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Fermentation Products of Cellulose[1]

C. S. Boruff with A. M. Buswell

ILLINOIS STATE WATER SURVEY DIVISION, URBANA, ILL.

IN WORKING on the products resulting from the anaerobic decomposition of biologic waste material, the writers, with others *(1)*, have observed that the reactions, which are brought about by bacteria, cause the formation of considerable amounts of gas. This gas is principally methane and carbon dioxide, with small amounts (3-5 per cent) of hydrogen and nitrogen, the latter probably from solution in the liquor. The ratio between CO_2 and CH_4 varies from about 1:10 to 1:1 when air is excluded and sugars are absent. In attempting to explain this variation in gas composition we have carried out experiments using various selected materials of known composition.

Our preliminary work on the digestion of cellulose, summarized in Table I, showed that the material decomposed or digested was converted practically quantitatively into gas and that the ratio between CO2 and CH_4 was about 1:1.5, except in the blank where it was 1:8.3.

The simplest equation for the decomposition of cellulose would be

$$C_6H_{10}O_5 + H_2O \longrightarrow 3CO_2 + 3CH_4$$

According to this equation, the CO_2:CH_4 ratio should be 1:1.

When the organic matter in inoculating material is reduced to a relatively small value, this ratio becomes practically the theoretical for the equation given (Table II).

As a gas containing 50 per cent methane has a calculated heat value of 500 British thermal units per cubic foot (coal gas runs 525-550), it seemed worth while to see whether or not crude plant material could be converted into gas in sufficient quantities to be of practical importance. Naturally, being in the heart of the Corn Belt, the material selected was cornstalks. The results were favorable (Table III).

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Table I—Cellulose Digestion Balances

DIGESTION COMPOSITION	VOLATILE MATTICR			CO_2	CH.	H_2	GAS LESS N_2	$CO_2:CH_4:H_2$	$CO_2:CH_4$
	At start	At close	Casided						
	Grams	*Crams*	*Crams*	*Cc.*	*Cc.*	*Cc.*	*Crams*		
Filter paper (inoculum + 9.56 grams, dry basis)	15.447	6.515	8.932	2864	3953	223	8.48	12.9:17.7:1	1:1.4
Cotton (inoculum + 10.429 grams, dry basis)	16.316	7.00	9.310	2961	4440	320	9.019	9.3:13.9:1	1:1.5
Toilet paper (inoculum + 9.3 grams, dry basis)	14.807	9.051	5.756	1786	2835	233	5.562	7.6:12.2:1	1:1.6
Wood pulp (inoculum + 10.12 grams, dry basis)	15.855	12.983	2.872	733	2083	99	2.946	7.4:21.0:1	1:2.8
Kotex (inoculum f 13.777 grams, dry basis)	19.5670	6.5611	13.0065	4750	5710	26	13.4534	18.2:21.8:1	1:1.2
Inoculum (200 cc. digested sludge + 2400 cc. settled sewage)	7.038	5.804	1.234	114	944	38	0.90	3.0:24.8:1	1:8.3

Table III—Digestion of Cornstalks

DIGESTION MIXTURE	PRETREATMENT OP CORNSTALKS	INITIAL TOTAL SOLIDS + VOLATILE ACIDS	Loss IN TOTAL SOLIDS + VOLATILE ACIDS	GAS RECOVERED (CO_2, CH_4, H_2)	TOTAL GAS RECOVERED S.T.P.	CORNSTALKS DIGESTED[a]
		Grams	*Grams*	*Grams*	*Cc.*	*Grams*
Inoculum + 8 grams cornstalks	Shredded	14.006	4.278	3.974	3282	2.691
Inoculum + 8 grams cornstalks	Shredded, 4-day water soak	14.006	4.597	4.710	3870	2.833
Inoculum + 8 grams cornstalks	Shredded, 2-hour water boil	14.006	4.904	5.068	4057	2.848
Inoculum + 8 grams cornstalks	Shredded, 4-day lime soak, neutralized	...	...	6.732	5600	4.688
Inoculum composition[b]		6.000[c]	1.21	1.21	1026	...

[a] These weights are all too low owing to difficulty in completely separating the fibers from the sludge.

