top	NA				
next-to-top	NA				
next-to-bottom	NA				
bottom	128	5	123	43	
Alfalfa (2nd cutting, vegetative)					
top	89	0	89	84	
next-to-top	112	1	112	77	
next-to-bottom	131	1	130	55	
bottom	148	4	144	41	

<sup>a</sup> by difference

<sup>b</sup> values obtained by dividing net hydrolysis by respective cellulose contents from Table 2 and multiplying by 100.

Table 2. Fiber composition of forage sorghum varieties as percent on dry weight basis.

	cell soluble material	acid detergent fiber	hemi-cellulose	cellulose	lignin
Dekalb FS-25A+					
vegetative	40.6	38.9	20.5	33.0	3.1
mature	37.6	39.0	23.3	30.4	6.5
silage	38.7	37.0	24.3	26.3	6.7
Frontier 214					
vegetative	44.2	38.8	17.0	30.3	3.9
silage	45.1	35.3	19.5	25.9	4.5
Sudan Grass					
vegetative	45.6	29.7	24.7	25.2	3.1
Brown Midrib Mutants					
vegetative					
bmr 6	51.0	26.5	22.5	20.5	4.4
bmr 12	48.3	25.4	26.3	22.3	1.9
bmr 16	51.9	26.9	21.2	22.0	2.5
bmr 17	50.1	24.2	25.7	20.5	2.2
bmr 18	51.7	26.4	21.9	22.7	1.9
Alfalfa (1st cutting)					
top	68.0	26.9	5.1	18.6	7.8
next-to-top	54.9	39.6	5.5	23.8	12.9
next-to-bottom	49.0	45.4	5.6	26.7	13.6
bottom	39.4	46.1	14.5	28.9	15.9
Alfalfa (2nd cutting)					
top	83.5	15.0	0.7	10.5	4.8
next-to-top	73.0	25.6	1.4	14.8	8.0
next-to-bottom	56.8	39.1	4.2	23.7	10.3
bottom	43.7	50.1	6.2	34.9	13.8

<sup>a</sup> Analysis by permanganate oxidation procedure of Goering and Van Soest (17).

Table 3. Estimated Capital Investment for a 25 x 10<sup>6</sup> Gallons/Year Ethanol Plant (U.S., \$1,000, Third Quarter 1979)

	Enzyme Production	Hydrolysis	Ethanol Production	Total
Major Equipment	17,243	13,350	15,186	45,779
Off-Site Investment	1,869	108	4,242	6,219
General Service Facilities	1,971	1,346	1,943	5,260
Total Fixed Investment	21,023	14,804	21,371	57,198
Start-up (8.5% IPI)				4,862
Working Capital (16.5% IPI)				<u>9,438</u>
Total Capital Investment				71,498

Table 4. Cost Analysis, Ethanol from Cellulose\*

	Enzyme Production	Hydrolysis	Ethanol Fermentation and Distillation	Total
Total Material	33.60	1.31	1.92	36.83
Total Utilities	5.93	4.54	11.96	22.43
Total Direct Labor	5.19	3.11	4.90	13.20
Total Direct Cost	44.72	8.96	18.78	72.46
Plant Overhead	4.15	2.49	3.92	10.56
Tax and Insurance	1.68	1.18	1.71	4.57
Depreciation	6.41	5.92	8.55	22.88
Factory Cost	58.96	18.55	32.96	110.47
% Total Cost	53	17	30	100

\*Basis: cents/gallon, 95% ethanol, no substrate charge

Table 5. Estimated Ethanol Yields from Several Forage Materials\*

Raw Materials	Total glucose yield (kg glucose /MT dry substrate-day)	Substrate yield (MT/ha-yr)	Ethanol Yield (liters /ha - yr)	Ethanol Yield (gallons /acre-yr)
Dekalb FS-25A+				
vegetative	155	17.3	1530	164
mature	151	17.3	1490	159
silage	188	17.3	1855	198
Frontier 214				
vegetative	103	17.3	1016	109
silage	175	17.3	1727	185
Sudan Grass				
vegetative	204	22.2	2583	276
Brown Midrib Mutants of Sorghum				
vegetative (average)	237	17.3	2338	250
Alfalfa				
vegetative (average)	120	13.2	903	97

\* Basts: ethanol yield during glucose fermentation = 45% on a weight basis

Table 6. Estimated Total Ethanol Production Costs from Several Forage Materials\*

Raw Materials	Substrate Cost (\$/MT)	Substrate Charge to EtOH Cost (\$/gal 95% EtOH)	Total EtOH Production Cost (\$/gal 95% EtOH)
Dekalb FS-25A+			
vegetative	22.71	0.97	2.07
mature	22.71	1.00	2.10
silage	22.71	0.80	1.90
Frontier 214			
vegetative	22.71	1.46	2.56
silage	22.71	0.86	1.96
Sudan Grass			
vegetative	17.75	0.58	1.68
Brown Midrib Mutants of Sorghum			
vegetative (average)	22.71	0.64	1.74
Alfalfa			
vegetative (average)	26.78	1.48	2.58

\* Ethanol processing costs = 110.474/gallon (from Table 4)  
Ethanol yield during glucose fermentation = 45% on a weight basis

Table 7. Relative Cost Factor Analysis of Ethanol Production Costs from Several Forage Materials

Raw Materials	Substrate Cost (\$ Total)	Enzyme Production Cost (\$ Total)	Hydrolysis Cost (\$ Total)	Fermentation and Distillation Cost (\$ Total)
Dekalb FS-25A*				
vegetative	47	28	9	16
mature	48	28	9	16
silage	42	31	10	17
Frontier 214				
vegetative	57	23	7	13
silage	44	30	9	17
Sudan Grass				
vegetative	34	35	11	20
Brown Midrib Mutants of Sorghum				
vegetative (average)	37	34	11	19
Alfalfa				
vegetative (average)	57	23	7	13

Table 8. Estimated Total Ethanol Production Costs from Several Forage Materials\*

Raw Materials	Substrate Charge to EthOH Cost (\$/gal 95% EthOH)	Total EthOH Production Cost (\$/gal 95% EthOH)
Dekalb FS-25A*		
vegetative	0.87	1.97
mature	0.90	2.00
silage	0.72	1.82
Frontier 214		
vegetative	1.32	2.42
silage	0.77	1.87
Sudan Grass		
vegetative	0.52	1.62
Brown Midrib Mutants of Sorghum		
vegetative (average)	0.57	1.67
Alfalfa		
vegetative (average)	1.33	2.43

\* Ethanol processing costs = 110.47 ¢/gallon (from Table 4). Ethanol yield during glucose fermentation = 90% on a weight basis.

## PILOT SCALE CONVERSION OF CELLULOSE TO ETHANOL

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### INTRODUCTION

Interest in cellulose as a renewable source of alcohol fuels and other chemicals has increased as the price of petroleum products continues to rise. Extensive research has been conducted in the area of cellulose utilization for a number of years (1, 2, 3, 4, 5). However, with the exception of The U. S. Army Natick Research Command which has operated a prepilot program for the enzymatic conversion of cellulose to glucose since 1976 (6, 7), these investigations have been confined to the laboratory.

The importance of piloting a complete process for the conversion of cellulose to ethanol was recognized by this laboratory in 1974. The complexity of combining the material handling of bulky slurries such as air classified municipal solid waste (MSW) and pulp mill waste (PMW) with the aseptic operation of an enzyme production facility posed a unique set of problems which could not adequately be addressed on a laboratory scale. In order to address these problems, it was believed that the design of a pilot plant should include the flexibility of handling feedstocks of widely varying composition and moisture content. Operation of a pilot plant would allow the identification and testing of equipment for the preparation and transfer of slurries, sterilization, and liquid/solid separation.

The economic feasibility of a capital intensive process such as the cellulose to ethanol process requires that the use of highly specialized exotic equipment be kept to a minimum. As a result of this, low cost chemical reactors would be evaluated as fermentation vessels. The vessels first tested as "off the shelf items" could then be modified as necessary to accommodate the individual requirements of each set of fermentation conditions. In this way parameters such as agitation, aeration, temperature and pH control, and sterility could be evaluated and adjusted as needed. Using these criteria the biochemical conversion of cellulose to ethanol was scaled-up approximately 100 fold from 10L laboratory fermenters to 1000L vessels in a pilot facility capable of processing 1 ton per day of cellulosic feedstock.

### METHODS AND MATERIALS

Three strains of yeast were used during the pilot investigations of simultaneous saccharification fermentation (SSF). (8, 9). These were *Saccharomyces cerevisiae* ATCC 4132, obtained from the American Type Culture Collection, Rockville, Maryland; *Candida brassicae* IFO 1664, obtained from the Institute for Fermentation, Osaka, Japan (2); and a strain of *Saccharomyces* obtained from Budweiser, Joplin, Missouri.

Stock cultures were stored on Difco YM agar slants at 4°C. Seed cultures of each yeast were prepared by the addition of a portion of a stock culture into a shake flask containing a medium shown in Table I.<sup>1</sup> Shake flasks were incubated at 28°C for 18 hours. The shake flask culture was used to inoculate a 130L fermenter made by Fermentation Design, Inc., containing 100L of the medium in Table II. This culture was incubated for 18 hours at 30°C, pH 5.0, with an agitation speed of 120 RPM. The yeast seed culture was harvested into sterilized 15 gallon aluminum barrels prior to use in SSF. If the yeast was not used immediately the barrels were stored in a cold room at 4°C for no longer than 48 hours.

The mold *Trichoderma reesei* QM 9414 was obtained from ATCC. This organism was grown on potato dextrose agar at 29°C until sporulation occurred. The spore plates were stored at 4°C until use. *T. reesei* seed cultures were prepared by inoculating shake flasks with a portion of a spore plate. The culture medium used in the shake flasks is shown in Table III. The 1 liter shake flasks were scaled-up to 100 liter fermenters. Physical parameters controlled in the fermenters were aeration at 0.5 v/v/m and agitation speed at 300 RPM (100L fermenter). The seed cultures were incubated for 24 hours and then harvested aseptically into 15 gallon aluminum barrels to be transported to the pilot facility where it was used as inoculum for enzyme production.

A 10% v/v inoculum was used for initiation of cellulase induction stage in both batch and continuous phases of enzyme production. The medium used in enzyme production is described in Table IV. Avicel PH 105, comparable to MSW in inducing cellulase enzymes, was chosen as a model substrate because of its ease of handling and uniformity. Avicel PH 105 was obtained from American Viscose Co., Division of FMC, Marcus Hook, Pennsylvania. The length of incubation of the culture depended on the mode of enzyme production being used. Batch enzyme production lasted 96 to 120 hours whereas continuous enzyme production had a residence time of 50 hours ( $D=0.02$ ). Batch SSFs were run for 24 hours unless experimental design dictated otherwise. Semi-continuous SSFs were run for 96 to 120 hours with the residence time varying from 24 hours to 48 hours. Three major types of feedstocks were used, 1) purified cellulose (Solka floc.), 2) PMW (digester rejects, primary sludges, and digester fines), 3) MSW. None of the feedstocks received any type of pretreatment before use in the SSFs. However, MSW was at times pasteurized depending on experimental conditions. The MSW used in the SSFs had been shredded so that it would pass a 4" screen and then air classified prior to arrival at the pilot plant.

Assays for measurement of enzyme activity and protein concentration were conducted as described by Blotkamp, et al (9). Glucose measurements were made with the use of a Yellow Springs Instrument Company Model 23A glucose analyzer. Total reducing sugars were measured by the dinitrosalicylic acid method (10). Ethanol was analyzed using a Perkin-Elmer Model 3920 B gas chromatograph or a Hewlett-Packard Model 5730 A gas chromatograph equipped with flame ionization

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<sup>1</sup> Chemicals used in media formulations were mostly technical or reagent grade, however in the past year many of the compounds used were either fertilizer or food grade.

detectors, an electronic integrator, and a 6 ft. column of Porapak Q. Isothermal analysis was performed at 150°C.

Yeast populations were monitored by using dilution plating. Cellulose concentration of samples used in SSF was determined by using a modified version of the Van Soest procedures (11, 12). Moisture determinations were performed on an Ohaus moisture balance.

### EQUIPMENT

The vessels used for enzyme production and SSF were 330 gal (1250 liter) capacity manufactured by Pfaudler (L/D=.78). Four of the five vessels were capable of aseptic operation. The vessels were constructed of stainless steel with carbon steel jackets. The vessels were fully jacketed for adequate temperature control and sterilization.

All process piping was stainless steel with welded connections except where piping entered the vessel. Flanged fittings with teflon gaskets were used at these points. No pumps were used as a precaution against contamination, the liquids and slurries were moved with pressure (sterile air or steam) or gravity. The agitator shafts were equipped with double mechanical seals filled with oil. Enzyme production vessels used two flat blade impellers, each having four blades ( $D_i/D_t=.456$ ). Agitation speed was 120 RPM, aeration was 0.5 v/v/m at which the  $k_L a$  was 84 hr<sup>-1</sup> vs 330 hr<sup>-1</sup> on a lab scale (with water).

The baffle tray stripping column was constructed from 9" (I.D.) glass pipe with trays made of monel to resist corrosion. Associated process lines on the stripper were stainless steel. Pumps were used on the beer feed lines on the stripping column and recirculation loops to maintain solids in suspension.

A brief process flow diagram is presented in Fig. 1. After the enzyme production vessels were filled with nutrients and sterilized, the seed inoculum was transferred aseptically from the aluminum barrels to the vessels using nitrogen to pressurize the barrels. From this point the enzyme production could be run in either a batch or continuous mode. When enzyme was ready to be harvested a portion of the whole culture enzyme broth was transferred to the SSF vessel into which the cellulosic feedstock (PMW or MSW) would be added, along with the yeast. The SSF could be run in either batch or semi-continuous modes in which one half of material was transferred out every one half residence time. As the SSF was harvested the resulting beer slurry was moved to the beer storage tank where it could be pumped into the stripper column for ethanol recovery.

### RESULTS

#### Enzyme Production

Performance of batch enzyme productions can be typified by the data presented in Figures 2 and 3. Relatively high levels of protein and  $\beta$ -glucosidase are present in the culture broth. These results compare favorably with those obtained in laboratory studies.

The pilot plant was modified to produce enzyme continuously in order to demonstrate feasibility on a large scale. The economical advantages of a

continuous process lie in reduced capital investment due to increased efficiency of vessel use. Results from continuous enzyme productions are shown in Figs. 4 and 5. From these graphs can be seen that the  $\beta$ -glucosidase is somewhat lower but the protein and FPRS remain almost as high as in batch culture. Use of the enzyme from batch as well as continuous enzyme production in small scale flask saccharification and SSFs indicate only small differences between the two enzyme preparations under the same conditions.

#### SIMULTANEOUS SACCHARIFICATION FERMENTATION

Batch SSFs were performed using a variety of substrates. Typical results for Solka floc. and pulp mill wastes are illustrated in Fig. 6 and Fig. 7 respectively. In both cases over 50% of the theoretical yield from cellulose to ethanol was achieved. Batch SSFs were run with cellulose concentrations ranging from 5 to 15%.

