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Converting Organic Wastes to Oil

A Replenishable Energy Source

By H. R. Appell, Y. C. Fu, Sam Friedman, P. M. Yavorsky, and Irving Wender

Pittsburgh Energy Research Center, Pittsburgh, Pa.

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CONVERTING ORGANIC WASTES TO OIL

A Replenishable Energy Source

by

H. R. Appell,[1] Y. C. Fu,[1] Sam Friedman,[2]
P. M. Yavorsky,[3] and Irving Wender[3]

ABSTRACT

The Bureau of Mines is experimentally converting cellulose, the chief constituent of organic solid waste, to a low-sulfur oil. All types of cellulosic wastes, including urban refuse, agricultural wastes, sewage sludge, wood, lignin, and bovine manure, have been converted to oil by reaction with carbon monoxide and water at temperatures of 350° to 400° C and pressures near 4,000 psig, and in the presence of various catalysts and solvents. Cellulose conversions of 90 percent and better (corresponding to oil yields of 40 to 50 percent) have been obtained.

A continuous reactor for use at maximum conditions up to 500° C and 5,000 psig has been operated successfully. Using sucrose as a feedstock, operation in this system has permitted a simplified and preliminary chemical study of the conversion process. Oil yields of over 30 percent have been obtained with this unit.

INTRODUCTION

There are essentially two kinds of solid wastes--inorganic and organic. The inorganic components include glass containers, tin and aluminum cans, junk automobiles, slags and wastes from mine ores, etc. Most people regard organic wastes (chiefly compounds of carbon, hydrogen, and oxygen) as simply the remainder after cans and bottles are removed from urban wastes. Although such urban wastes are indeed a huge source of organic material, other replenishable and continually increasing sources of organic solid wastes are now adding each year to the glut spreading over our land. Not only can essentially all of them be recycled, but they can furnish much of our energy in the form of low-sulfur liquid fuels.

The total of various solid organic wastes generated yearly in the United States is about 3 billion tons.[4] Agricultural wastes generated total

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[1]Research chemist.
[2]Supervisory chemical research engineer.
[3]Project coordinator.
[4]Knapp, E. C. Agricultural Poses Wastes Problems. Environ. Sci. and Technol., v. 4, December 1970, pp. 1098-1100.

2.5 billion tons, of which about 2 billion tons are manure.[5] Total urban wastes generated, including domestic, municipal, industrial and commercial, is 400 million tons per year. The population is rising and so is the amount of solid wastes rejected per person. Discards collected by private and municipal agencies have almost tripled in the last 40 years, from 2.2 pounds to 6.0 pounds per day per person. Predictions call for doubling even this latter rate long before the end of the twentieth century.[6]

The Bureau of Mines has developed a process for converting solid organic wastes to a low-sulfur oil potentially suitable for use by powerplants or for conversion to gasoline and diesel fuels. Two billion tons of waste per year, containing about 50 percent organic matter, could yield some 2 billion barrels of oil annually; this is about 50 percent of the 1970 U.S. demand for oil. In a fundamental sense, this process is a means of utilizing solar energy which is, of course, the basis of cellulose production.

An earlier report[7] described a method of converting organic urban refuse, waste paper, and sewage sludge to oil by treating these materials with carbon monoxide and water. A heavy oil was obtained when this reaction was carried out at high temperatures and high pressures; at low temperatures and moderate pressures, the product was a soft, bitumenlike solid.

This paper describes the results of experimental work conducted since the first report. Of special interest is that the process has been found applicable to wood wastes and to the conversion of bovine manure (animal wastes constitute over a billion and a half tons per year). This report also describes a continuous bench-scale unit that was recently constructed and operated. Initial trials were successful in converting sucrose, a typical carbohydrate, to oil.

BACKGROUND

The work on the conversion of solid wastes to oil is an outgrowth of the Bureau's efforts to help solve the problem of energy shortage in the United States in keeping with the demands of good environment. Almost all previous work on conversion of coal to low-sulfur liquid fuels involved use of hydrogen at high pressures and temperatures in the presence of a catalyst. In searching for a novel system that did not use hydrogen, the Bureau discovered that treating low-rank coals with carbon monoxide and water converted them to a low-sulfur, benzene-soluble oil in good yields.[8] Indeed, at 350° to 400° C the reaction of coal with carbon monoxide and water is more rapid than the reaction of coal with hydrogen.

