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PRODUCTION OF FUEL GAS BY ANAEROBIC FERMENTATIONS

By

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Production of Fuel Gas by Anaerobic Fermentations[1]

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This paper traces the early studies of production of methane by anaerobic fermentation, and summarizes recent work in that field. The chemical reactions involved in the decomposition of fats, proteins, and carbohydrates by anaerobic bacteria are discussed. A general formula is proposed for the reaction of the acids of the aliphatic series of acids, and data are presented to show that the fermentations described result in a 90 per cent conversion of the material used into stoichiometric yields of carbon dioxide and methane. The commercial possibilities of the use of this fermentation process for the production of power gas from waste material are pointed out.

UNTIL recently anaerobic fermentations have not been recognized as means for producing valuable products, although they have been used for many years for the purpose of stabilizing waste organic matter and rendering it inoffensive. The septic tank is the most commonly known example of this use. Unfortunately the early investigators of waste treatment had their attention so firmly focused on the recovery of fertilizer in the form of the solid sludge that the importance of the gaseous products of the process escaped their attention.

It has long been known that one of the products of the decomposition of organic matter by bacteria is methane. The presence of methane in bubbles which rise from swamps or from the bottom of lakes or ponds where there is considerable decomposing organic matter was early recognized, and this accounts for the common name "marsh gas." Some of the early workers in the field of bacteriology, studying the decomposition of pure cellulose, obtained methane among their products, but the quantities obtained were not generally re-

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corded, and the time required for the fermentation to take place was so great that no practical importance was attached to the formation of this gas.

It was not until 1897 that a waste-disposal tank serving a leper colony in Matunga, Bombay, was equipped with gas collectors and the gas used to drive gas engines. At about the same time the waste-disposal tanks at Exeter, England, were partially equipped with gas collectors and the gas was used for heating and lighting at the disposal works. In 1911 a company was formed in Australia for the purpose of producing and using fuel gases which resulted from the biological decomposition of municipal wastes. In this country in 1915 Hommon equipped some waste-treatment tanks with gas collectors and used the gas. In 1920 John Watson, of Birmingham, England, reported a study of methane production from sludge digestion and called attention to the fact that a considerable amount of methane can be produced in this way. Following his suggestion, the new disposal plant which has just been put into operation by his successor, Mr. Whitehead, is equipped with gas engines that are being operated on the gases produced from sludge digestion. This use of the gas cuts down very materially the operating cost of the disposal works. In the meantime (1925) Imhoff in Germany had equipped the sludge-reduction tank in Essen (Figure 1) with gas collectors and connected them to the city mains. The gas is found satisfactory for general municipal use and is sold to the city. In the same year Buswell and Strickhouser observed that the sludge-reduction tanks at Decatur, Ill., were producing about 200,000 cubic feet of gas a day. This large yield is due to a considerable amount of wastes from a starch works which are discharged into the city drainage system. The average yield at Decatur is about 125,000 cubic feet of gas per day.

The composition of the gases evolved by sludge-digestion tanks varies somewhat. In open tanks the methane is frequently as low as 20 per cent; in closed or covered tanks it amounts to 60 or 70 per cent. The remainder is largely carbon dioxide with a small amount of hydrogen and some nitrogen. The total amount of gas that can be produced from municipal wastes does not constitute a large economic factor. The yield is somewhere in the neighborhood of 1 cubic foot of gas per capita per day, and amounts to about one twenty-fifth of the gas required for general domestic use.

Analyses of Sludge

It was with the hope of increasing the yield of gas from waste materials that we started our investigation about five years ago. Our first interest was to analyze the sludge and find, if possible, what constituents were responsible for the methane formation.

The solids settling from municipal wastes were found to consist approximately of the following materials: 25 per cent of ash; 25 per cent of protein or nitrogenous material; 25 per cent of "fat" or material soluble in petroleum ether, which incidentally is largely lime soap; and 25 per cent of carbohydrate material, which is almost entirely fibrous cellulosic material. This mixture is known to decompose to the extent of about 65 per cent when acted upon by anaerobic bacteria. The optimum temperature is 25° C. or a little above.