Semi-continuous SSFs utilized pulp mill wastes and municipal solid waste as primary feedstocks. Ethanol production can be seen in Fig. 8. Both MSW and PMW showed the same trend (Fig. 9) concerning ethanol yield, base utilization for pH control, and bacterial contaminant population. The presence of contaminants and increased base usage indicates the production of other acidic products. Lab scale continuous SSF operation has proved to be significantly better than batch SSF per unit time.

#### STRIPPING OPERATIONS

After the SSFs were completed the resultant beer slurry was pressured to the beer storage tank (Fig. 1). From the beer storage tank the slurry was pumped to the top of the baffle tray column (13) while steam was injected into the bottom of the column. As the beer slurry cascaded down the column the hot vapor from below contacted the descending liquid and effected the stripping of the ethanol from the beer feed. The column was designed to handle beer slurries with solids content as high as 10% and deliver a product stream of approximately 25% w/v ethanol from a feed containing 2.0 to 3.5% ethanol. The still bottoms ethanol concentration remained as low as 0.04%. In a large-scale plant the product from the slurry stripper will be rectified further to yield 95-100% industrial or motor grade ethanol as necessary.

#### DISCUSSION AND CONCLUSION

Many pieces of equipment used for materials handling were tested in the pilot plant. An example is a 750 gallon pulper which worked with some wood products but not very well with MSW because of the plastics and metal cans in the material. A rotary vacuum filter was used for dewatering some slurries but for the majority of feedstocks it was not acceptable. For these reasons the feedstocks used at the pilot plant, as outlined in this paper, received no pretreatment and were used in the process just as they were received.

The operation of the pilot plant in both a batch and continuous mode using potential industrial feedstocks demonstrated the enzymatic cellulose to ethanol technology on a substantially larger scale than had previously been reported. The size of the plant enabled the use of bulky materials, such as MSW, which was difficult on a laboratory scale. The results from the pilot plant enzyme

production compared very favorably with the laboratory results, however in the case of the SSFs the data from the pilot plant and the laboratory are only comparable for approximately the first 24 hours after which the pilot plant results lagged behind. For example, on batch SSFs that ran longer than 24 hours at the pilot plant the percent conversion to ethanol did not continue to rise as in the laboratory. With pulp mill wastes in laboratory studies, SSFs of 85 to 90% of theoretical conversion to ethanol was achieved in 48 hours compared to 55 to 60% conversion at the pilot plant. The reasons for the difference in results can be explained in part by the lack of adequate environmental controls such as temperature and pH due to poor heat and mass transfer in the high solids slurry of the SSFs. Contamination was also a problem in SSFs that ran for extended periods as evidenced by the increase in base utilization for pH control and the concomitant decrease in ethanol yields (Figs. 8, 9).

The data gathered from the operation of the pilot plant was used for extensive economic analysis of the cellulose to ethanol technology (14). The results of this analysis along with the problem areas mentioned above indicate further scale-up of the process from the 1 ton/day to a 50 ton/day facility should be carried out in order to identify specific equipment to be used on a commercial scale and execute process modifications toward enhancing the economic viability of the technology.

#### NOMENCLATURE

a	area
D	dilution rate
$D_i$	impeller diameter
$D_v$	vessel diameter
I.D.	internal diameter
$k_L$	mass transfer coefficient
L	vessel length
m	minute
v	volume

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Table IYeast growth medium (flask)

	g/l
D - glucose	20.0
yeast extract	5.0
malt extract	5.0
bacto-peptone	5.0

Table IIYeast growth medium (fermenter)

	g/l
D - glucose	20.5
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.5
MgSO <sub>4</sub> ·7H <sub>2</sub> O	0.11
CaCl <sub>2</sub>	0.06
Cornsteep Liquor	7.5

Table III*T. reesei* growth medium

	g/l
D - glucose	20.0
KH <sub>2</sub> PO <sub>4</sub>	2.0
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	1.23
MgSO <sub>4</sub> ·7H <sub>2</sub> O	1.0
CaCl <sub>2</sub>	3.0
FeSO <sub>4</sub>	0.05
ZnSO <sub>4</sub>	0.014
MnSO <sub>4</sub>	0.016
CoCl <sub>2</sub>	0.04
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	2.62
(NH <sub>2</sub> ) <sub>2</sub> CO	1.7
Cornsteep	7.5

Table IV*T. reesei* enzyme production medium

	g/l
Cellulose (Avicel 105)	20.0
KH <sub>2</sub> PO <sub>4</sub>	2.0
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	1.23
MgSO <sub>4</sub> ·7H <sub>2</sub> O	1.0
CaCl <sub>2</sub>	3.0
FeSO <sub>4</sub>	0.05
ZnSO <sub>4</sub>	0.014
MnSO <sub>4</sub>	0.016
CoCl <sub>2</sub>	0.04
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	2.62
(NH <sub>2</sub> ) <sub>2</sub> CO	1.72
Cornsteep Liquor	7.5
Tween 80	0.2%