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[5]Vaughn, R. D. Solid Waste Management--Everybody's Problem. Environ. Sci. and Technol., v. 5, April 1971, p. 293.

[6]Work cited in footnote 5.

[7]Appell, H. R., I. Wender, and R. D. Miller. Conversion of Urban Refuse to Oil. BuMines Tech. Prog. Rept. 25, 1970, 5 pp.

[8]Appell, H. R., I. Wender, and R. D. Miller. Solubilization of Low Rank Coal With Carbon Monoxide and Water. Chem. and Ind. (London), Nov. 22, 1969, p. 1703.

In an effort to understand why the reaction of coal with carbon monoxide and water went so well, a comparison was made of the reactions of several model compounds with hydrogen and with carbon monoxide plus water. Olefins, aromatics, etc., added more hydrogen in the presence of hydrogen gas; but for two model substances tested (cellulose and lignin, the chief constituents of growing plants), the reaction with carbon monoxide and water was more rapid and complete. Urban refuse, waste paper, and even sewage sludge were converted to oil in this way.[9]

REACTANTS

Substrates

Cellulosic materials, all other carbohydrates, wood wastes (largely cellulose and lignin), urban wastes (mostly cellulose plus other carbohydrates, proteins, fats, and small amounts of other organic materials), sewage sludge, agricultural wastes, and bovine manure can be converted to oil with carbon monoxide and water. Some plastics depolymerize and dissolve in the product oil; some remain as part of the unconverted residue. But since the plastic content of urban refuse is relatively small, the presence of these materials is expected to have only a minor influence on oil composition and yield.

Carbon Monoxide

Carbon monoxide and water react to form hydrogen and carbon dioxide in the following water-gas shift reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2.$$

Because some hydrogen adds to cellulose during its conversion to oil, it seemed at first reasonable to suppose that the hydrogen gas formed in the water-gas shift was responsible for converting cellulose. But when hydrogen was added to the reactor, it had little effect; an equivalent molar amount of carbon monoxide was much more effective.

Since the water-gas shift reaction cannot be entirely avoided, it must be minimized. Carbon monoxide is somewhat costly, and as little of it as possible should be used. Earlier work[10] showed that carbon monoxide consumption at lower temperatures (250° C) was low; this finding offered a promising lead to less carbon monoxide use. Since both carbon monoxide and hydrogen are usually made from synthesis gas (mixtures of CO and H_2), it would be best to use the cheaper synthesis gas directly. This is entirely possible, and although its use will raise the total pressure somewhat, synthesis gas may ultimately be the gas used.

When cellulose is heated to 250° to 400° C, it eliminates water, some carbon dioxide, and carbon monoxide, and then forms a solid black material, called char, which many people have termed "artificial coal." It does

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[9] Work cited in footnote 7.
[10] Work cited in footnote 7.

resemble coal in many ways. A similar char forms when cellulose is heated to the same temperatures in the presence of hydrogen. The addition of water along with hydrogen has little effect. But heating cellulose with carbon monoxide and water converts it to an oil. This oil yield increases if a catalyst such as sodium carbonate is present.

The exact function of the carbon monoxide is not yet known. It may take part in the water-gas shift reaction. It could react with water and alkaline salts to form some intermediate compound, possibly an alkali formate, which transfers hydrogen, probably as hydride ion, to the substrate, thus leading to oil formation. Or it could function to remove oxygen from cellulose by formation of carbon dioxide. It probably has other, additional roles. Dehydration of cellulose leads to unsaturated substances that polymerize easily to char. It is known that carbon monoxide often inhibits or prevents such polymerizations. In the presence of carbon monoxide, the extent of decarboxylation (loss of CO_2) is greater and dehydration is less when compared with reaction in the presence of hydrogen.

Water

The original experiments with carbon monoxide on low-rank coal (lignite) were successful without added water, because this coal has a large amount of moisture. However, addition of water was beneficial. It serves as the source of hydrogen which is added to the substrate and as the vehicle (solvent) for the reaction. Cellulose forms water on being heated; and adding water plus carbon monoxide improves the oil yield. However, added water also shifts the water-gas reaction in the direction of more carbon dioxide and hydrogen (more carbon monoxide is consumed); this side reaction may not be desirable.

The critical temperature of water is 375° C; above this temperature all the water is in the gaseous state. There are indications that the presence of liquid water is desirable;[11] this may be accomplished by adding enough water so that some liquid is always present. The temperature must of course be below 375° C. If insufficient water is added, all of it will be in the gas phase, even below 375° C.