Table I—Effect of Two-Stage Digestion on Sewage Solids

MATERIAL	ADDBD	RESIDUE	DLGESTED	PRODUCHD	LIQUEFIED	DIGESTION	LIQUEFACTION
	Lbs.	*Lbs.*	*Us.*	*Lbs.*	*Lbs.*	%	%
Total solids[a]	2305.0	858.8	1446.2	...	....	62.6	..
Grease[b]	747.96	72.9	675.06	...	....	90.3	..
Cellulose[c]	40.3	3.0	37.3	...	....	92.5	..
Protein[d]	308.0	195.7	195.7	...	....	63.5	..
Sulfate (SO_4)[e]	90.0	112.3	75.0	...	....	83.0	..
Crude fiber[f]	.....	15.0	294.0	...	....	..	..
Dehydration[g]	.....	...	169.2	...	....	..	..
Ammonia compds.	24.5	130.9	.....	106.4	....	..	..
Settling-solids	2250.0	567.6	.....		1682.4	..	74.8

GAS PRODUCED (CH_4, CO_2, H_2)[h]

	Cu. ft.	*Lbs.*
1st tank	15,687	1063.4
2nd tank	2,036	138.6
Total	17,723	1202.0

[a] Includes ammonium compounds (acetate and carbonate).
[b] Petroleum ether extract.
[c] Alpha-cellulose.
[d] Protein = 6.25 (total nitrate-ammonium nitrate).
[e] Estimated from data of Elder (5).
[f] Crude fiber = gas — (grease + cellulose + protein digested).
[g] Solids digested — (gas + sulfate) = dehydration.
[h] Includes dissolved and bicarbonate CO_2.

Sludge Fermentation Experiments

The process was said to take place in two stages, the preliminary or acid formation and the secondary or methane production stage. Rather large tanks were deemed necessary for this digestion, and it was reported that attempts to force the rate of the reaction in smaller tanks resulted in acid production and the interruption of methane production. Our first experiments were carried out in a tank similar to that shown in Figure 2, and the results confirmed this observation. The top of the tank became clogged with scum and considerable acid was produced but practically no methane. The manner in which this difficulty was solved has been previously described (4). Briefly, it consisted in pumping the liquor from beneath the scum and allowing it to flow down upon the top of the scum as shown in the figure. Circulation of this sort softens the scum and allows the action of methane-producing organisms to proceed. Apparently these organisms are able to decompose the acid as fast as it is formed, so that the acid stage may thus be avoided. Operating under these conditions we were able to obtain 90 per cent of the total possible gas production in about a week, while previously 60 to 90 days had been allowed for this process.

The effect of anaerobic fermentation on mixed organic matter is shown in the quantitative summary given in Table I.

The data on gas production were collected under favorable conditions and are believed to be accurate to within 1 per cent.

It will be observed that practically 90 per cent of the gas was produced in the first tank, although the sludge during the major part of the experiment remained in that tank for only 7 or 8 days. It is also interesting to note that 90 per cent of the grease was digested and that the weight of grease digested corresponded to more than 56 per cent of the gas. The gas produced was 0.39 cubic foot per capita per day from