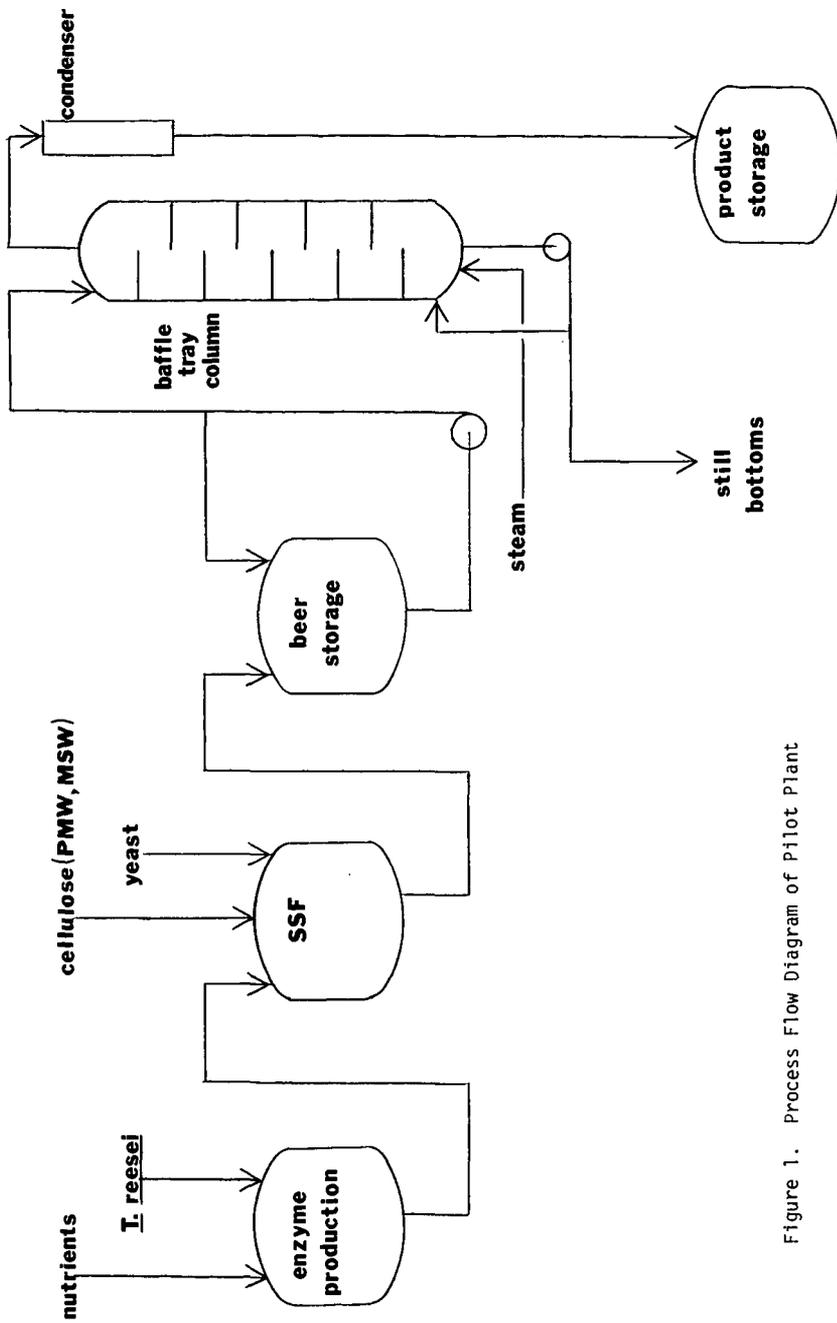


Figure 1. Process Flow Diagram of Pilot Plant

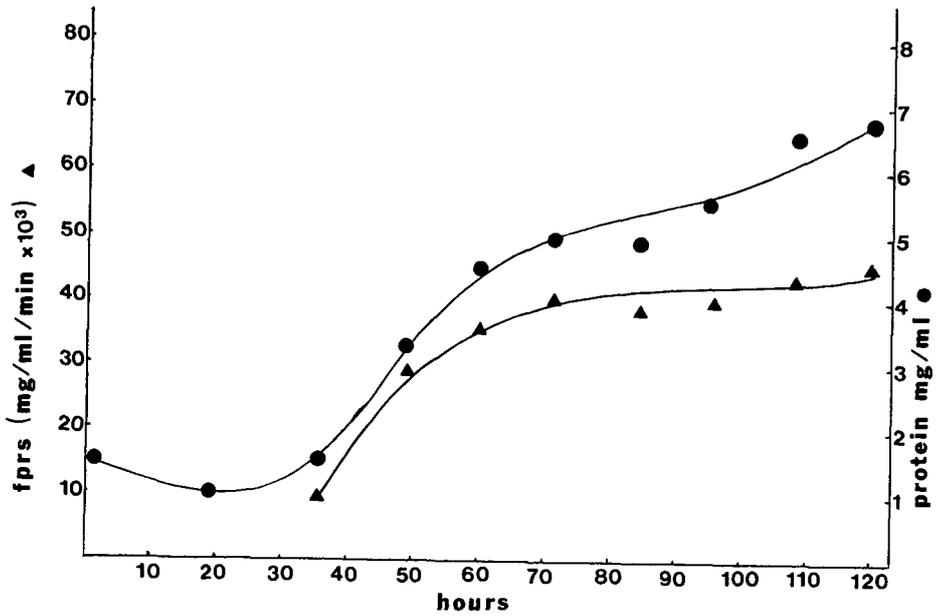


Figure 2. Batch Enzyme Production FPRS Activity and Protein Concentration

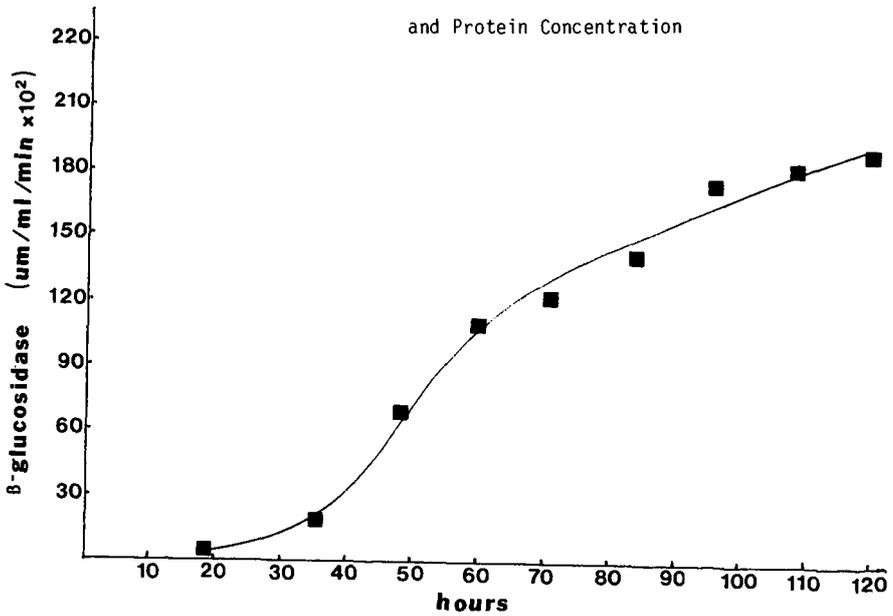


Figure 3. Batch enzyme production  $\beta$ -glucosidase Activity

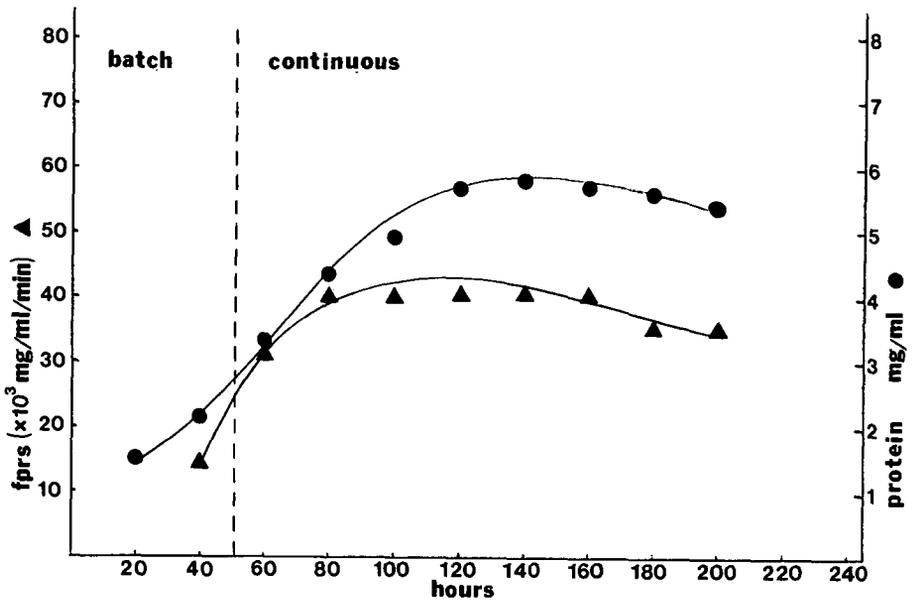


Figure 4. Continuous Enzyme Production FPRS Activity

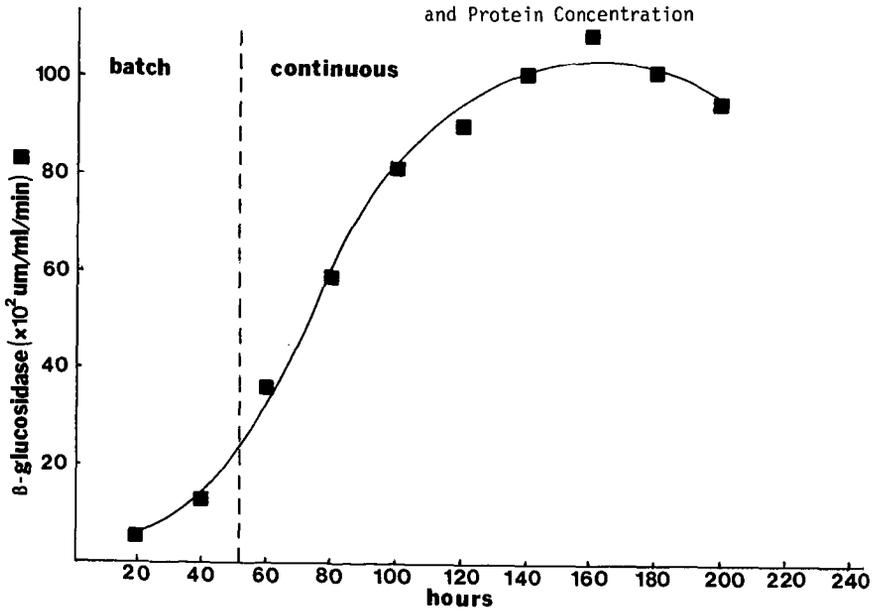


Figure 5. Continuous Enzyme Production  $\beta$ -glucosidase

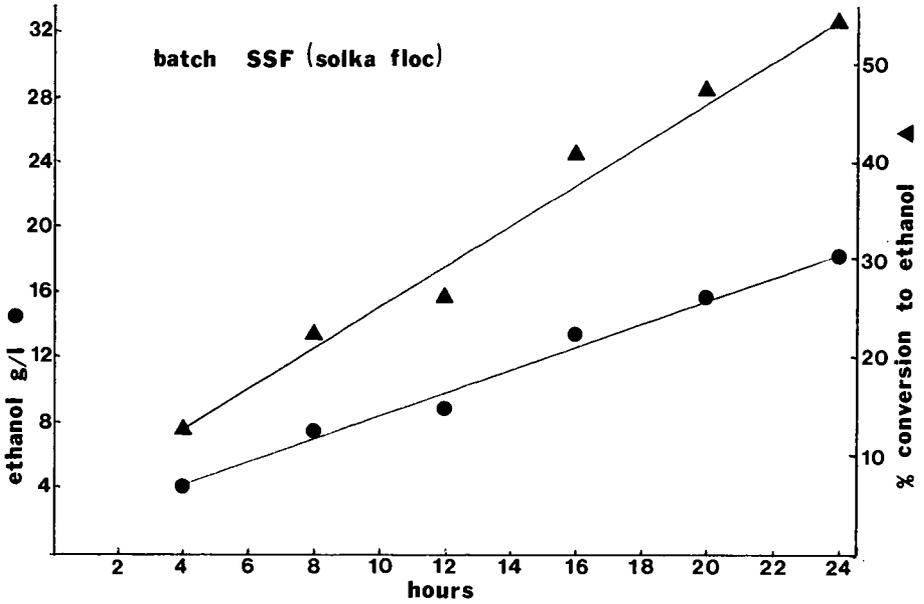


Figure 6. Batch SSF Using Solka Floc. Ethanol Production

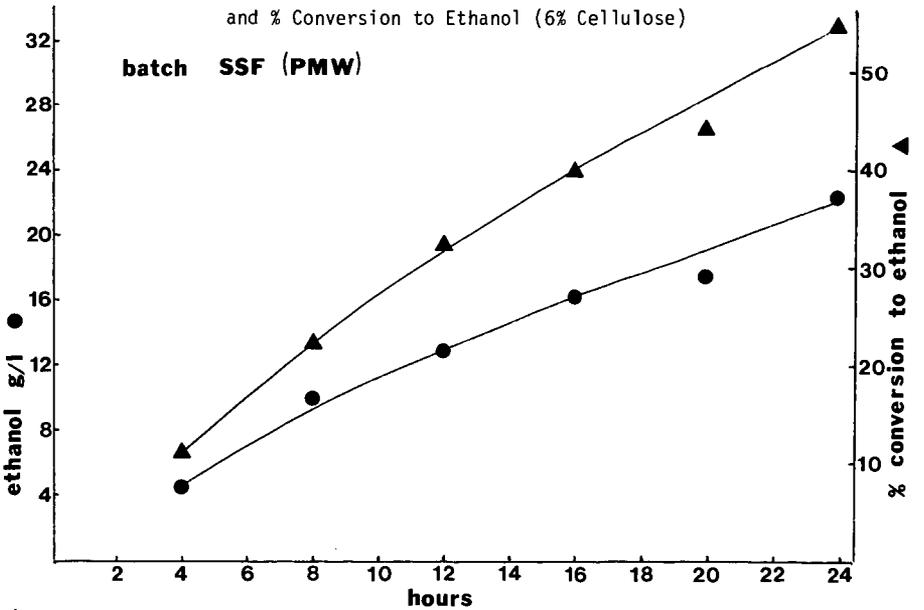


Figure 7. Batch SSF Using Pulp Mill Wastes, Ethanol Production and % Conversion to Ethanol (7% Cellulose)

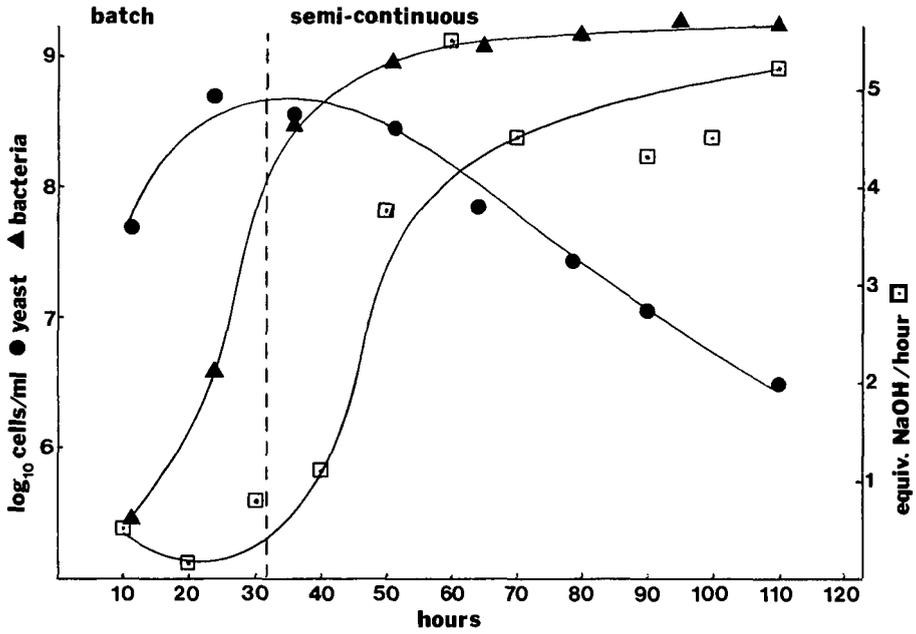


Figure 8. Semi-continuous SSF Using Pulp Mill Waste or Municipal Solid Waste, Ethanol Production (8% Cellulose)

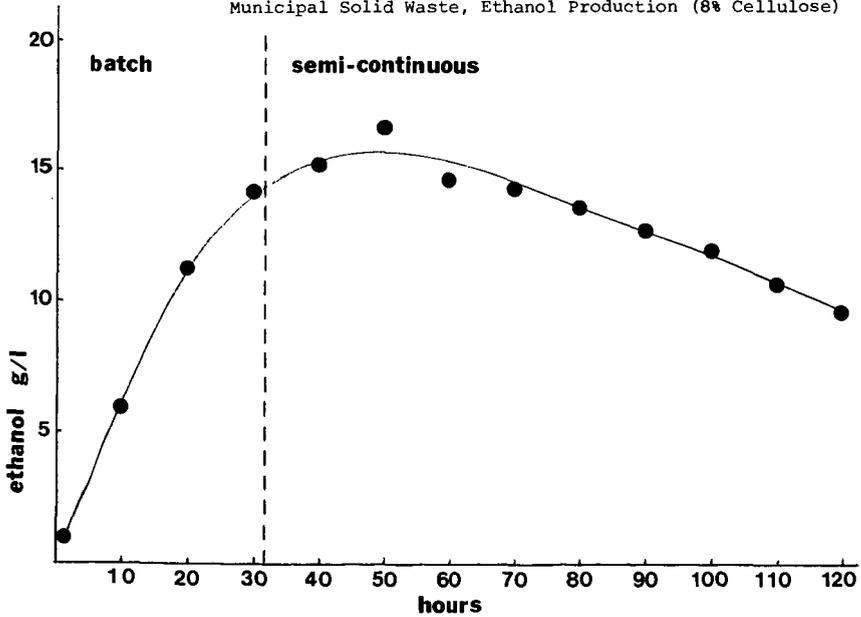


Figure 9. Semi-continuous SSF Using Pulp Mill Wastes or Municipal Solid Waste, Yeast Cell Count, Bacterial Cell Count and Base Utilization

## LOW ENERGY DISTILLATION SYSTEMS

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### ABSTRACT

Much work, aimed at improvements in the manufacture and recovery of ethyl alcohol, is currently being conducted in connection with the production of substitute liquid fuels; e.g., Gasohol. A primary consideration in all schemes for producing substitute liquid fuels lies in the energy consumed to produce the fuels. By energy re-use, pressure cascading and waste heat recovery, the expenditure of energy in distillation (alcohol recovery) can be greatly reduced. Such energy savings have been industrially demonstrated in three systems described in this paper. For high grade industrial ethanol production, a steam consumption of 3.0-4.2 Kg/liter (25-35 lb/U.S. gallon) of 100° G.L. alcohol is realized. For motor fuel grade anhydrous alcohol, the steam consumption is 1.8 to 2.5 Kg/liter (15-20 lb/U.S. gallon) of 99.5° G.L. alcohol, and for hydrous motor fuel grade alcohol, the steam consumption is 1.2 to 1.4 Kg/liter (10-12 lb/U.S. gallon) of 96° G.L. alcohol.

### ALCOHOL DISTILLATION

Over the past two decades, Raphael Katzen Associates International, Inc. has developed a series of highly efficient alcohol distillation systems for recovery of various grades of ethyl alcohol from synthetic and fermentation feedstocks. For each of these systems, the prime goal is minimization of energy consumption.

The RKAll distillation system for production of high quality spirits or industrial grade alcohol, uses a four tower distillation train. The product is first quality neutral spirits at 96° G.L. (192° U.S. proof) ethanol. When the crude ethanol feed is obtained by the synthetic process, e.g., direct hydration of ethylene, only 3 towers are required. For motor fuel grade alcohol, where a high quality product is not necessary, simpler abbreviated systems are used to reduce investment and operating costs.

### PRODUCTION OF 96° G.L. HYDROUS INDUSTRIAL ALCOHOL

The distillation system is shown in Figure 1 (1, 2). The process has been successfully operated commercially with four different fermentation feedstocks, namely, molasses, grain (corn or milo), corn wet milling middlings, and sulfite waste liquor. In addition, it has been operated with an ethylene-based synthetic crude.

Beer from the fermenters, containing approximately 6-8 wt % alcohol and 8-10% total solids (suspended and dissolved) is preheated to near saturation temperature and fed to the beer still. An overhead condensed product, at 75-85° G.L. (150°-170° U.S. proof) is taken to the high wines drum, and the bottoms liquid (stillage), containing not more than 0.02 wt % alcohol, is treated further for animal feed production.

The high wines distillate from the beer still is mixed with recycled alcohol from the concentrating tower and the combined stream is fed to the extractive distillation tower.

The extractive tower is designed to separate substantially all impurities; aldehydes, esters, and higher alcohols from the ethanol. The extraction technique relies on the volatility inversion of the higher alcohols with respect to ethanol in solutions containing high concentrations of water. The net result is that a substantially pure ethanol/water mixture is removed from the bottom of the extractive tower while the impurities are taken overhead.

Dilute alcohol from the base of the extractive tower is stripped and concentrated to product strength in the rectifying tower. A heads purge is taken from the overhead condensate. Product ethanol at 96° G.L. (192° U.S. proof) is withdrawn near the top of the rectifying tower, and a water stream, containing trace amounts of alcohol, is discharged from the base. Heads and side draw fusel oil purges are fed to the concentrating tower to prevent any buildup of impurities in the rectifying tower. The overhead stream from the extractive tower also is fed to the concentrating tower. Heads and fusel oil are concentrated in this tower and removed from the system, with the recovered alcohol being recycled to the extractive tower.

Steam economy is achieved by multi-stage preheating of beer feed, and by operating the extractive and concentrating towers at higher pressures. The overheads from these pressure towers supply thermal energy to the reboilers of the rectifying tower. Such pressure cascading results in a 30 to 50% reduction in virgin steam.

The key features of the RKAll high quality alcohol distillation system are:

1. Extractive distillation accomplishes a higher degree of impurity removal than is possible in more conventional systems. Product ethanol contains only 20-30 ppm of total impurities.
2. The use of pressure cascading permits substantial heat recovery and re-use. In the system described above and in figure 1, the extraction tower and concentrating tower are operated at a pressure higher than the rectifying tower. The overhead vapors

from these pressure towers supply thermal energy to the rectifying tower reboilers. By operating in this manner, the steam usage is kept to a minimum. Commercial facilities using this pressure cascading technique, show steam usages of only 3.0 to 4.2 Kg of steam per liter (25 to 35 lb/gal) of 96° G.L. (192° U.S. proof) ethanol compared to 6.0 Kg/liter in earlier conventional systems.

3. Substantially all (95 to 98%) of the ethanol in the crude feed is recovered as first grade product.
4. Design of highly efficient tower trays permits high turndown capability. These trays are designed to be self-descaling in the stripping section of the beer towers.
5. A highly advanced control system, developed through years of experience, provides for sustained stable operation, with only part-time attention of an operation required. Product quality is maintained with less than 30 parts per million of total impurities. Permanganate time is in excess of 60 minutes.

#### PRODUCTION OF ANHYDROUS (99.5°-99.98° G.L.) ALCOHOL

Anhydrous alcohol is produced by azeotropic distillation. A high grade product of 99.98° G.L. (199.96° U.S. proof) concentration is produced for use in food and pharmaceutical aerosol preparations. A product of 99.5° G.L. (199° U.S. proof) concentration is produced for blending with gasoline for motor fuel.

The Katzen two-tower dehydrating system design (see Figure 2) has been installed and successfully operated in seven different alcohol plants in North America and the Carribean.

The 96° G.L. (192° U.S. proof) product is withdrawn from the side of the rectifier in the hydrous distillation process. The hydrous alcohol is fed to an atmospheric dehydrating tower. Removal of water from the feed is achieved by the use of benzene, heptane, cyclohexane, or other suitable entraining agent. A ternary azeotrope is taken overhead from the dehydrating tower. The overhead vapors are condensed and the two liquid phases are separated in a decanter.

The entrainer-rich phase is refluxed to the dehydrating tower. A reboiler is used to supply vapor to this tower with heat supplied by either low pressure steam, recovered flash vapor, or hot effluent and condensate streams from the hydrous alcohol unit.

The aqueous phase from the decanter is fed to a stripper. The entraining agent is recovered, along with alcohol, in the overhead vapor. Water is removed from the bottom of the stripper. Direct steam may be used in this stripper.