[b] Inoculum composition: 50 cc. active sewage sludge, 650 cc. settled sewage, 300 cc. distilled water, and 0.75 gram each of $NaHNH_4PO_4$ and K_2HPO_4. 49.6 per cent volatile matter.

e Calculated on the basis that initial total solids are equivalent to the final total solids plus weight of gas collected.

Four digestion mixtures were prepared with cornstalks which had been shredded, soaked, boiled, and soaked in lime, respectively. The cornstalks were decomposed to the extent of 35 to 50 per cent and an equivalent weight of gas was produced. The rate of gas evolution from the eight grams of cornstalks used is shown in Figure 1. The best results were obtained with material which had been soaked in lime water.

Table II—Cellulose Digestion Balance Sheet

DIGESTION COMPOSITION	VOLATILE MATTER			GAS COLLECTED	CO_2 AND CH_4	CO_2:CH_4:H_2	CO_2:CH_4
	At start	At close	Cabined				
	Grams	*Crams*	*Crams*	*Cc.*	*Grams*		
Inoculum + filter paper	12.950[a]	2.466	10.484	7734	9.357	12:11:1	1:0.94
Inoculum[b] + toilet paper	12.313[c]	5.544	6.769	5560	6.728	12:12:1	1:1

[a] Of this, 3.390 grams are inoculum and 9.560 grams are paper.
[b] Hg from gas seal sucked into digestion bottle. Digestion not complete.
e Of this, 3.390 grams are inoculum and 8.923 grams are paper.

The gas analyses (Table IV) show that here again the reaction appears to follow the equation. It is interesting to note how nearly quantitatively the agreement with the equation is. A variety of side reactions might have been anticipated.

Table IV—Composition of Gases

COMPONENT	ANALYSIS COR. FOR DISSOLVED CO_2	Av. GAS ANALYSIS AS DRAWN
CO_2	44.2	37.0
H_2	2.4	2.7
CH_4	48.6	54.8[a]
N_2	4.8[b]	5.5[b]

[a] Some samples drawn run as high as 70 per cent CH_4.
[b] The first samples of gas drawn contain from 8 to 15 per cent N_2, but later samples contain only from 1 to 3 per cent.

At this point it seemed advisable to calculate the energy consumed by the bacteria in bringing about this hydrolysis. As data on the free energy of formation of cellulose are not available, heat data taken from the International Critical Tables, Vol. V, p. 163, were used. The calculation follows:

(1) $C_6H_{10}O_5 + 6O_2 = 6CO_2\ (g) + 5H_2O\ (l)$; $\Delta H_{150} = 678,000$ calories

(2) $3CH_4 + 6O_2 = 3CO_2\ (g) + 6H_2O\ (l)$; $\Delta H_{150} = 632,400$ calories

(3) $C_6H_{10}O_5 + H_2O = 3CO_2\ (g) + 3CH_4\ (g)$; $\Delta H_{150} = X$

(1) - (2) = (3); 678,000 - 632,400 = 45,600 calories

45,600/678,000 = 6.7 per cent

6.7 per cent of total heat of oxidation is consumed in the biological hydrolysis of cellulose to form equal parts of CO and CH_4.

The loss of 6.7 per cent of the heat value appears small in comparison with the advantages of a gaseous fuel. On the basis of the data in Table III, we calculate that a ton of cornstalks will yield from 10,000 to 20,000 cubic feet of gas. Taking the lower figure, a ton of cornstalks would furnish gas for 400 people for one day, allowing 25 cubic feet per capita per day. From the data given by Webber *(5),* for yields from regions where 30 per cent of the land is planted to corn a circle with an 8-mile radius would produce enough cornstalks to supply a city of 80,000 inhabitants with gas. The 'process is not difficult to carry out and the equipment, which will consist largely of covered tanks, will not be expensive. A typical digestion tank is shown in Figure 2. Naturally, the bacteria require some nitrogen and this is to be supplied from domestic wastes.