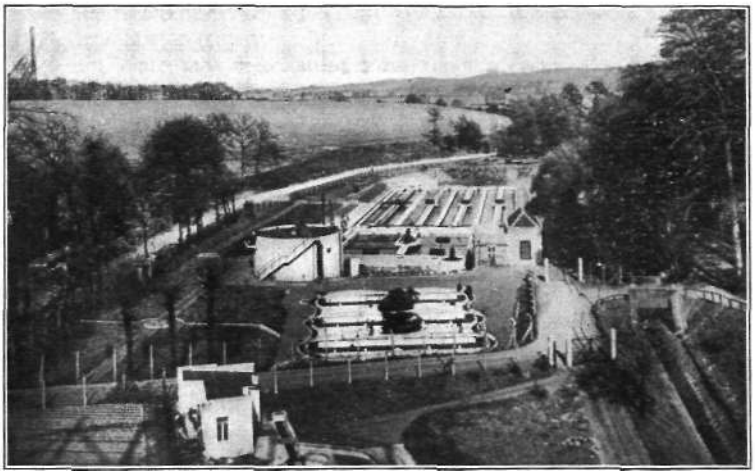
Courtesy of Dorr Company

Figure 1—Essen-Rellinghausen Sewage Treatment Plant near Essen, Germany

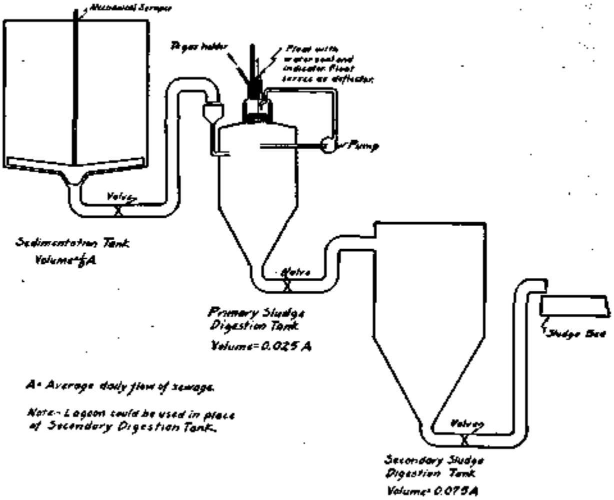

Figure 2—Two-Stage Sludge Digestion

both tanks, or 0.34 cubic foot per capita per day in the primary stage. The gas produced in the primary tank was 12.3 cubic feet per pound of solids digested.

An average of 150 analyses of the gas indicated that it consisted of 64 per cent methane, 28 per cent carbon dioxide, 3.4 per cent hydrogen, and 4.3 per cent nitrogen, with a calculated heat value of 640 B. t. u. per cubic foot.

From these figures it is evident that a fuel gas can be produced by the anaerobic fermentation of the solids settling out of domestic wastes and that the amount of gas thus available is sufficient to justify its collection for use. But this amount is small in comparison with the total needs of the community—namely, 1 cubic foot per capita per day against a consumption of 20 to 25 cubic feet per capita per day. The production of gaseous fuel in large quantities requires considerable additional supplies of raw material. A survey of the possible sources of such raw materials is best preceded by a brief summary of present knowledge of the biochemical reactions involved in the anaerobic decomposition of typical pure substances.

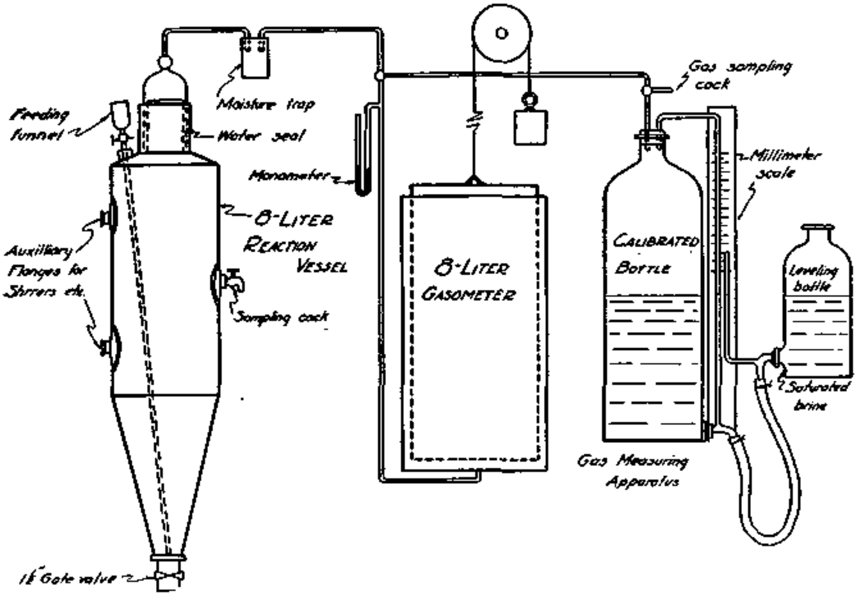

Figure 3—Apparatus for Anaerobic Metabolism Studies

Experiments with Pure Substances

Some recent work with pure substances throws considerable light on the chemical reactions which occur during anaerobic fermentation.