The bottoms stream from the azeotropic dehydrating tower is the anhydrous alcohol product.

Design know-how consists of optimizing the balance between capital costs and utility consumption, with stable control. Specific features which contribute to overall process efficiency and reliability of the RKAll anhydrous alcohol distillation system are:

1. Use of a common condenser and decanter for the dehydration and stripping towers to reduce capital costs.
2. Design of highly efficient tower trays for high turndown capability.
3. Low consumption of entraining agent (less than 0.1 Kg per 1,000 liters of anhydrous alcohol).
4. Low consumption of steam (1 to 1.5 Kg/liter or 8.3 to 12.5 lb/gallon of anhydrous alcohol), or equivalent hot condensate or waste streams.

#### PRODUCTION OF ANHYDROUS MOTOR FUEL GRADE ALCOHOL

For motor fuel grade alcohol, the beer feed is preheated in a multi-stage heat exchange sequence. A pressure stripper-rectifier (see Figure 3) is used to separate the beer feed into an overhead fraction of about 95° G.L. (190° U.S. proof) alcohol and a bottoms stream containing less than 0.02 wt % alcohol. Side draws are made to remove fusel oils. These oils are recovered by water washing, and rebled as a component of the motor fuel grade alcohol. In addition, a pasteurizing section is used to concentrate low boiling impurities. These are removed by taking a small heads draw which is burned in the plant reboiler. Dehydration of the hydrous product is accomplished in two additional towers. Energy is supplied to the reboilers of the two towers in the dehydration step by condensing the overhead vapors from the pressure stripper-rectifier. By operating the beer stripper-rectifier at a higher pressure (3) than the two-tower dehydration system, very low total steam consumption can be achieved. The steam usage is 1.8 to 2.4 Kg/liter (15 to 20 lb/gallon) of 99.5° G.L. (199° U.S. proof) motor fuel grade alcohol product (5).

## PRODUCTION OF HYDROUS MOTOR FUEL GRADE ALCOHOL

For a product to be utilized in NEAT alcohol engines (no gasoline in the blend), further steam economy can be achieved when only 85-95° G.L. (170°-190° U.S. proof) alcohol product is desired. This is accomplished by splitting the stripping-rectifying duties between two towers (see Figure 4, Ref. 4). The first stripper-rectifier tower is operated at a pressure higher than the second tower and receives 50 to 60% of the beer feed. The overhead vapors from the first tower are used to boil up vapor in the second tower.

The steam usage is 1.2 to 1.5 Kg/liter (10 to 12 lb/gallon) of 85°-96° G.L. (170°-192° U.S. proof) motor fuel grade alcohol (on a 100% ethanol basis). Along with steam economy, cooling water requirements are reduced proportionately.

### SUMMARY

A summary of investment for typical low energy distillation systems (shown in Figures 1 through 4) for production of 190 MM liter/year (50 MM USGPY) alcohols is given in Table 1. Also, shown are the steam, cooling water and electric energy requirements for each system.

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3. U.S. Patent Application No. 958,533, Distillation Method and Apparatus for Making Motor Fuel Grade Anhydrous Alcohol, November 7, 1978.
4. U.S. Patent Application, Novel Energy Efficient Process for Production of 170 to 190° Proof Alcohol.
5. Raphael Katzen Associates, Grain Motor Fuel Alcohol, Technical and Economic Assessment Study, U.S. DOE Contract No. EJ-78-C-6639, June, 1979.

TABLE 1

LOW ENERGY DISTILLATION SYSTEMS  
SUMMARY OF INVESTMENT AND UTILITIES

190 MM liters/yr (50 MM gallons/yr)

	High Grade (96° G.L.) Industrial Alcohol	Anhydrous (100° G.L.) Industrial Alcohol	Anhydrous (99.5° G.L.) Motor Fuel Alcohol	Hydrous Motor Fuel Grade Alcohol
Figure	1	2	3	4
Alcohol Product, U.S. Proof	190	200	199	190
Distillation Unit Investment \$MM U.S.	7.3	2.8	6.1	3.4
Steam Usage Kg/liter (lb/gallon)	4.1 (34)	1.4 (11.7)	2.2 (18)	1.2 (10)
Cooling Water MT/hr	1866	934	1311	182
Electric Power kw	289	31	133	177

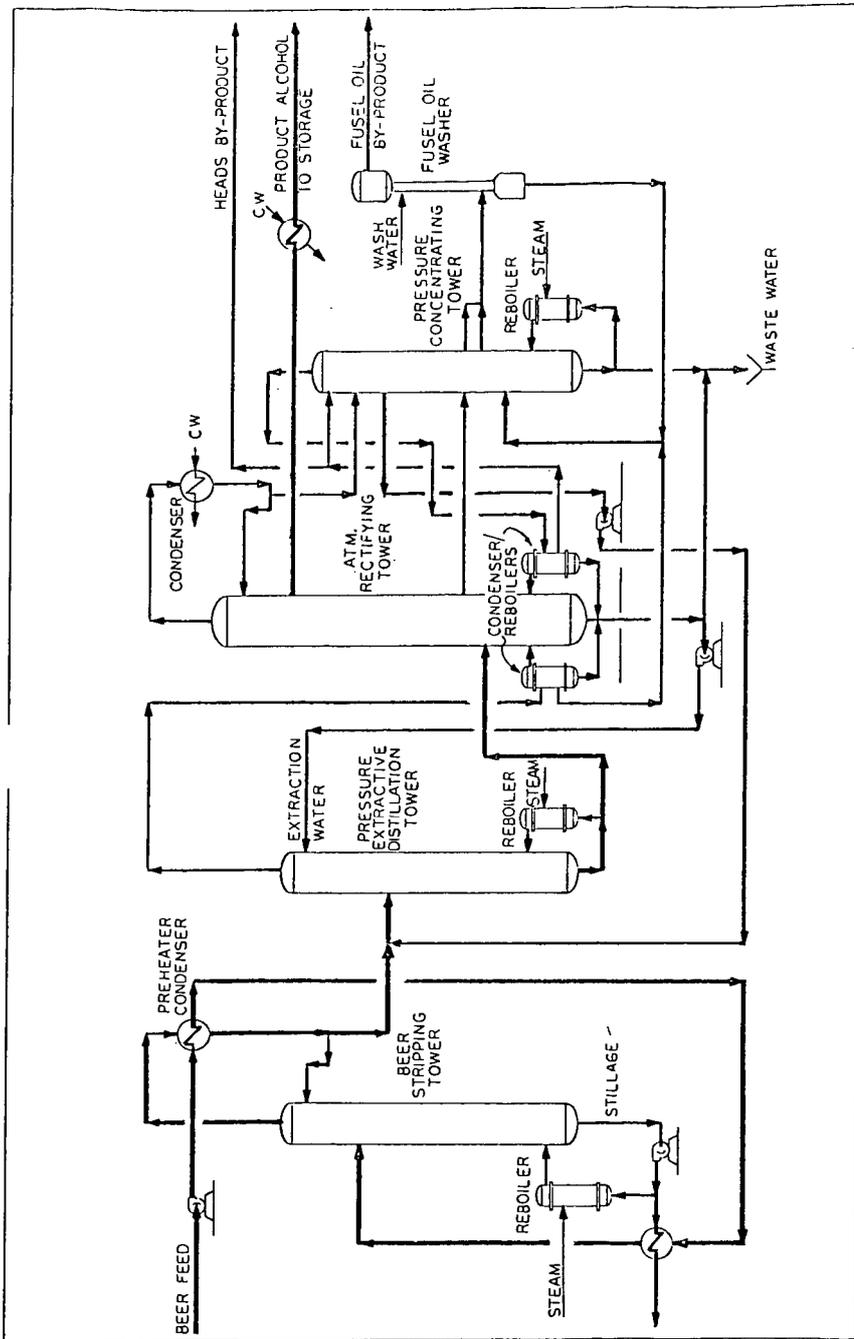


FIGURE 1. HIGH-GRADE HYDROUS ALCOHOL SYSTEM

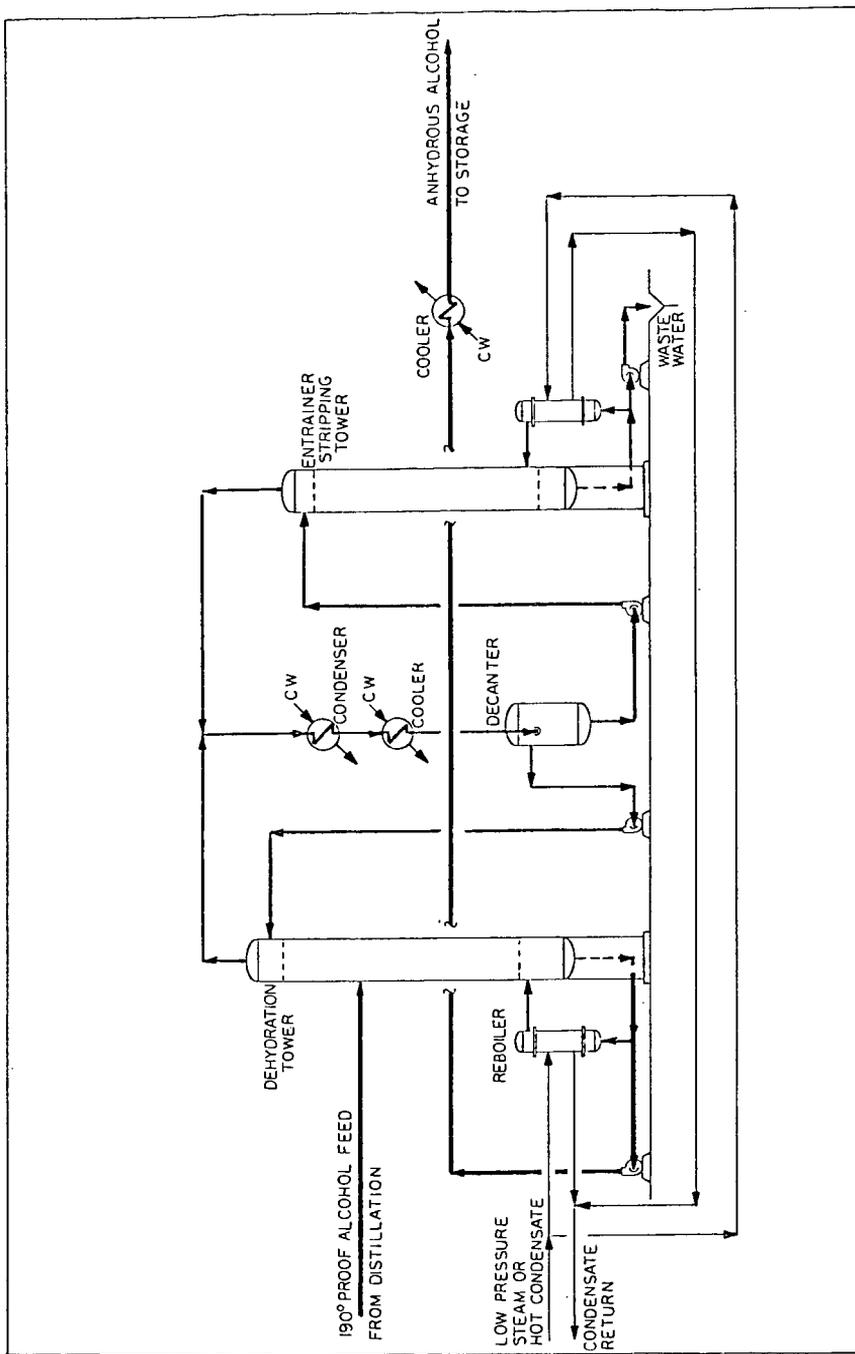


FIGURE 2. HIGH-GRADE ANHYDROUS ALCOHOL SYSTEM

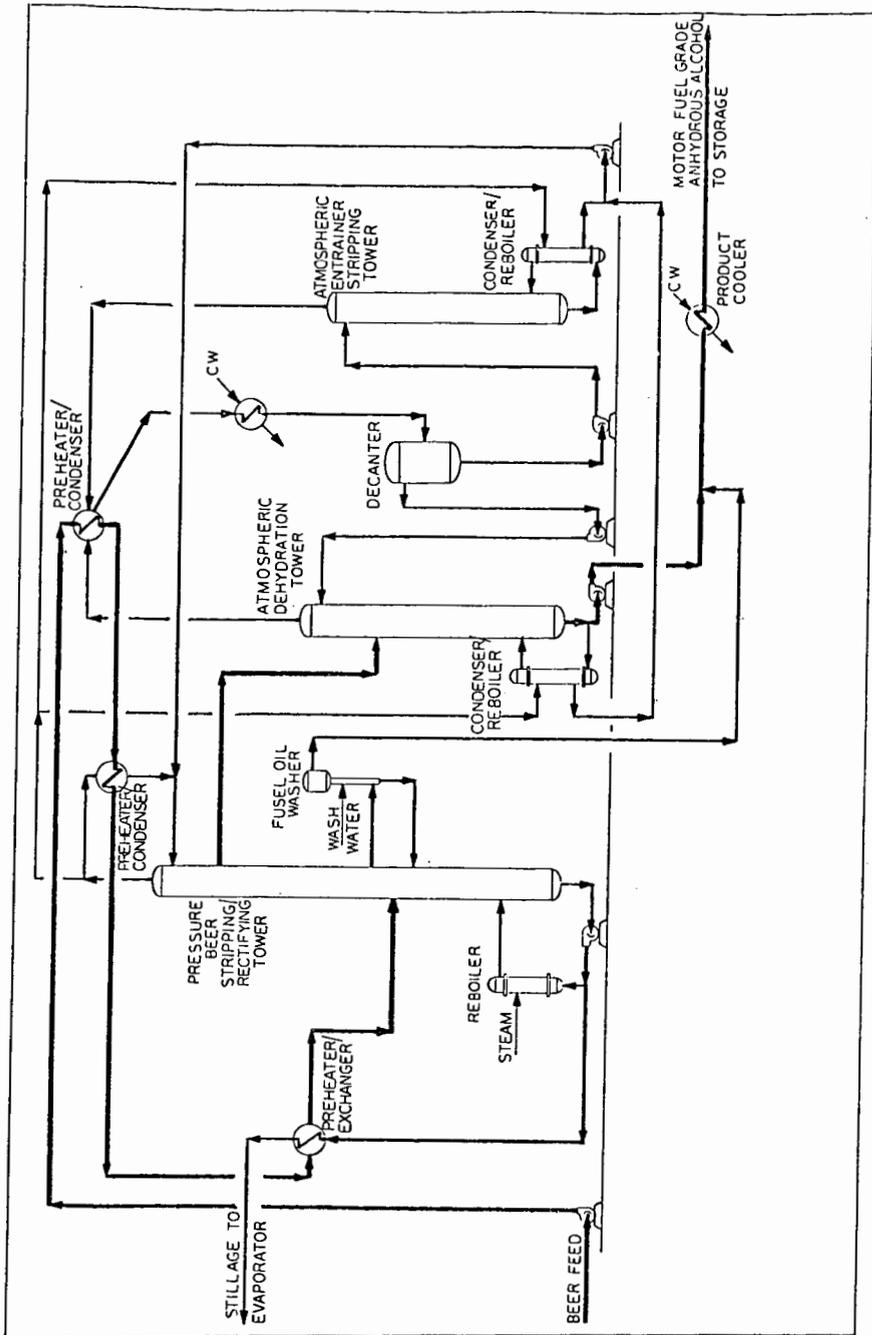


FIGURE 3. MOTOR FUEL GRADE ANHYDROUS ALCOHOL SYSTEM



# CHEMICAL FEEDSTOCKS FROM WOOD: AQUEOUS ORGANIC ALCOHOL TREATMENT

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## INTRODUCTION

The current world petroleum crisis has caused renewed interest in alternative and renewable sources of fuel and feedstock chemicals. One such alternative receiving attention involves the separation of wood into its components, cellulose, hemicellulose and lignin, followed by conversion to feedstock chemicals. Treatment of wood with an aqueous organic solvent has been found to be effective in removing lignin and hemicellulose from the cellulose fibers.