In summary, water is the source of hydrogen added to the substrate and serves as a vehicle (solvent) for the reaction.

Catalyst

No catalyst was added in the initial experiment with cellulose, in which ordinary tan paper towels were used; nor was catalyst added in converting low-rank coals to oil with carbon monoxide and water. But it was soon found that both the coals and the paper towels contained alkali salts which functioned as catalysts. The conversion of pure cellulose with carbon monoxide and water is poor (a conversion rate of 63 percent and an oil yield of 15 percent). The conversion rate rises nicely when sodium carbonate is added (conversion rate and oil yield of 90 percent and 40 to 43 percent, respectively).

[11] Work cited in footnote 7.

Vehicle (Solvent)

A liquid phase is helpful as a vehicle for feeding substrates and for keeping reactive, unsaturated organic intermediates apart so that they do not condense to a char. Water may be the best vehicle, since it dissolves the catalyst and some organic intermediates; it is the least expensive; and in any case, it must be present to some extent. Urban refuse, sewage sludge, and other substrates may contain sufficient water so that no more need be added. However, as detailed later, the use of anthracene oil and other high-boiling organic solvents permits operation at lower pressures.

NATURE OF CONVERSION REACTIONS

Cellulose $(C_6H_{10}O_5)_n$ is found in the cell walls of plants and trees. It consists of long chains of glucose units. Second to cellulose in importance is starch, a widely distributed polysaccharide that is stored in the seeds, roots, and fibers of plants as a food reserve; it too consists of glucose units, but these are linked differently than in cellulose.

Cellulose, starch, and other carbohydrates can undergo a large number of reactions on treatment at elevated temperatures and pressures with carbon monoxide, water, and sodium carbonate or other alkaline salts. Since almost every carbon atom in a carbohydrate is bonded to an hydroxyl group (-OH), some dehydration will take place. Hydrolysis of the polysaccharides to glucose will also occur; glucose and the smaller units formed from it are soluble in water. Hydrolysis of the fats in the refuse to long-chain palmitic and stearic acids will also occur.

Probably the most important overall reaction in converting cellulose to oil is the splitting out of oxygen to form molecules with high hydrogen-to-carbon ratios. Cellulose and other carbohydrates lose water and carbon dioxide just on being heated. Oxygen can also be lost by reaction with the added carbon monoxide to form carbon dioxide, by hydrogenation, by various disproportionation reactions, and by combinations of these reactions. The vast number of reactions should result in an oil made up of a complex mixture of different molecules. This is what has been found.

EXPERIMENTAL PROCEDURES

Batch studies were conducted in 0.5-liter and 1-liter stainless steel autoclaves at temperatures of 250° to 400° C.[12] White pine wood chips and newsprint were used as a source of crude cellulose. Dextrose, filter paper, and cellulose were used as a source of pure carbohydrates. Bovine manure was obtained from a local dairy barn.

The feedstock, water, and catalyst were charged to the cold autoclave; carbon monoxide was added to the desired initial pressure; and the autoclave was then heated to the desired temperature. The reaction time reported in the tables does not include the heating and cooling periods, only the time at

[12]Work cited in footnote 7.

reaction temperature. The heating and cooling periods in the autoclave runs, where significant amounts of reaction may have occurred, are about 1 hour for runs at 250° C, and about 2 hours for runs at 350° C and above.

The reaction product was flushed from the autoclave with solvent, and the oil was exhaustively extracted in a Soxhlet. Benzene was used to extract the product, except for runs made at 250° C, where acetone was used. The oil or bitumen was recovered by stripping off the solvent and then drying at room temperature. In some runs (tables 1 and 4), the product was dried overnight in an oven at 100° C. This treatment resulted in the loss of some volatile product, and the oil yields in these cases are low. The percent conversion is determined by subtracting the percent of insoluble residue remaining after solvent extraction from 100. All calculations are on a moisture- and ash-free basis. The gaseous products were analyzed by mass spectrometry.

Complete conversion of all the carbon in cellulose would give an oil yield of about 57 percent if the average carbon content of the oil is assumed to be 78 percent. Since some carbon would be converted to gaseous products, mostly carbon dioxide, the actual oil yield would be smaller. A conversion of 100 percent means that about half the cellulose is converted to oil; the remaining liquid product is mostly water.