FATTY ACIDS—Neave and Buswell *(9)* have found that the fatty acids are quantitatively converted into methane and carbon dioxide, the recovery being better than 90 per cent of the theoretical, as shown in Table II. These experiments were conducted in 8-liter reaction vessels, equipped for gas collection, to which several hundred grams of fatty acid can be treated. (Figure 3) To avoid lethal osmotic effects and hydroxyl-ion concentrations, either the calcium salt or the sodium salt plus some free acid is fed in daily rations, the displaced supernatant liquor being saved for analysis. Twenty-five to 50 grams of acid per week can be metabolized in such an apparatus, and the experiment continued until the organic matter in the initial inoculum is a negligible percentage of the total metabolized.

Table II—Anaerobic Fermentation of Fatty Acids

	ACETIC ACID		PROPIONIC ACID	
	Crams	%	*Grams*	%
Metabolized	114.18		130.06	
Methane produced	28.08		48.587	
Yield		92.9		98.7
Carbon dioxide produced	79.22		96.320	
Yield		94.7		99.6
Hydrogen produced	0.106		0.243	
Volume ratio, CH_4:CO_2	1:1.03		7:5.05	
Theoretical volume ratio	1:1		7:5	

The experimental data on the acids studied bring out the following points.

For acids higher than acetic the total carbon dioxide produced (not merely that evolved) is more than that contained in the carboxyl group of the acid metabolized; therefore, some of the carbon atoms of the chain are oxidized, and the only source of oxygen for this reaction is shown analytically to be water.

A simple relation has been found between the number of water molecules required by each molecule of fatty acid decomposing and the number of carbon atoms in the acid. If *n* is the number of carbon atoms, then *n/2* — 1 molecules of water are required, the general equation for the digestion of saturated monocarboxylic acids being:

$$C_nH_{2n}O_2 + \frac{(n-2)}{2} H_2O = \frac{(n+2)}{4} CO_2 + \frac{(3n-2)}{4} CH_4$$

Thus acetic acid, with 2 carbon atoms, requires no water; each propionic acid molecule requires ½ molecule of water; each butyric, 1 water molecule, etc. The experimental verification of the general equation may be summarized thus:

ACID	THEORETICAL EQUATION	OBSD. CO_2:CH_4	No. OF RUNS
Formic	$4CH_2O_2 - 2H_2O = 3CO_2 + CH_4$	2.5 : 1[a]	1
Acetic	$C_2H_4O_2 = CO_2 + CH_4$	1.03:1	2
Propionic	$4C_2H_6O_2 + 2H_2O = 5CO_2 + 7CH_4$	5.04:7	8
n-Butyric	$2C_4H_6O_2 + 2H_2O = 3CO_2 + 5CH_4$	2.7 :5[a]	3
n-Valeric	$4C_5H_{10}O_2 + 6H_2O = 7CO_2 + 13CH_4$	6.7 : 13[a]	1
Lactic	$2C_3H_6O_2 = 3CO_2 + 3CH_4$	1.06: 1	1

[a] From preliminary tests which require repetition with the tank apparatus.

Lactic acid, while not a member of this fatty acid series, is included for comparison with propionic acid because the difference in gas ratio between propionic and its hydroxy derivative (lactic) supports the anaerobic oxidation mechanism proposed for these fermentations.

A consequence of this oxidation by water is that, for acids above acetic, the weight of carbon dioxide plus methane produced exceeds the weight of acid metabolized; thus, while 100 grams of metabolized acetic would yield the same weight of gas, a like quantity of propionic would yield 112 grams of gas; of butyric, 120 grams; and of stearic, 151 grams. The mathematical nature of this relationship is such that the weight of gas approaches a theoretical limit of 164 per cent of the acid metabolized for an infinite number of carbon atoms, but the greatest increase, up to 151 per cent, occurs with acids up to 18 carbon atoms (stearic).