Early work by Aronovsky and Gortner (1) studied the use of aqueous solutions of organic alcohols to remove lignin and produce wood pulp. They determined that aqueous n-butanol was the most effective solvent for producing a well pulped residue and for the removal of lignin.

Kleinert (2,3) found that organosolve bulk delignification occurred in two distinct pseudo-first order stages. Delignification was found to be considerably faster during the first part of the batch cook.

More recently, Katzen et al. (4) showed that a continuous alcohol pulping process using aqueous ethanol is economically feasible if the by-products (lignin and hemicellulose hydrolysis products) can be upgraded and sold. A pay out time of 3.2 years with a 22% return on investment was calculated.

This paper reviews the recent work with aqueous organic solvents conducted at The University of Alabama. Emphasis on the rate of lignin removal and the extent of pulp recovery is included. The use of the data to make preliminary process calculations regarding technical and economic feasibility is also addressed with comparisons to recent work reported in the literature.

## BATCH DELIGNIFICATION STUDIES

A majority of the work reported in the literature was accomplished using batch equipment. Initial screening studies at The University of Alabama likewise followed this mode of investigation. A summary of the various conditions investigated is shown in Table 1.

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Table 1 - Summary of Experimental Conditions

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Wood Type	-	Southern Yellow Pine, Sweet Gum
Wood Size	-	Meal (-10 +70)
Solvent Type	-	Ethanol, Butanol, Phenol
Solvent/Water	-	50/50 by Volume
Solvent/Wood	-	15 ml Solvent/1 g Wood
Temperature	-	175-205°C
Pressure	-	1140-2180 kPa
Catalysts	-	Alum, AlCl <sub>3</sub> , Anthraquinone

---

A summary of the results of the batch experiments is shown in Table 2.

Table 2 - Summary of Batch Results

Southern Yellow Pine			
Conditions	Time	% Residual Pulp	% Lignin Removed
Solvent: nBuOH	0.0	85.3	15.0
Temp: 175 °C	0.5	74.1	36.0
Pressure: 1140 kPa	1.0	71.8	36.0
	4.0	67.5	22.0
Solvent: nBuOH	0.0	65.3	27.2
Temp: 205 °C	2.0	60.7	36.0
Pressure: 2170 kPa	4.0	56.0	35.0
Solvent: Phenol	0.0	58.0	35.9
Temp: 205 °C	0.5	43.0	83.1
Pressure: 1490 kPa	1.0	41.1	84.7
	1.5	39.5	87.0
	2.0	38.0	89.3
	4.0	36.2	89.7
Sweet Gum			
Conditions	Time	% Residual Pulp	% Lignin Removed
Solvent: nBuOH	0.00	90.8	17.2
Temp: 175 °C	0.67	69.1	45.3
Pressure: 1140 kPa			
Solvent: nBuOH	0.0	69.2	42.2
Temp: 205 °C	0.5	56.5	60.9
Pressure: 2170 kPa	1.0	50.4	78.6
	1.5	47.8	83.6
	2.0	45.7	88.8
	4.0	43.1	85.7

These data are graphically illustrated in Figures 1 & 2 in which the fractional residual pulp versus time-at-temperature is plotted on rectangular and semi-log paper, respectively. A rapid decrease in the residual pulp during the early stages of the cook is observed.

Figure 2 shows the characteristic, two stage process that has been described by Kleinert and others (5,6) by a two step, first order expression. For the systems investigated in this study the rate constants for each step were calculated to be between  $5.0 \times 10^{-3}$  and  $2.0 \times 10^{-2} \text{ min}^{-1}$  for the rapid initial step and between  $4.0 \times 10^{-4}$  and  $4.0 \times 10^{-3} \text{ min}^{-1}$  for the subsequent slower rate.

Figures 3 and 4 show the lignin removed versus time and the log of lignin removed versus time. The percent lignin removed reaches a maximum level in the batch studies (see Figure 3) and then decreases. This decrease in the amount of lignin removed is due to repolymerization and precipitation of removed lignin,

and/or to the decrease in solubility of lignin in the solvent as it cools to room temperature. Figure 4 shows that the removal of lignin occurs in several first order stages paralleling the results noted for residual pulp (Figure 2). Corresponding rate constants for lignin are in good agreement with those values reported for residual pulp ( $2 \times 10^{-2}$  to  $6.0 \times 10^{-2} \text{ min}^{-1}$  and  $3.0 \times 10^{-4}$  to  $1 \times 10^{-3}$ ) indicating a common mechanism during initial stages of hydrolysis. Kleinert (2,3) reported values for the rate constants between  $1.5 \times 10^{-2}$  and  $3.0 \times 10^{-2} \text{ min}^{-1}$  for times corresponding to the initial first order removal presented here.

#### SEMI-BATCH DELIGNIFICATION STUDIES

In order to eliminate problems of solubility and repolymerization/redeposition of lignin, and, to simulate more closely commercial delignification processing, a series of data have been collected using a semi-batch apparatus. In this scheme, the solvent phase is continuously passed over a fixed bed of wood chips. The results obtained from these runs are summarized in Table 3.

Table 3 - Semi-Batch Results

Solvent	Wood	Temp, °C	Time hrs	Flow cc/min	% Residual Pulp	% Lignin Removed	Catalyst*
EtOH	SYP	175	2.50	7.20	91.1	3.7	-
EtOH	SG	175	0.67	7.20	74.0	47.3	-
EtOH	SG	175	0.67	7.20	73.2	48.9	-
EtOH	SG	175	0.67	7.20	30.6	97.9	Anthraquinone AlCl <sub>3</sub>
EtOH	SYP	205	1.33	3.20	52.1	59.4	-
EtOH	SYP	205	2.50	7.20	65.4	38.9	-
EtOH	SYP	205	4.00	7.20	47.0	62.2	-
BuOH	SG	175	0.67	7.20	95.5	20.0	-
BuOH	SG	175	0.67	7.20	96.8	15.3	Alum
BuOH	SG	175	0.67	7.20	43.2	87.2	AlCl <sub>3</sub>
BuOH	SG	175	0.67	7.20	74.6	37.9	Anthraquinone
BuOH	SG	200	0.67	7.20	67.8	45.2	-
BuOH	SYP	205	4.00	5.43	65.0	43.7	-
BuOH	SYP	205	4.00	6.30	69.3	43.6	-

\*Catalyst concentration is 0.005 % wt

These values show that for delignification to proceed at an appreciable rate with Southern Yellow Pine, the temperature must be above 175°C. It is also seen that more lignin is removed using aqueous ethanol as a solvent (over n-BuOH) but the amount of residual pulp decreases due to increased hydrolysis of the carbohydrates.

The results show that anthraquinone has no catalytic affect in aqueous ethanol at 175°C. The use of AlCl<sub>3</sub> as a catalyst causes a severe loss of the carbohydrates. The high loss of carbohydrates makes AlCl<sub>3</sub> an undesirable catalyst for the production of wood pulp.

In aqueous nBuOH solvent at 175°C Alum has no catalytic effect. The use of anthraquinone catalyst cause the percent lignin removal to increase from 20.0% to 37.9% with a corresponding decrease in residual pulp from 95.5% to 74.6%. The use of AlCl<sub>3</sub> again leads to high lignin removals with rapid hydrolysis of the carbohydrates.

Recovery data from a four hour semi-batch extraction of Southern Yellow Pine with aqueous ethanol at 205°C are shown in Figure 5. This data was collected by sampling the effluent at 100 ml intervals. These samples were stripped of solvent using a rotary evaporator followed by analysis of the residue for lignin content. The corresponding rate of removal of the lignin was described by a first order model producing a rate constant of  $1.5 \times 10^{-2} \text{ min}^{-1}$ ; well within the rate of values calculated for batch treatment.

Using the above information and data on the physical properties of the solvents, a preliminary engineering analysis can be made evaluating commercial application of the treatment method.

Commercial applications various process schemes have been proposed for organic solvent delignification including the more recent one by Katzen (4) for aqueous ethanol extraction. Figure 6 shows a form of that process modified for n-butanol-water treatment. This process is comprised of four sections: Extraction, Solvent Separation, Solvent Recovery and Product Recovery. A fifth, pretreatment of the wood may also be included as a major section of hemicellulose recovery is considered as an option. The values shown tabulated are based on the recovery data and extraction efficiencies generated in the experimental investigation for n-butanol-water treatment.

In general, 1000 kg of wood is needed to produce 650 kg of pulp ( 25% lignin), 150 kg of dry extracted lignin and 200 kg of hemicellulose hydrolysis products. The pulp could be further processed for use as a paper stock or could be acid hydrolyzed to glucose. There are existing processes for converting glucose to ethanol or n-butanol, making either solvent process totally independent of petroleum sources.

Approximately 1% of the solvent would be held up by the pulp and 1% would be removed with the lignin slurry. Approximately 80-90% of this could be easily removed by steam stripping giving an overall alcohol loss of 25 kg of nBuOH per 1000 kg of wood processed. It is also estimated that 275 kcal/kg of wood processed/extractor would be required assuming 20% energy loss. This compares quite favorably with the value of 268 kcal/kg wood given by Katzen (4) using a battery of nine extractors.

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#### ACKNOWLEDGEMENT

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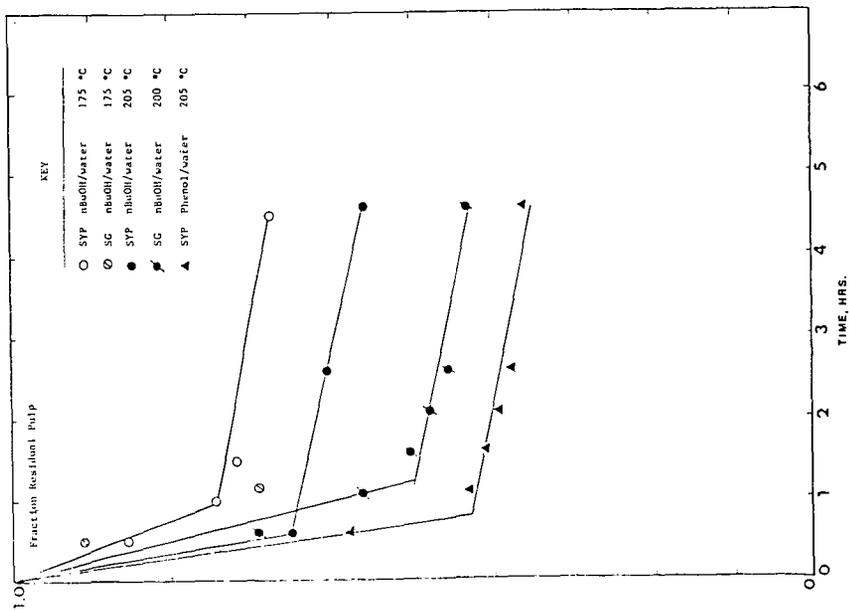


Figure 1. Fraction Residual Pulp vs. Time-at-Temperature for Aqueous Alcohol Delignification of Sweet Gum (SG) and Southern Yellow Pine (SYP).

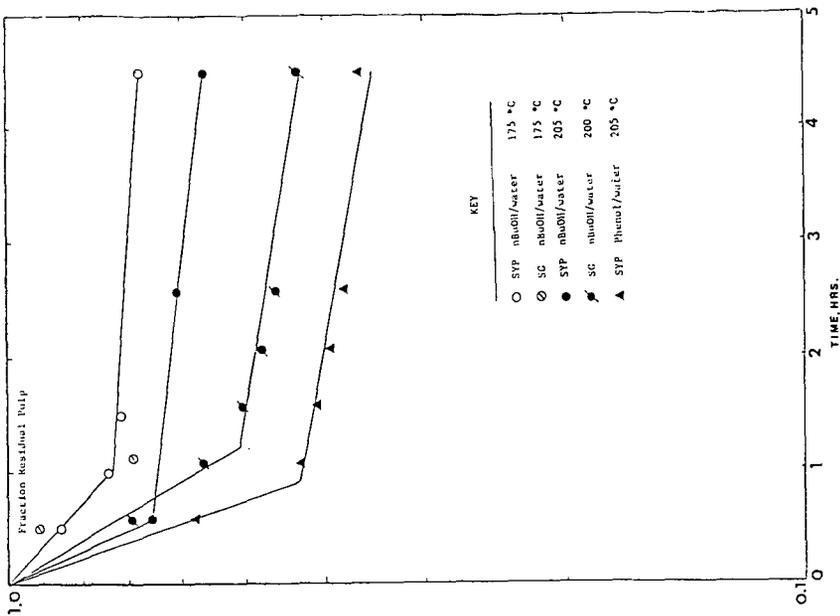


Figure 2. Fraction Residual Pulp vs. Time-at-Temperature for Aqueous Alcohol Delignification of Sweet Gum (SG) and Southern Yellow Pine (SYP).

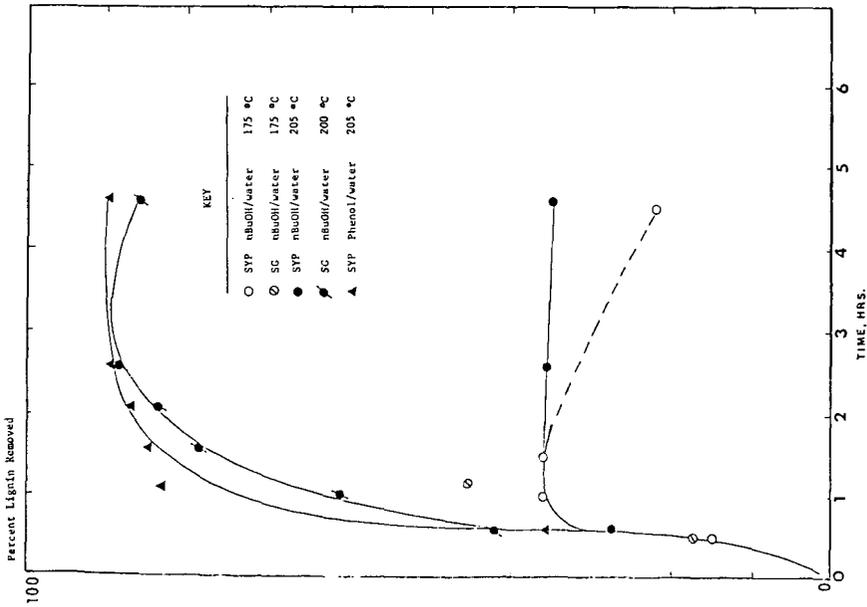


Figure 3. Percent Lignin Removed vs. Time-at-Temperature for Aqueous Alcohol Delignification of Sweet Gum (SG) and Southern Yellow Pine (SYP).