A continuous bench-scale unit for converting waste to oil by carbon monoxide-water treatment has been constructed and recently placed in operation. Figure 1 presents a simplified schematic diagram of the unit, and figure 2 shows the control section on the protective barricade enclosing the

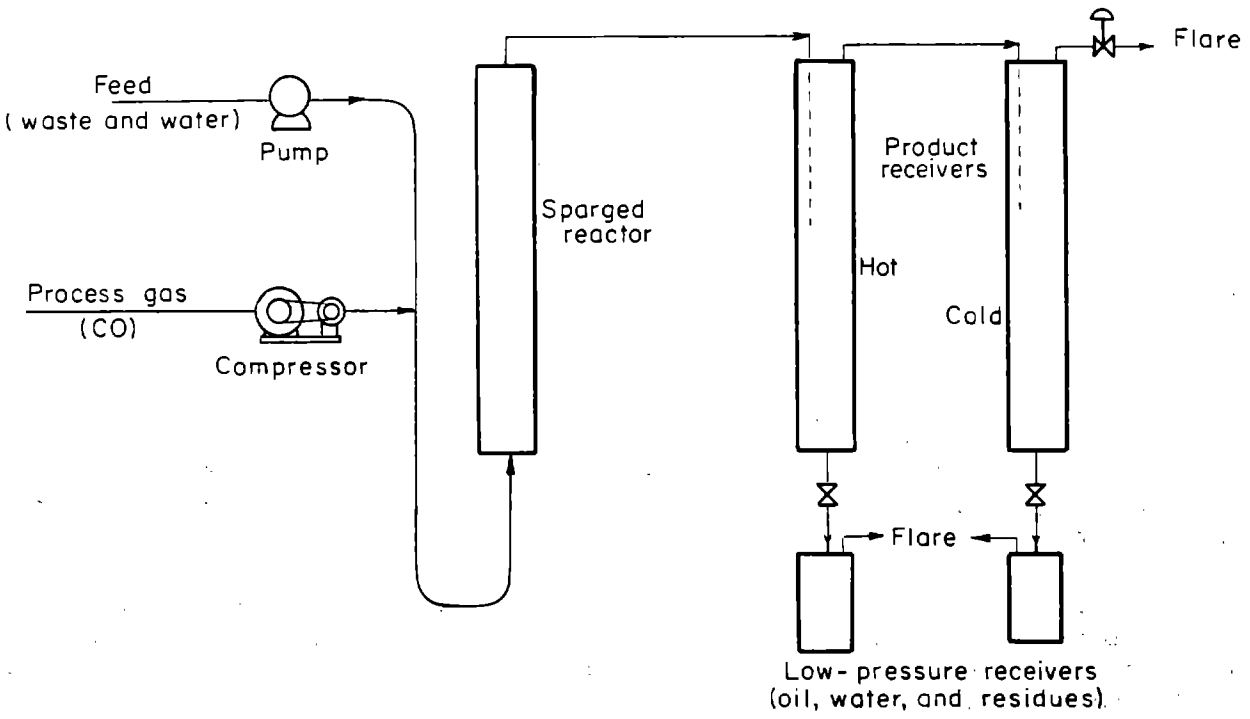

FIGURE 1. - Continuous Unit for Converting Carbohydrates to Oil.