From the above general equation it follows also that the percentage of methane in the gaseous products increases with increasing length of the carbon chain undergoing digestion, and attains a theoretical limit of 75 per cent by volume, or a CO_2 :CH_4 ratio of 1:3, for an acid chain of infinite length. In practice, of course, much of the carbon dioxide is not evolved as gas, but remains dissolved and chemically combined in the medium, and with highly buffered digestion mixtures even acetic acid can give evolved gases containing 80 to 90 per cent of methane.

A review of biological oxidation theories has revealed no mechanism applicable to the methanic degradation of fatty acids. The experimental results require an oxidation of some carbon atoms in the fatty acid chain to carbon dioxide by water molecules, while other carbon atoms act as hydrogen acceptors and yield methane.

PROTEINS—In the anaerobic decomposition of proteins the reactions as far as they have been studied are analogous to those of the fatty acids. The amino groups behave essentially like hydroxyl in the oxidation-reduction processes.

CARBOHYDRATES—The decomposition of the carbohydrates is apparently a much simpler matter than that of the fatty acids. It follows the equation for simple hydrolysis suggested for cellulose by Omelianski:

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

Boruff with Buswell (*1, 2)* has recently shown that pure cellulose (filter paper) decomposes quantitatively according to the above equation (Table III).

Table III—Cellulose-Digestion Balance Sheet

Cellulose (filter paper) digested		496.2 grams
Composition of gas as drawn:		
Carbon dioxide	47.5 per cent	
Methane	47.5 per cent	
Hydrogen	2.9 per cent	
Total volume		411.4 liters[a]
Total weight		543.4 grams[a]

[a] Corrected for dissolved CO_2.

The simpler carbohydrates, starch and sugars, may decompose in a similar manner, but frequently, a different type of reaction is encountered. This type is characterized by the conversion of 25 per cent or less of the material to gas, the remaining material being converted in varying amounts to acids, aldehydes, and ketones. The gas from this type of fermentation differs radically in composition from that produced in the fermentation of cellulose. It is composed principally of carbon dioxide and hydrogen, methane being either entirely absent or present in very small amounts. From the standpoint of the composition of the gaseous end products the carbon dioxide—hydrogen fermentations are capable of subdivision into two sub-groups—(*a*) those in which more hydrogen is produced than carbon dioxide (fermentation of lactose by *B. coli* in which the H_2:CO_2 ratio is 2:1), and (*b*) those in which the amount of carbon dioxide exceeds the hydrogen produced (the various acetone and butanol fermentations).

Figure 4—Digested Cornstalk Node

Fuel Gas Production

The above data indicate that fuel gas containing 50 per cent or more of methane can be produced from any type of organic matter, if proper conditions are maintained. The outlook for a cheap raw material in large quantity has not been considered very promising, for the following reasons.

If we consider the three general classes of organic matter—fats, proteins and carbohydrates—all of which give methane on digestion, we see, first, that waste fats are too valuable either for the production of soap or for direct burning, to serve as a fermentation material, and that the amount of these substances produced is not very large. Second, waste nitrogenous material, if produced in a suitable manner, may be used for animal food or, if not suitable for this purpose, it may be used for fertilizer. Here again the amount of waste material is not great. It is only in the third class of substances, the carbohydrates, that we find a large amount of material which at the present time has practically no economic value. It will be readily realized that the amount of waste cellulosic material in the form of stems and leaves of crop plants and cuttings such as sawdust shavings and brush from the production of lumber is very considerable, and that if it can be made to serve as a source of energy enough power can be produced to have a real effect on the world's power bill. However, the previous experiments on the bacterial destruction of cellulosic material were very discouraging. The literature indicated that at best not more than 6 or 8 per cent of the weight of the material could be converted into methane, and also that the entire group of cellulosic materials which about ten years ago went under the unfortunate misnomer of lignoeellulose was entirely immune to bacterial action. These so-called lignocelluloses constitute a large percentage of the substance of most plants. Fowler *(6),* for example, states that "cellulose is not attacked when it is in combination with pectin, lignin, etc., which are always present in raw vegetable tissues."