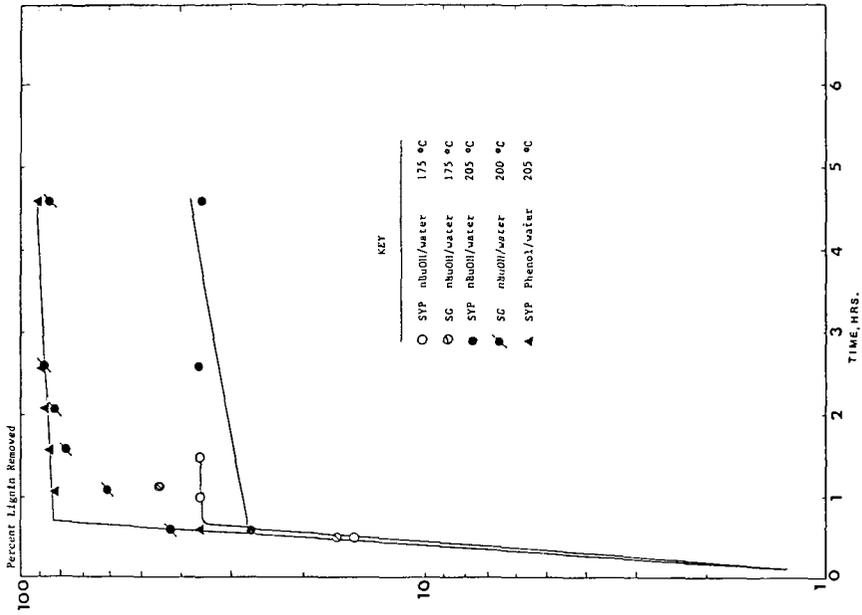


Figure 4. Percent Lignin Removed vs. Time-at-Temperature for Aqueous Alcohol Delignification of Sweet Gum (SG) and Southern Yellow Pine (SYP).

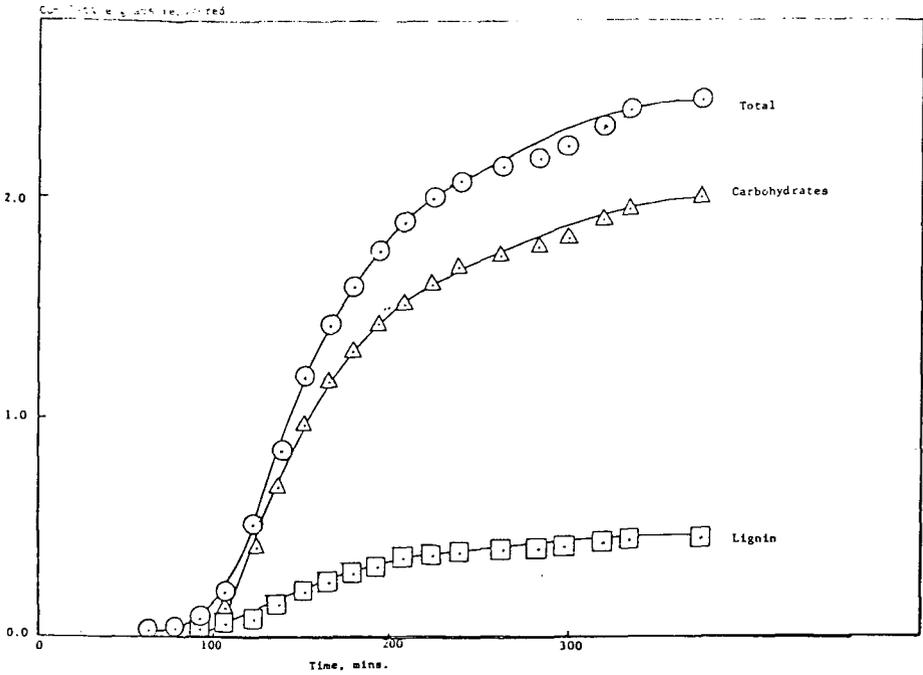
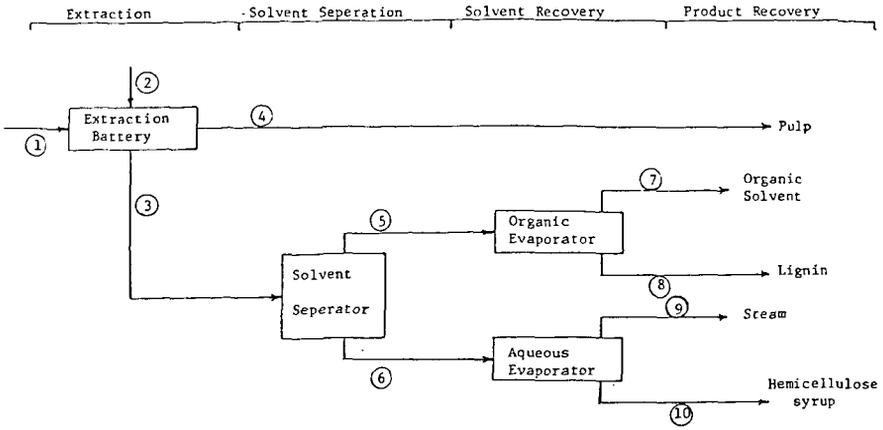


Figure 5. Cumulative Weight of Wood Components Recovered vs. Contact Time in a Semi-Batch System using Aqueous Ethanol as the Delignification Agent at 205°C.



Stream	1	2	3	4	5	6	7	8	9	10
nBuOH (kg)	-	10840	10740	90	9990	750	9910	80	750	-
H <sub>2</sub> O (kg)	-	13470	13370	110	2720	10640	2720	-	10450	200
Cellulose (kg)	400	-	-	400	-	-	-	-	-	-
Hemicellulose (kg)	300	-	200	100	-	200	-	-	-	200
Lignin (kg)	300	-	150	150	150	-	-	150	-	-
Total Mass (kg)	1000	24310	24400	850	12860	11590	12630	230	11200	400
Temp (°C)	25	205	205	205	40	40	117	117	100	100
Q kcal x 10 <sup>6</sup>	0.005	8.89	-	-	0.518	1.064	3.411	0.005	7.144	0.014

Figure 6. Process Schematic for the Aqueous n-Butanol Delignification of Southern Yellow Pine.

## ENVIRONMENTAL ASSESSMENT OF WASTE-TO-ENERGY CONVERSION SYSTEMS

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### Introduction

Increased emphasis on energy and material recovery and the need for alternatives to solid waste disposal in landfills have generated growing interest in waste-as-fuel processes. The processes include, on a generic basis, waterwall incinerators, pyrolysis systems, combined fuel-fired systems (coal plus refuse derived fuel [RDF], RDF plus municipal sewage sludge, coal plus wood waste, and biochemical conversion of waste to methane.

The Fuels Technology Branch of EPA's Industrial Environmental Research Laboratory in Cincinnati is sponsoring a program at Midwest Research Institute (MRI) to conduct environmental assessments of some of the above waste-to-energy conversion processes. The overall objective of this program is to evaluate the potential multi-media environmental impacts resulting from using combustible wastes as an energy source and thereby identify control technology needs. As part of this program, MRI has undertaken fairly extensive sampling and analysis efforts at the following waste conversion facilities.

- A 200 ton/day refuse pyrolysis system
- A 120 ton/day municipal incinerator fired with Municipal Solid Waste (MSW)
- A 10 MW power plant boiler fired with wood waste and No. 2 oil
- A 70,000 lb/hr steam boiler fired with coal and densified refuse-derived fuel (d-RDF)
- A 20 MW power plant boiler fired with RDF

A description of the facility, the sampling and analysis methods used, and the results obtained are individually presented below for each of the above facilities tested.

### Refuse Pyrolysis System

The Union Carbide refuse pyrolysis system (PUROX) at South Charleston, West Virginia, was designed to pyrolyze 200 tons/day of refuse-derived fuel. The refuse fuel was produced by shredding MSW to a 3 in. size and then removing magnetic materials from the shredded waste. The PUROX system is a partial oxidation process that uses oxygen to convert solid wastes into a gas having a higher heating value (HHV) of about 370 Btu/scf.

Figure 1 is a schematic illustration of the Purox process. Raw refuse is received by truck in the plant's storage building. It is moved and stacked in the storage area by a front end loader. The same loader picks up the stored waste, weighs it on a platform, and dumps it on a conveyor leading to the shredder, where it is shredded to a 3-in. size. Ferrous material is removed by a magnetic recovery system.

The refuse fuel is fed into the top of the reactor, the principal unit on the process, by two hydraulic rams. There are three general zones of reaction within the reactor (drying, pyrolysis, and combustion). The reactor is maintained essentially full of refuse, which slowly descends by gravity from the drying zone through the pyrolysis zone into the combination zone. A counterflow of hot gases, rising from the combustion zone at the bottom, dries the incoming, moist refuse. As the material progresses downward it is pyrolyzed to form fuel gas, char, and organic liquids.

Oxygen is injected into the bottom hearth section at a ratio of about 20% by weight of incoming refuse. The oxygen reacts with char formed from the refuse to generate temperatures of 1370 to 1650°C in the lower zone, which converts the noncombustibles into a molten residue. This residue is discharged into a water quench tank where it forms a slag.

The hot gases from the hearth section are cooled as they rise through the zones of the reactor. After leaving the reactor, the gases are passed through a recirculating water scrubber. Entrained solids are separated from the scrubber water in a solid-liquid separator, and recycled to the reactor for disposal. The water product discharged from the separator system is sent to a plant treatment system. The gas leaving the scrubber is further cleaned in an electrostatic precipitator (ESP) and then cooled in a heat exchanger prior to combustion in a flare combustor. During the tests the gas was burned in a package boiler transported to the site for these tests. The fuel gas consisted of about 40% CO by volume, 23% CO<sub>2</sub>, 5% CH<sub>4</sub>, 26% H<sub>2</sub>, and the rest being N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, etc.

Sampling at the Purox facility was directed to the three effluent streams; slag, scrubber effluent, and gaseous emissions from a boiler when fired with Purox gas and when fired with natural gas. An overview of the sampling and analysis scheme is shown in Figure 2. As can be seen in this figure, sampling and analysis of each stream was rather complex, being directed to conventional pollutants but including, among others, priority pollutants in water samples and sampling of both liquid and gaseous emissions for most of the analyses prescribed under EPA's Level 1 environmental assessment protocol. Particulate emission sampling in the boiler stack was conducted according to EPA Method 5, but using a High Volume Sampling System (HVSS) because of the expected low particulate loading. Boiler stack sampling also included use of the Level 1 SASS\* train.

Water samples also underwent analysis for priority pollutants, but the data are too lengthy for inclusion in this paper. The results of these analyses showed that a few of these pollutants were present at detectable levels in the scrubber effluent, but that the Unox system did effectively reduce their concentrations.

\* Source Assessment Sampling System.

Results of the testing effort showed that, of the criteria pollutants, only NO<sub>x</sub> and particulate emissions increased when burning Purox gas as compared to natural gas. NO<sub>x</sub> and particulate levels were of the order of 350-400 ppm and 0.002-0.005 gr/scf respectively. SO<sub>2</sub> emissions averaged 70-100 ppm. Particulate and SO<sub>2</sub> emissions were below present standards, whereas NO<sub>x</sub> will require further reduction. Also, analysis for metals and other pollutants indicate that these should not present any problems.

Because of the difficulty involved in interpreting much of the data collected in this test, especially the Level 1 analysis results, the environmental assessment work was extended to include application of the methodology known as the Source Analysis Model (SAM/1A) developed by EPA. Basically, this model compares the measured concentrations of pollutants with approximate emission concentration guidelines known as MATE values (minimum acute toxicity effluents). These MATE values have tabulated for several compounds or classes and there is a specific MATE concentration for each compound and for each type of effluent stream (solid, liquid, or gaseous). The MATE values are used to compute the ratio of the measured concentration to the MATE concentration, and this ratio is termed the "degree of hazard." The "degree of hazard" for each pollutant is then summed to provide the "degree of hazard" for the effluent stream under consideration. This value, when multiplied by the effluent flowrate, in specific units (e.g., liters per second), establishes the "toxic unit discharge rate" (TUDR) for the stream.

The SAM/1A methodology, as described above, was utilized to analyze the data obtained for each of the three primary effluent streams from the Purox process (slag, scrubber effluent, and boiler stack gas). Based on the SAM/1A methodology, the scrubber effluent had the highest "degree of hazard," being considerably greater than the "degree of hazard" for the input river water. However, the slag stream had the highest "toxic unit discharge rate." The boiler flue gas effluent had the lowest "degree of hazard" and the lowest "toxic unit discharge rate." Both of these values were comparable to the baseline values computed for boiler flue gas when burning natural gas.

#### Municipal Incinerator Fired With MSW

The Braintree municipal incinerator (Braintree, Massachusetts) is a mass-burn facility consisting of twin water-wall combustion units, each with a design capacity of 120 tons of MSW for 24-hr period. A portion of the steam produced (20-35%) is supplied to neighboring manufacturers and the remainder is condensed. Each furnace is equipped with an ESP and both ESP's exhaust to a common stack.

The Riley Stoker boilers are of the single pass design, each having a rated capacity of 30,000 lb of steam/hr at 400°F and 250 psig. The ESP units are single field, 12 passage precipitators with a specific collection area of 125 ft<sup>2</sup>/1000 acfm; each has a design collection efficiency of 93%.

Environmental assessment of the incinerator facility was conducted using EPA approved sampling and analysis procedures similar to these identified in Figure 2. Results and conclusions of the testing effort are summarized below.

Of the criteria pollutants, SO<sub>2</sub>, NO<sub>x</sub>, and hydrocarbon emissions were low. However, CO levels were high and could not be explained considering the large quantities of excess air that were used. The average particulate concentration was 0.24 gr/dscf, corrected to 12% CO<sub>2</sub>. This level exceeded the federal and state regulations. However, subsequent tests for compliance had an outlet particulate loading of 0.074 gr/dscf, which shows compliance.

Elemental analysis of the glass-and metal-free bottom ash revealed an overall increase in the elemental concentrations when compared to the refuse feed. The collected fly ash contained levels of chlorides, sulfates and some trace metals which may be of concern. PCB's were not detected in the collected fly ash; 4 PAH compounds were identified.