It should be possible for the individual farmer to have a small digestion tank arranged to receive both cornstalks and

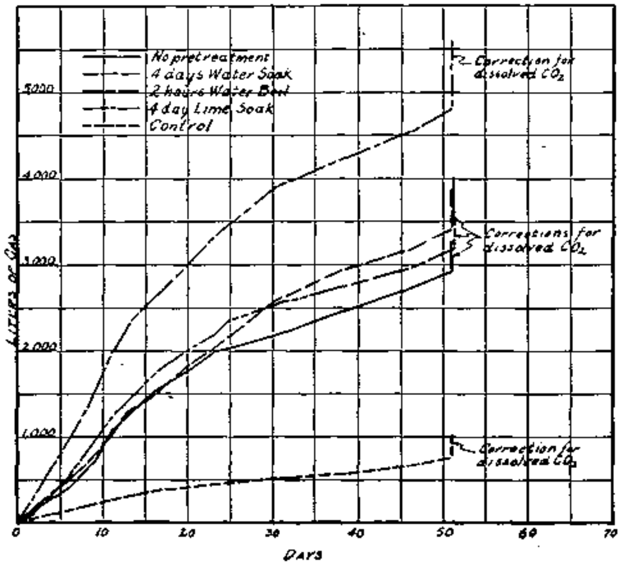

Figure 1—Effect of Pretreatment on Digestion of Cornstalks

household wastes. This would solve the sanitary and the fuel problem alike. As the corn borer hibernates in the cornstalk, their removal from the fields will help to control this pest.

Digestion as a Step toward Paper-Making

In the experiments just discussed the digestion was not complete. The pith and finer fibers are digested first, leaving behind that portion of the cornstalk which is most valuable for paper-making. According to Sutermeister (4), the removal of the pith is a serious handicap in the manufacture of cornstalk paper. He makes the following statement:

Bagasse and Cornstalks. These two materials are so similar *** that they may be considered as practically identical. The pulp from both raw materials *** includes serrated cells *** and many pith cells which are so thin-walled that nearly all become flattened during the reduction process. The pith cells are much larger than those from straw and are therefore much more difficult to remove by washing. They impart to the paper made from this fiber a hardness and rattle which are undesirable in many products, and as their separation from the rest of the fiber has proved very difficult the presence of pith has proved one of the chief stumbling blocks in the way of using either bagasse or cornstalks.

If the pith is removed by digestion, with the production of methane, the process should be more profitable.

The volume per pound is decreased by 25 to 30 per cent as the result of removing the pith. This is considered an advantage in paper-making.

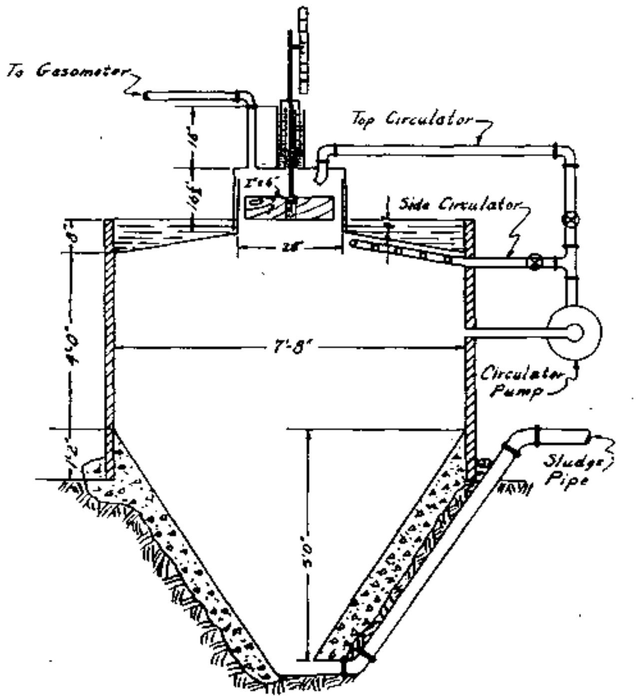

Figure 2—Design of Proposed Cornstalk Digestion Tank

Use of Carbon Dioxide

As the percentage of carbon dioxide in the gases from cellulose digestion is much higher than that in the usual commercial sources of carbon dioxide *(2, S)*, its recovery would seem feasible.

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(5) Webber, IND. ENG. CHEM., 21, 270 (1929).