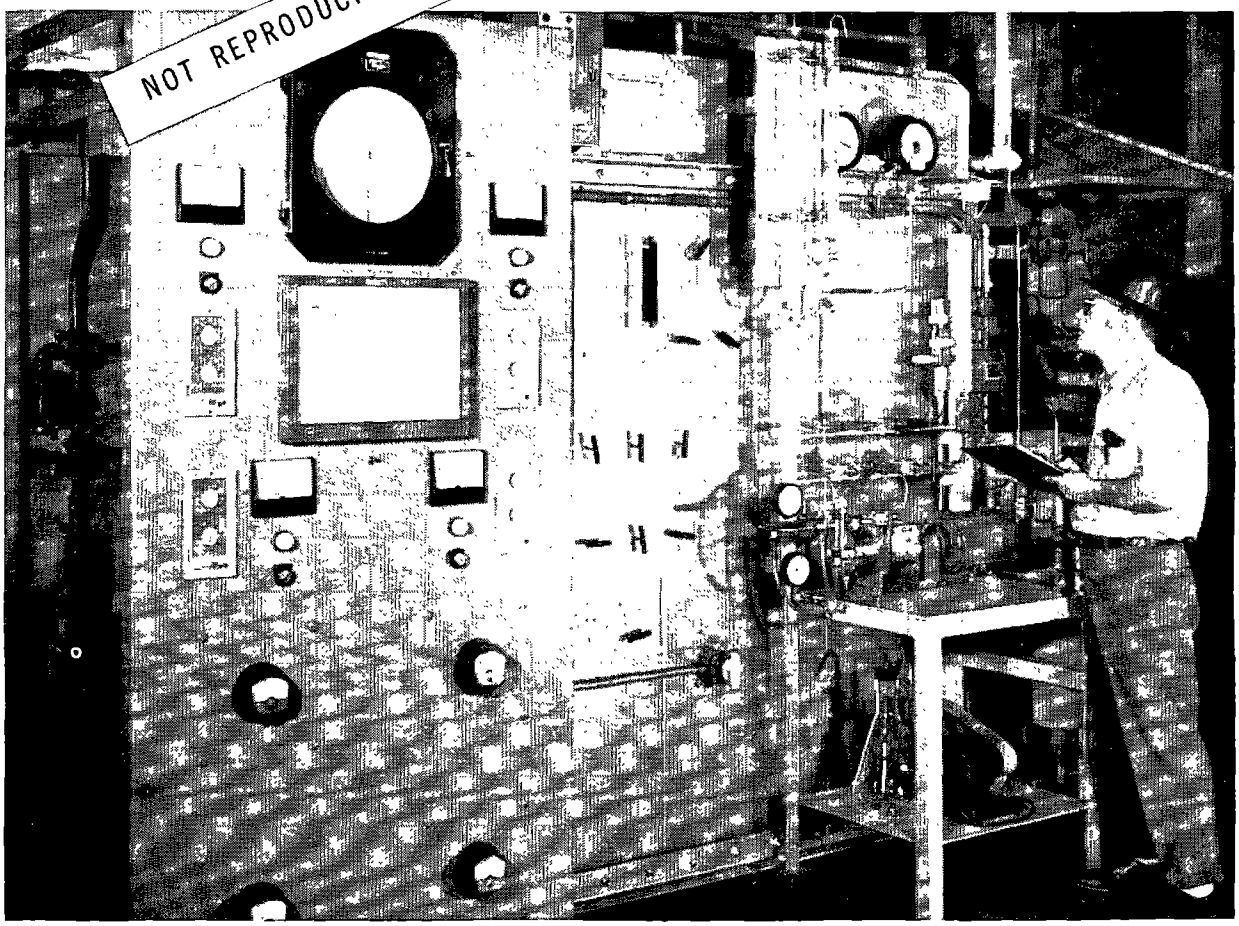

FIGURE 2. - Control Panel Barricade for Continuous Unit.

unit. The system was designed to operate at maximum conditions of 5,000 psig and 500° C, with feed rates of 100 to 500 g/hr of waste slurry and 10 standard cubic ft per hr (scfh) of carbon monoxide. The combined stream of carbon monoxide and liquid feed was preheated under pressure and injected into the bottom of the heated reactor. The liquid and gas exited from the top of the reactor and separated in the high-pressure recovery system. The liquid collected was intermittently discharged into secondary receivers at atmospheric pressure, while gas was continuously released through a back-pressure regulator.

RESULTS AND DISCUSSION

Effect of Temperature

The conversion of carbohydrates to oil has been investigated over the range 250° to 400° C. At 350° to 400° C, cellulosic wastes are readily converted to an oil by combined action of carbon monoxide, water, and catalyst. Within this range, temperature has little effect on conversion and oil yield, probably because the tendency of the product to carbonize at higher

temperatures balances out the small amount of additional conversion of organic matter to oil. Temperatures near 400° C may be preferred if synthetic polymers, such as polystyrene and polyolefins, are also present in cellulosic waste in more than trace amounts. These polymers, especially the polyolefins, do not depolymerize significantly below 400° C.

The reaction temperature does have a significant influence on the viscosity and oxygen content of the product. The product obtained from urban refuse at 250° C is a soft, bitumenlike solid at room temperature, but becomes readily pourable as its temperature is raised to near 100° C. On the other hand, the oil formed at 380° C is a free-flowing liquid with a viscosity of 650 cs (centistokes) at 50° C and 102 cs at 88° C.