Levels of BOD, COD, oil and grease, TSS and TDS in the bottom ash quench water do not appear to be of concern. The phenolic content was found to be < 0.1 mg/liter in all samples.

Levels of gaseous chlorides and other halides were low. Presence of PCB's was confirmed only in the SASS train XAD-2 resin at a concentration of 3.6 µg/m<sup>3</sup>.

Results of the SAM/1A environmental assessment procedure showed the incinerator stack emissions to have the highest apparent degree of health hazard. Further analysis is needed to determine the exact composition of the organic components of the stack emissions to better ascertain the hazard potential. SAM/1A also showed that the bottom ash effluent had the largest toxic unit discharge rate due primarily to the abundance of phosphorus and metals in this stream.

#### Power Plant Boiler Fired With Woodwaste and Fuel Oil

The No. 1 unit at the Burlington Electric Plant (Burlington, Vermont) was originally a coal-fired boiler which has since been modified to fire wood chips with supplementary No. 2 fuel oil. Because of the high moisture content of the chips, the boiler cannot provide the desired steam output on wood alone. Therefore, No. 2 fuel oil is used. Steam production is rated at 100,000 lb/hr, which powers a 10 MW turbine generator. Residual ash from the boiler is discharged at the end of the grate into a hopper and is then pneumatically transported to an emission control system consisting of two, high efficiency mechanical collectors in series. For a flue gas flow rate of 60,000 acfm at 330°F, the collectors were designed for an overall pressure drop of 6.5 in. H<sub>2</sub>O and a collection efficiency of 97.75%.

Sampling and analysis was based on the matrix shown in Figure 3. Major results and conclusions of the tests are as follows:

On a heat input basis, wood accounted for 80% of the boiler fuel, and oil the remainder. The heat of combustion of wood was 5870 Btu/lb (as received) and for oil, the heat of combustion was 19,500 Btu/lb.

Bottom ash analysis indicated that most elements were more concentrated in the ash relative to the input fuels. No PCB's were detected in bottom ash but one PAH compound, phenanthrene, was present at a concentration of 0.89 µg/g. Primary and secondary collector ash contained no PCB's but several PAH compounds were identified in the secondary ash, with one sample containing 10 µg/g of phenanthrene.

Particle sizing at the collector inlet and outlet, could not be established due to constant plugging of the optical counters dilution system. Stack concentration of particulates averaged 0.08 gr/dscf and the collector had a particulate efficiency of 94.2%. NO<sub>x</sub> and SO<sub>2</sub> concentrations averaged 66 and 138 ppm respectively. CO averaged 213 ppm and hydrocarbons 9 ppm. Analysis of Method 5 particulate indicated concentrations approaching 100 µg/dscm for Pb, Ba, Sr, Fe and Ti in the stack gases. PCB and PAH tests of the stack gases were negative.

EPA's SAM-1A analysis indicated that the secondary collector ash contained the highest degree of hazard although all three ash streams were similar in the magnitude of their hazard values. Stack emissions showed a low degree of hazard. The primary collector ash had the highest toxic unit discharge rate.

#### Steam Boiler Fired With Coal and Densified Refuse-Derived Fuel (d-RDF)

Emission tests were conducted on the GSA/Pentagon facility's No. 4 boiler in Arlington, Virginia during a test burn program coordinated by the General Services Administration (GSA) and the National Center for Resource Recovery (NCRR). The No. 4 unit is an underfeed-retort stoker boiler with a rated steam capacity of 70,000 lb/hr at 125 psig and 350°F. During the tests, the boiler was equipped with a multiclone collector for removal of particulates from the exhaust gases.

The test burn program included three fuel firing modes: 100% coal (baseline conditions), 20% d-RDF + 80% coal, and 40% d-RDF + 60% coal. Samples of coal, d-RDF, and the coal/d-RDF mixtures were collected hourly by NCRR and analyzed for moisture, ash, heating value, and chemical composition. Several daily samples of bottom ash were also collected by NCRR and analyzed for loss-on-ignition and chemical composition. MRI conducted sampling and analysis of the stack effluent. Parameters measured included particulate concentration, gaseous criteria pollutants (SO<sub>2</sub>, NO<sub>x</sub>, CO and total hydrocarbons), and chlorides. The particulate samples were further analyzed for lead content.

Results of the emission tests showed that:

- \* Particulate emissions were reduced from 22 to 38% when d-RDF was blended with the original coal fuel. Filterable particulate emissions were lowest when using the 20% d-RDF blend and rose again when the proportion of d-RDF was raised to 60%. This finding may not be conclusive, however, since the boiler load was held steady during the 20% RDF firing but not during the 60% mode.

- \* The amount of particulate lead emitted when burning d-RDF with coal is substantially higher than that from combustion of coal alone (an average of 1000  $\mu\text{g}/\text{m}^3$  with 20% d-RDF, and 2,260  $\mu\text{g}/\text{m}^3$  with 60% d-RDF, versus 330  $\mu\text{g}/\text{m}^3$  with coal only).
- \* Chloride emissions showed no definite trend which could be used to correlate chloride emissions with RDF modes, though slightly higher concentrations of HCl were observed in two of the samples collected during combustion of the 60% d-RDF blend.
- \* Concentrations of sulfur dioxide, nitrogen oxides and carbon monoxide all appeared to decrease slightly when the RDF was used with coal. Because of the very low sulfur content of d-RDF,  $\text{SO}_2$  emissions were reduced progressively as the proportion of d-RDF with coal was increased. However, the reduction in  $\text{NO}_x$  and CO levels, may or may not have been the direct result of burning d-RDF since they are highly dependent on boiler combustion conditions.

#### Power Boiler Fired With RDF

The Hempstead Resource Recovery Plant (Long Island, New York) receives municipal solid waste, produces a refuse-derived fuel and converts the fuel to electrical power. The facility consists of two distinct segments: a refuse processing operation, utilizing the Black Clawson Hydrosposal system; and a power house, which contains two steam boilers and two, 20 MW electrical turbine generators, plus the associated control equipment.

Tests were conducted by MRI on the No. 2 unit of the power house, which is an air-swept spreader stoker, waterwall boiler with a nominal capacity of 200,000 lbs/hr of steam at 625 psig and 750°F. The boiler was fired with 100% refuse-derived fuel (RDF), although auxiliary oil burners are used for start-up and during fuel feed interruptions. Air pollution controls for the boiler consist of a bank of 12 mechanical cyclones followed by an electrostatic precipitator.

The purpose of the assessment was primarily to investigate organic constituents of the stack gases and to quantify odorous components. However, other tests were also included. Emission streams evaluated included the boiler bottom ash, cyclone ash, ESP ash and the stack effluent gases. Samples of the RDF were also collected and analyzed for moisture plus chemical and elemental composition. The three ash streams were analyzed for elemental composition. Stack emissions were continuously monitored for  $\text{SO}_2$ ,  $\text{NO}_x$ , CO,  $\text{O}_2$  and total hydrocarbon concentrations, and were also tested to determine levels of vaporous mercury and aldehydes. In addition, a sample was collected using the EPA Source Assessment Sampling System (SASS) for analysis under EPA's Level 1 protocol.

Results of the test program did not indicate any pollutant emissions of major concern. Stack gases contained relatively low concentrations of  $\text{SO}_2$ ,  $\text{NO}_x$ , and hydrocarbons. Carbon monoxide levels were slightly greater than anticipated.

Emissions of carbonyl compounds (aldehydes) were detected at a maximum level of 7 ppm (6.5 lb/hr).

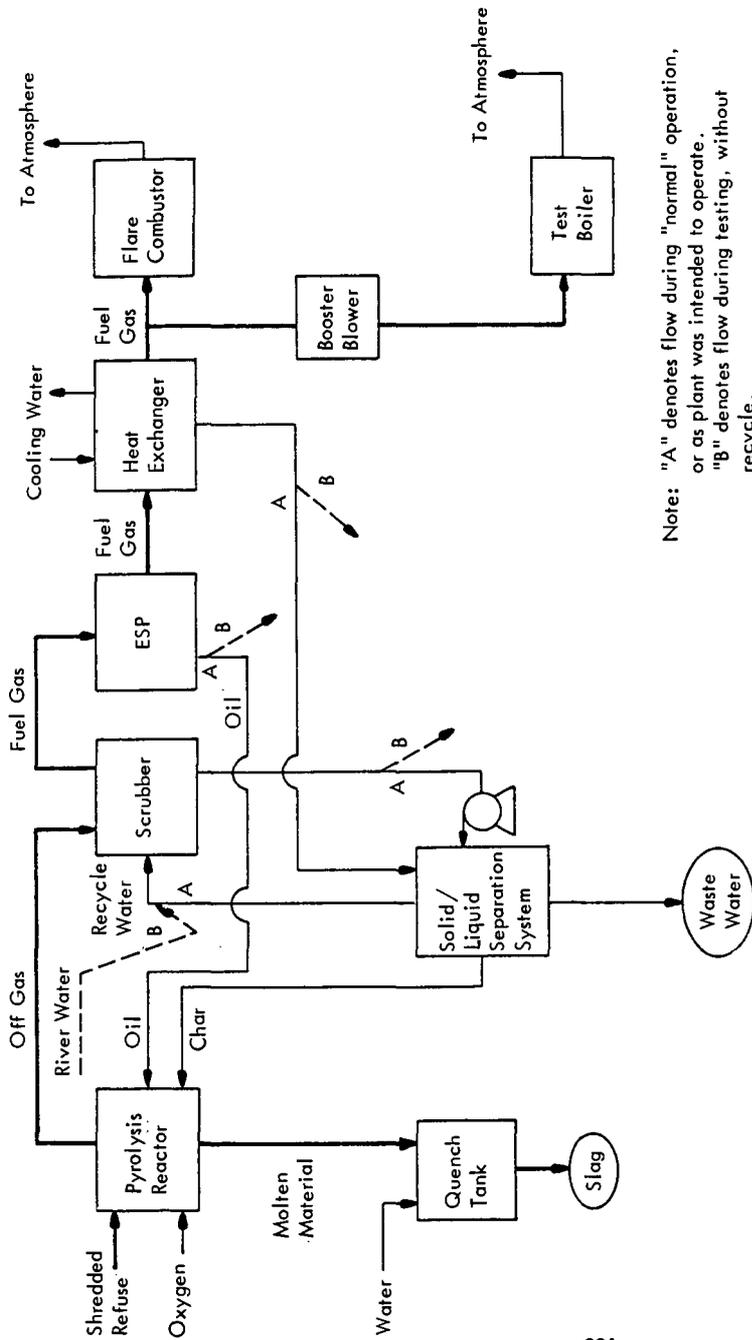
Mercury vapor concentrations in the stack effluent were very low ( $< 0.12 \text{ mg/m}^3$ ), and it appears that mercury levels are greatest in the fly ash collected by the electrostatic precipitator. The concentration of mercury in samples of the RDF was constant at about  $3 \text{ } \mu\text{g/g}$ .

Several trace metals were detected in the stack gases at relatively high concentrations. Of these, lead, antimony, chromium, and arsenic were most notable. Their respective concentrations in the SASS sample were 580, 460, 640, and  $560 \text{ } \mu\text{g/m}^3$ . Elemental analysis of the bottom ash, cyclone ash, and ESP ash streams also indicated that many of the more volatile elements were associated with the smaller sized particles.

Organic analysis of the SASS sample, using EPA Level 1 and additional GC/MS analytical techniques, showed a variety of organic constituents. No single compound group appeared to predominate, although several polynuclear aromatic hydrocarbons were detected. All organic results were qualitative.

Compounds consistently observed in all SASS component extracts included naphthalene, fluoranthene, acenaphthylene, pyrene, phenanthrene/anthracene, bis(2ethylhexyl) phthalate, and diphenylamine. The majority of additional compounds were found in the XAD-2 resin extract and included two chlorobenzenes, hexachlorobenzene, fluorene, and di-butylphthalate.

FLOW DIAGRAM FOR PUROX<sup>®</sup> PROCESS



Note: "A" denotes flow during "normal" operation, or as plant was intended to operate.  
 "B" denotes flow during testing, without recycle.

Figure 1. Flow diagram for Purox<sup>®</sup> process.

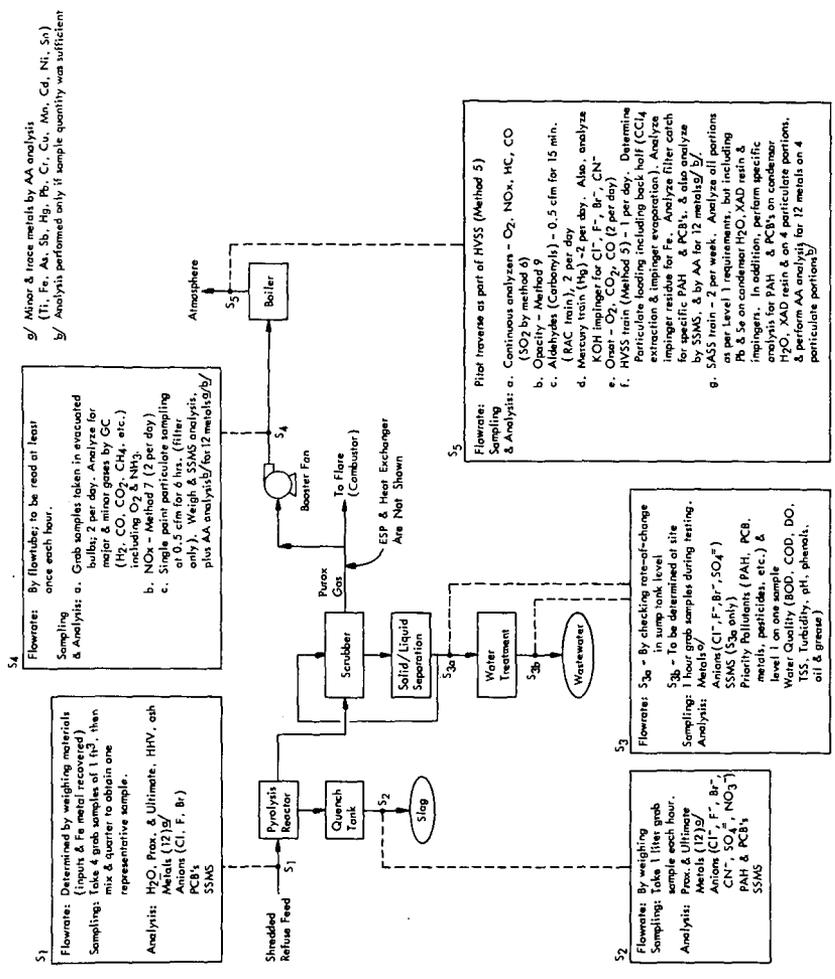


Figure 2. Sampling and analysis scheme for Purox® process.