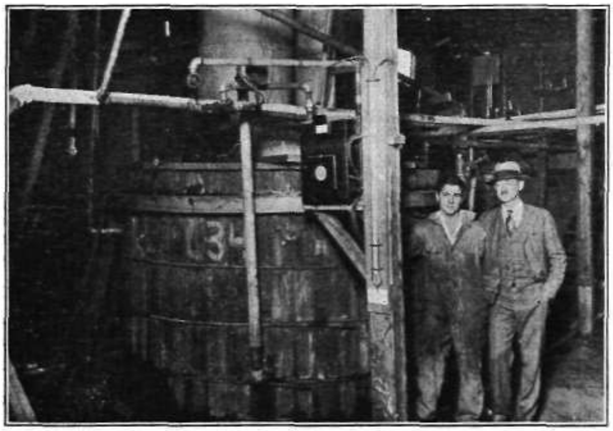

Figure 5—Experimental Plant

More recently Sen, Pal, and Gosh *(10)* reported that the fermentation of water hyacinth resulted in acid formation and a drop in pH to 3.8.

Boruff and Buswell *(2, 3)* were led to doubt the correctness of the general belief that crude plant tissue was resistant to anaerobic fermentation. They carried out numerous experiments with cornstalks and other waste cellulosic material, and reported rapid and complete fermentation of the thin-celled tissues with slower fermentation of the more dense structure such as the cortex. (Figure 4) A typical set of results is shown in Table IV.

Table IV—Distribution of Products Formed in the Digestion of Cornstalks

	WEIGHT *Grams*	STALKS ADDED %
Cornstalks added	1535.0	
Cornstalks recovered	832.2	54.3
Cornstalks digested	702.8	45.7
Recovered as:		
Soluble and suspended solids:		
Ash	80.8	5.3
Organic matter	155.6	10.0
Acids, volatile organic	86.3	5.6
Gas	465.0	30.3
Total	787.7	51.2

These authors operated a pilot plant (Figure 5) for 6 months from which a yield of 60 cubic feet per day was obtained. The yield was about 20 per cent less than had been obtained in the laboratory and some mechanical difficulties were encountered. A change in construction and operation routine has now made it possible to operate the plant smoothly and the yield has equaled or bettered those obtained in the laboratory.

The present estimate is that from 5 to 10 cubic feet of gas can be obtained per pound of cornstalks, and that the rate of production will be from Vs to 1 cubic foot of gas per day per cubic foot of tank volume. 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 *(12)* for yields from regions where 30 per cent of the land is planted to corn, an area with an 8-mile radius will produce enough cornstalks to supply a city of 80,000 inhabitants with gas continuously. In other words, the cornstalks from one acre will produce the gas for one person for a year. Naturally, the bacteria require some nitrogen, and this may be supplied from domestic wastes.

In the experiments discussed above the digestion was not complete. The pith and finer fibers are digested first, leaving behind that portion of the cornstalks which is most valuable for paper-making. According to Sutermeister *(11)* the removal of the pith is a serious handicap in the manufacture of cornstalk paper. 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.

As intimated above, the more fibrous and resistant portions of the stem are too slowly attacked to be allowed to remain in the digestion tank. This residue is the most desirable portion of the stalk for the manufacture of wallboard and paper. In fact, the first step in the production of either wallboard or paper is to remove the pith. It is probable that the anaerobic fermentation may serve instead of the usual cooking process to prepare the fibers for subsequent use in manufacture.

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 *(7, 8)* its recovery would seem feasible.

Conclusion

It is believed that the completion of some development work now in progress will make it possible for farms and ranches to install digestion tanks in which various crop residues may be converted in considerable amounts to a gaseous fuel of high heat value. The undigested residue could be composted and returned to the soil. The operation can be combined with other routine farm work in such a way that the cost of the gas should compare favorably with city gas prices.

It is also probable that small towns located in the corn belt could be supplied with gas in the same way. In this case the undigested residue would be baled and shipped to a nearby wallboard or paper mill.

As our coal, oil, and gas supplies become exhausted the installation of pipe lines fed by fermentation plants located along them at short distances would seem the most probable line of development.

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