The transition of the physical state of water at its critical temperature (375° C) may complicate interpretation of results from work in the 350° to 400° C range. A moderate decrease in temperature may sometimes result in more of the reaction mixture existing as a liquid phase, and thus improve product quality. But when much of the reactants are already in the liquid phase, a decrease in temperature can be expected to result in a product of higher viscosity and oxygen content.

A major advantage of low temperature (250° C) in batch tests is that the pressure developed by the steam and gases is usually about 1,500 psig compared with almost 5,000 psig at 400° C. Another is that very little carbon monoxide is consumed by the water-gas shift reaction at 250° C. As the temperature is raised, the liquefaction reaction proceeds well but the water-gas shift reaction begins to consume carbon monoxide, and a major advantage of low-temperature operation starts to disappear.

Table 1 shows some data on the effect of reaction temperature on cellulose conversion. The water-to-cellulose ratio is high, causing water to be present in both liquid and vapor states. The observed pressure varies with temperature, increasing with progress of the reactions.

The analysis of cellulose and its products in table 2 reveals that treatment of cellulose with carbon monoxide and water results more in oxygen removal than in hydrogen addition. The oxygen contents of the oil products and the residues are lower at higher temperatures, indicating that oxygen removal is more effective at higher temperature. The hydrogenation effect will not be apparent from the product analysis, because the starting cellulose contains many hydroxyl groups which contribute to the hydrogen content.

Interestingly, the extent of the water-gas shift reaction at 250° C was reduced to less than 10 percent, and most of the accompanying hydrogen was quite effectively taken up by the cellulose conversion processes.

TABLE 1. - Effect of temperature on cellulose conversion

	Temperature, ° C		
	250	300	350
Initial pressure of CO[1].....psi..	610	620	595
Operating pressure.....psi..	2,000	2,850	4,140
Time at temperature.....min..	120	120	120
Input, g:			
Cellulose.....	40	40	40
Water.....	120	120	120
Sodium carbonate.....	2	2	2
Carbon monoxide.....	37.2	37.8	36.1
Output, g:			
Benzene-extractable.....	[2]11.8	8.1	6.4
Residue.....	5.2	5.0	4.6
Water[3].....	120	120	120
Gas.....	41.2	45.7	45.9
Gas products, mole:			
Carbon dioxide.....	0.17	0.49	0.85
Hydrogen.....	Trace	0.29	0.70
Recovery.....percent..	89.5	89.5	89.3
Cellulose conversion.....do..	87.0	87.5	88.5
Oil yield.....do..	30	21	16
Carbon monoxide consumed.....mole..	0.13	0.51	1.03
Shift reaction.....percent..	9.8	37.8	79.8

[1]Values are corrected to 25° C.
[2]Acetone used as solvent instead of benzene.
[3]The water contained some oxygenated organic materials derived from the cellulose.

TABLE 2. - Analysis of cellulose and products,[1] percent

Element	Untreated cellulose	250° C		300° C		350° C	
		Oil	Residue	Oil	Residue	Oil	Residue
Carbon.....	45.6	72.4	73.9	78.5	76.6	81.2	83.1
Hydrogen.....	6.9	7.0	5.3	8.0	5.9	8.4	5.3
Nitrogen.....	.0	.004	.3	.03	.2	.1	.2
Sulfur.....	.04	.2	.2	.04	.04	.003	.1
Oxygen (by difference)	47.5	20.4	20.3	13.4	17.3	10.3	11.3
H/C atomic ratio.....	1.81	1.16	.86	1.22	.92	1.24	.76

[1]See table 1 for operating conditions.

Effect of Pressure

Batch experiments on converting organic solid wastes to oil usually consist of placing the waste material in an autoclave, adding water and catalyst (if not already present in the waste material), and then adding carbon monoxide to the desired pressure. The initial pressure is thus due essentially to carbon monoxide. In addition to the normal pressure increase of carbon monoxide upon heating, contributions are also made by water vapor and the evolved

carbon dioxide and hydrogen. Carbon dioxide forms in two ways: by the water-gas shift reaction and by decomposition of cellulose or other waste material. Most of the hydrogen forms via the water-gas shift reaction.

If the temperature is above 375° C, all the water is in the vapor phase, and the pressure becomes as high as dictated by the quantity of water put into the autoclave. Below 375° C, if liquid water is present at reaction temperature, the vapor pressure of water is regulated by the solution concentration, thus making this pressure somewhat less than the known steam pressure of pure water. If a relatively small amount of water is added initially to the autoclave, all water will be in the vapor phase, and the steam pressure at a given temperature will depend on the volume of the autoclave.