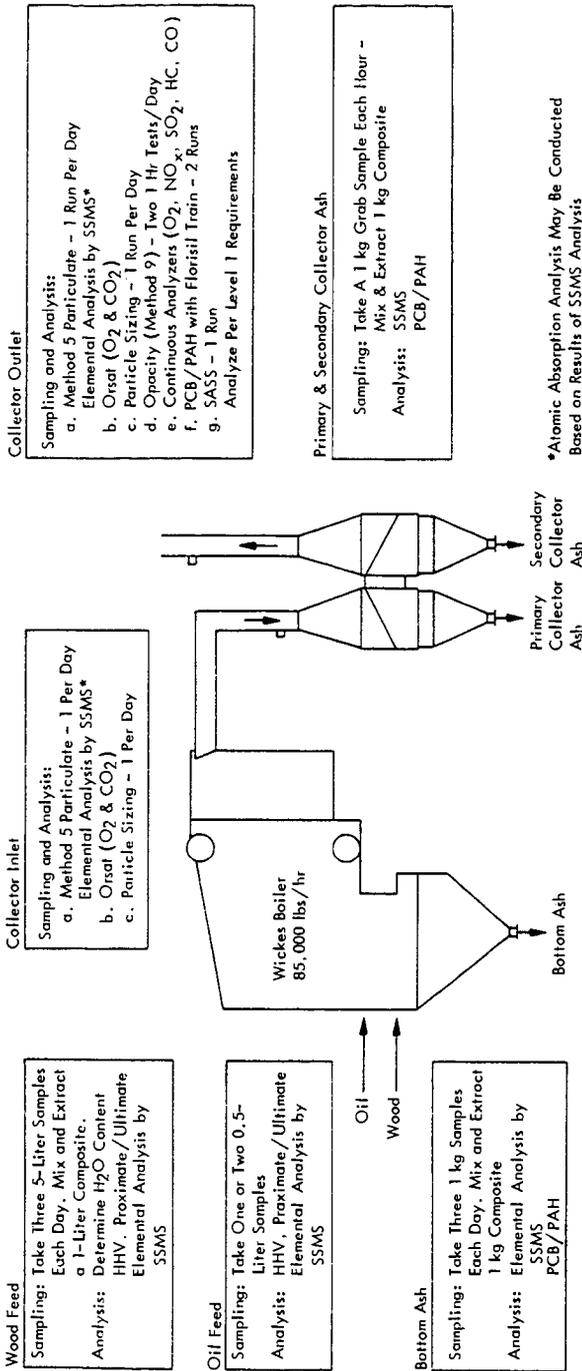


Figure 3. Test matrix for Burlington Electric's wood and oil-fired power plant.

## ENVIRONMENTAL AND HEALTH ASPECTS OF BIOMASS ENERGY SYSTEMS\*

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In a recent study (1) undertaken to ensure the early incorporation of environmental considerations in decisions concerning biomass-to-energy systems, a number of issues emerged indicating the need for early attention to environmental, socio-economic and health concerns. Both production of biomass as well as conversion can lead to environmental impact, and although most impacts will be site-specific, some generic effects can be identified. The most important potential impacts arise first, from the need for large-scale commitment of resources for production, and second, from uncontrolled widespread small-scale utilization.

Because biomass-related impacts cover a very broad spectrum of materials, processes, end products, and effects, the discussion presented here, except for an overview of generic effects and comment on production impacts, will be directed primarily to those resulting from residential wood combustion.

Table I summarizes the potential negative impacts associated with biomass energy systems. Small scale refers to on-farm, residential or small commercial facilities and large-scale implies industrial size. It is assumed that implementation of completely effective environmental control for either biomass production and harvesting or small-scale conversion will be difficult to attain whereas industrial installations will be subject to existing or future regulation on air, water, and solid waste emissions. This accounts in some cases for a greater severity of impacts projected for small-scale application compared to industrial-scale deployment of the same technology. A note of caution is essential in interpreting the data in Table I. Because biomass systems are not yet well defined and because many of the issues are complex and far-reaching, assessment of the severity of environmental impact at this time must be considered only as an indicator of potential for negative effect and definitely not as a prediction of unavoidable impact. This is especially applicable to the as-yet-unripe technologies involving energy cultivation, such as silviculture, agriculture, and mariculture (marine farming).

Potential impacts of biomass production, which can be summarized in terms of:

- Land use (and abuse)
- Water use (and abuse)
- Erosion and sedimentation
- Agricultural and forest runoff
- and ● Disturbance of ecosystems,

can be attributed directly to the necessary properties of an energy farm:

- Intensive species management
- Fast growing and regenerative species (monocultural)
- Short rotation time
- Weed and pest control
- Large land tracts
- and ● Use of presently underutilized land.

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Table I: SUMMARY OF POTENTIAL IMPACTS OF BIOMASS ENERGY SYSTEMS

Conversion impact categories	Wood combustion small-scale	Wood combustion large-scale	Agriculture residue combustion	Gasification small-scale	Gasification large-scale	Liquefaction <sup>c</sup>	Pyrolysis <sup>c</sup>	Anaerobic digestion small-scale	Anaerobic digestion large-scale <sup>c</sup>	Fermentation herbaceous small-scale	Fermentation herbaceous large-scale <sup>c</sup>	Fermentation lignocellulosic large-scale <sup>c</sup>
	VL	L	VL	L	M	M	L	VL	M	VL	M	M
Solid waste disposal	VL		VL	L	M	M	L	VL	M	VL	M	M
Air quality	VH	M	H <sup>e</sup>	L	L	L	L	VL	L	VL	L	M
Water quality	VL	VL	VL	M	M	M	L	VL	L	VL	L	M
Institutional and social	M	M	VL	L	L	L	L	M	L	M	VH	L

<sup>a</sup> Impact severity index  
 VH - Very high L - Low  
 H - High VL - Very low  
 M - Moderate U - Uncertain

<sup>b</sup> Estimates of potential for marine systems development are widely divergent. Impacts in every category could vary from low to very high, depending on the eventual extent of deployment.

<sup>c</sup> Assumes larger scale facilities are subject to environmental control technology

<sup>d</sup> Refers to use of ocean surface rather than land

<sup>e</sup> Assumes that NO<sub>x</sub> scrubbers are not yet commercially available in the U.S.  
 Source: Reference (1)

Production and harvest impact categories	Wood from marginal forests	Wood from small-scale	Wood from large-scale	Plantations	Agricultural residues	Agricultural	Manure	Freshwater	Marine biomass <sup>d</sup>
	VL	M	M	VH	VL	VH	VL	H	H <sup>d</sup>
Land use	M	M	M	H	VH	H	VL	-	-
Soils	M	M	M	H	H	H	VL	VL	U
Air quality	M	M	M	M	H	H	VL	M	H
Water quality	M	M	M	M	H	H	VL	M	H
Institutional and social	H	VH	VH	VH	L	VH	L	M	VH
Wildlife and ecosystems	M	H	H	H	L	H	VL	M	H

Because biomass energy production systems are projected as operating on a very large scale, the projected environmental impacts tend to be an exaggeration of well-defined effects which are now controlled or mitigated in existing production and harvest schemes. For example, land use impacts of energy production arise from the need for a large commitment of land (it requires 38 million acres to produce one quad of energy). Land is unavailable except either in competition with food, fiber, or live-stock production, or by using underutilized land. Land is only underutilized when it is of low quality and unsuitable for cultivation because of problems such as wetness, dryness, or high erosion potential. Potential environmental impacts of intensive monoculture cultivation of low quality, marginal, or uncultivated lands have been well documented (1). In addition to possible water and soil nutrient depletion, and air and water pollution, conversion of such areas to biomass plantations could result in destruction of the last remnants of once-extensive wildlife habitats.

In order to effect the release of the energy in biomass materials, they must be converted either directly, by combustion, or indirectly, by thermochemical or biochemical conversion. This involves a wide variety of technologies, many different processes, and various-size operations. Of the resulting array of biomass-to-energy options, one of the most familiar and readily available is residential wood combustion. Unfortunately, few definitive environmental impact data exist for this use. Because wood burning is relatively free of some of the most serious environmental problems associated with coal combustion such as solid waste disposal and sulfur dioxide emission, and because environmental control is difficult to implement at the home-owner level, little attention has been focused on environmental management of this biomass application. However, home wood burning, which is becoming increasingly more popular and widespread, produces air emissions which, if uncontrolled, can pose a threat not only to the environment but also to human health. The important thermal decomposition products of wood are smoke (a mixture of solid particles and condensed liquid particulates), volatile hydrocarbons, and carbon monoxide. Significantly, even when wood burning produces low concentrations of smoke, large quantities of carbon monoxide may be produced (2). Additionally, the conditions that promote abundant emission of both smoke and carbon monoxide are exactly those prevalent in the conventional residential wood stove or fireplace (1).

Unfortunately, attempts to estimate the air quality impacts of small-scale residential combustion are hindered by the lack of standard techniques such as exist for assessing the emissions associated with large centralized sources. The latter commonly employ sophisticated emission abatement devices, uniform fuels, and carefully designed, operated, and maintained combustion devices. None of these assumptions apply to the residential wood stove. Nonetheless, the rapid pace with which wood stoves are replacing more conventional heating sources and the consequent potential for environmental impact, demands an evaluation.

Available predictive techniques were utilized to predict ground-level concentrations of pollutants from wood combustion devices. These techniques (3) assume Gaussian distributions of pollutants, and are most applicable in flat to gently rolling terrain. Concentrations can be calculated for a variety of pollutant emission rates, wind speeds, and wind directions. Using this typical Gaussian dispersion approach, the values in Tables II and III were obtained. The time and distance dependence were determined for groundlevel concentrations of emissions from one wood combustion device burning 3 kg of wood per hour under the following typical meteorological conditions:

wind speed	2m/sec
effective emission height	10 m
atmospheric stability	stable, class E.

Table II - Maximum One-hour Ground Level Concentrations Of Emissions  
From One Wood-burning Device ( $\mu\text{g}/\text{m}^3$ )

Downwind Distance (m)	Stove (oak)		CO <sup>e</sup>	Stove (pine) <sup>b</sup> Particulates	Fireplace Particulates <sup>c</sup>
	Particulates <sup>d</sup>	Hydrocarbons <sup>d</sup>			
10	-	-	-	-	-
25	1.5	1 - 32	114	8.8	13.2
50	4.6	3 - 98	354	27.2	40.7
75	4.2	3 - 87	320	24.6	36.8
100	3.3	2 - 70	254	19.5	29.2
150	2.1	1 - 45	161	12.4	18.6
200	1.5	1 - 31	111	8.5	12.8
250	1.1	0.7 - 23	82	6.3	9.4
300	0.8	0.5 - 17	62	4.8	7.2

Table III - Peak Concentrations ( $\mu\text{g}/\text{m}^3$ )

Time <sup>f</sup> (hrs)	Particulates <sup>d</sup>	Hydrocarbons <sup>d</sup>	CO <sup>e</sup>	Stove (pine) <sup>b</sup> Particulates	Fireplace Particulates <sup>c</sup>
1	4.7	3 - 99	356	27.4	41.1
3	3.2	2 - 67	242	18.6	28.0
24	1.5	1 - 32	116	8.9	13.3

Table IV - Short-term Worst-case Estimates From A Study Area<sup>g</sup> ( $\mu\text{g}/\text{m}^3$ )

10	-	-	-	-	-
25	53	31 - 1071	4017	309	463
50	52	30 - 1070	3991	307	459
100	51	30 - 1050	3939	303	453
150	51	30 - 1040	3900	300	445
200	50	29 - 1029	3809	293	439
250	49	29 - 1009	3718	286	428
300	48	28 - 988	3666	282	422

- a) ref. (5). Emissions: 1.7 g/kg wood
- b) ref. (5). Emissions: 10.0 g/kg wood
- c) ref. (6). Emissions: 15.0 g/kg wood
- d) ref. (7). Emissions: range 1 g/kg to 35 g/kg wood
- e) ref. (8). Emissions: 130 g/kg wood
- f) Time scaling factors from ref. (3)
- g) Study area:

Size 1/2km x 1/2km  
Housing density 4 units/acre = 247 dwellings  
Wood use 3 kg/hr/house  
Emissions rates same as in Table II

In the Clean Air Act Amendments of 1977 (PL 95-95), the EPA defined that amount of adverse effect on air quality allowed in the prevention of significant deterioration (PSD) regulations. Presently, only large facilities such as industrial sources and power plants are reviewed for PSD compliance. However, the allowable deterioration represents reasonable levels of air quality degradation deemed acceptable. PSD increments for particulates (none exist for carbon monoxide or hydrocarbons) are given for Class I & II areas (4). For presently pristine (Class I) areas increments are  $10 \mu\text{g}/\text{m}^3$  maximum for a 24 hour period with an overall mean maximum of  $5 \mu\text{g}/\text{m}^3$ ; for typical (Class II) areas, particulate concentrations are limited to a 24 hour maximum increment of  $37 \mu\text{g}/\text{m}^3$  and a mean of  $19 \mu\text{g}/\text{m}^3$ . Clearly, values in Table II show that of several woodburning stoves located within 100 meters of each other would exceed allowable increased in pristine areas and would consume much of the allowable increases in typical areas.

Were a community of houses to convert to wood heat, under adverse meteorological conditions (inversion with a 15 meter stable layer), the air quality impact would be far more severe, as indicated in Table IV. The study area in Table IV represents a typical small community, and the dispersion conditions are representative of small Appalachian region. The assumed adverse conditions represent a realistic worst case situation that could be expected to occur nightly in some locations in the southeastern U.S. and in New England occasionally lasting for up to 24 hours. If all 247 houses in the community heat with wood for four months the total particulate emissions from a 1000 MWe coal-fired power plant serving the needs of approximately 500,000 people using a state-of-the-art particulate removal system (99.5% efficient) would emit approximately 13 tons of particulate during the same time period (10). In addition, although little is known about the potential health effects of long-term exposure to wood combustion particulates, many of the identified hydrocarbons are known carcinogens (1). Additionally, preliminary studies indicate the potential for adsorption of polycyclic aromatic hydrocarbons onto the surface of respirable-size wood ash particles (11).

The level of carbon monoxide downwind of the small community is within the current ambient 8 hour maximum standard of  $10,000 \mu\text{g}/\text{m}^3$  (4). However, the  $4,000 \mu\text{g}/\text{m}^3$  should perhaps not be considered inconsequential. Animal studies indicate that exposure to low levels of carbon monoxide for periods as short as four hours converts the myocardium from aerobic to anaerobic metabolism leading to ultra-structural heart damage (12).

Biomass-to-energy systems, by utilizing a renewable resource, can make an important contribution to our overall energy needs. However, insurance of environmental acceptability will require close attention to the possible impacts of rapid, impulsive, and uncontrolled implementation. Our habit has been to accommodate dispersed, small-scale environmental alterations and to consider local effects as insignificant relative to the large centralized source. Implicit in this accommodation is the doctrine that environmental dilution is equivalent to environmental dissipation. But because a renewable technology is a long-term technology, an in-depth evaluation will require knowledge about low-level, long-term effects. Unfortunately, this is an area that we know little about. Thus, until this information is available, it may be difficult to assess long-term effects of the large number of relatively small, dispersed disturbances that can arise from this broad-based technology.

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