The effects of carbon monoxide pressure and steam pressure were delineated by several experiments. The effect of very low carbon monoxide pressure on cellulose conversion was observed visually as well as by determining oil yield. If insufficient carbon monoxide is present, some oil is made, but much of the cellulose chars and retains the shape and volume of the original material. If adequate carbon monoxide is present, as well as water and catalyst, the cellulose structure collapses and yields more oil. The data in table 3 were obtained with high concentrations of water at 250° C. Under these conditions, liquid water is always present, but very little water-gas shift occurs because of the low temperature. Here the difference in operating pressure at temperature is almost entirely due to carbon monoxide, because the steam pressure is constant. Note in table 3 that oil yield is strongly influenced by the applied carbon monoxide pressure.

TABLE 3. - Effect of CO pressure on cellulose conversion

(50 g newsprint, 200 ml water, 10 g $NaHCO_3$, 1 hr at 250° C)

Initial CO, psig	Operating pressure, psig	Oil yield, percent	Conversion, percent
0.....	960	24	78
100.....	1,150	24	76
200.....	1,380	32	83
300.....	1,480	32	82
400.....	1,500	34	84
500.....	1,640	35	87
600.....	1,840	40	90

But a gradual decrease in oil yield and conversion is observed as the initial pressure is decreased below 600 psig. Below 200 psig initial pressure, the yields and conversions drop more sharply. At 100 psig or less, the product contains so much solid that it resembles a friable char coated with oil. At higher pressures, the product resembles a heavy tar or a soft solid.

Effect of Water

Some information on the effect of water and resultant steam pressure on cellulose conversion is given in table 4. Here the reaction was run at 350° C, a temperature at which the water-gas shift can be very large (table 1).

TABLE 4. - Effect of water to cellulose ratio on cellulose conversion

	Experiment			
	1	2	3	4
Initial pressure of CO[1]....psi..	585	600	600	585
Operating pressure....psi..	2,340	2,810	3,360	3,560
Temperature....° C..	350	350	350	350
Time at temperature....min..	120	120	120	120
Input, g:				
Cellulose....	20	20	20	20
Water....	20	40	60	80
Sodium carbonate....	1	1	1	1
Carbon monoxide....	40.6	40.6	39.8	38.0
Output, g:				
Benzene-extractable....	2.9	2.6	3.2	4.6
Residue....	3.9	3.2	3.7	2.7
Water....	18	39	52	75
Gas....	49.8	47.0	50.8	47.6
Recovery....percent..	91.4	90.4	90.8	93.5
Cellulose conversion....do..	80.5	84.0	81.5	86.5
Shift reaction....do..	18.6	18.6	19.0	39.0
Oil yield....do..	14.5	13.0	16.0	23.0

[1]Values are corrected to 25° C.

The water-to-cellulose ratio was varied from 20:20 to 80:20. The amount of water collected was usually more than 90 percent of the water added. It should be noticed that only in experiment 4 with a water-to-cellulose ratio of 80:20 did water exist both in the liquid and vapor phases in the reactor at 350° C. The calculated amount of water required to give the saturated vapor pressure of 2,390 psi at 350° C in the reactor is 53 grams. Considering the amount of water recovered and that some water would be expended in forming hydrogen and carbon dioxide, it is apparent that only enough water was present to supply the vapor phase during other runs with lower water-to-cellulose ratios. Under these conditions, the pressure of the system reached a plateau as soon as the desired temperature was attained. On the other hand, in experiment 4 the pressure steadily increased during the reaction time owing to the water-gas shift reaction.

Examination of the data in table 4 reveals that variation of the water-to-cellulose ratio had little effect on the results as long as water was present only in the vapor phase. Under these conditions, the conversion of cellulose was 80 to 84 percent, and the products were heavy oil, water, and gases, in yields as shown. The offgas contained carbon monoxide, carbon dioxide, hydrogen, and very small amounts of low-molecular-weight hydrocarbon

gases. The extent of the water-gas shift reaction is about 19 percent, when it is assumed to be equivalent to carbon monoxide consumption.

For the run with the high water-to-cellulose ratio (80:20) and with water present in both the liquid and vapor states, cellulose conversion and oil yield seemed to improve slightly. The extent of the water-gas shift reaction also increased to 39 percent, indicating that formation of carbon dioxide and hydrogen also increased.

Generally, formation of carbon dioxide was approximately equimolar to carbon monoxide consumption, but formation of hydrogen, as analyzed in the final gaseous products, was about 30 percent lower than that of the carbon dioxide, which suggests that some hydrogen was taken up in hydrogenating cellulose at 350° C.

In an experiment with a water-to-cellulose ratio of 40:160 under essentially the same conditions, the cellulose conversion was 90 percent and the water-gas shift reaction was as high as 78.1 percent. Here the operating pressure reached 3,900 psi because of increased formation of hydrogen and carbon monoxide. Under these conditions too much carbon monoxide is consumed.

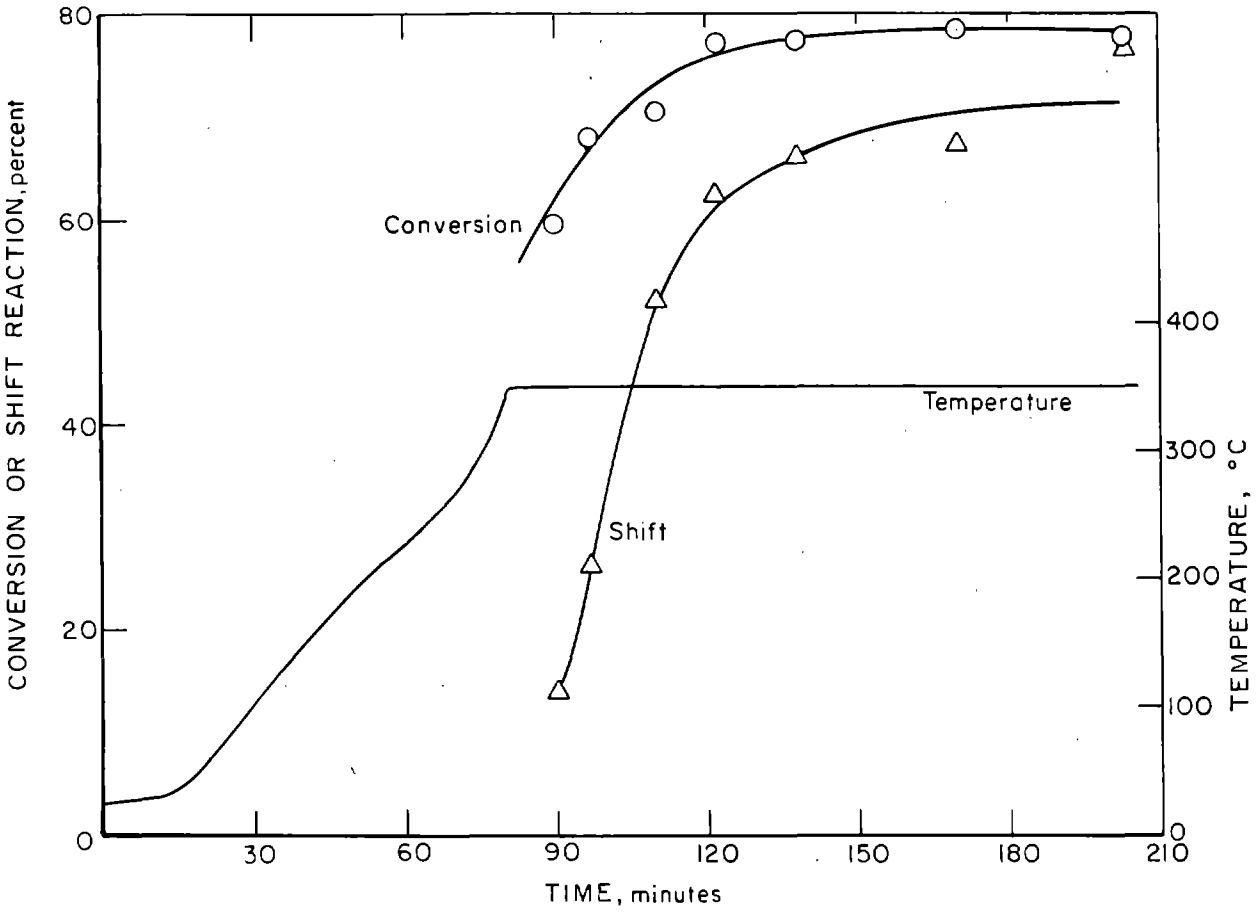

FIGURE 3. - Conversion of Cellulose and Concurrent Water-Gas Shift at 350° C.

A basic problem is to find reaction conditions that minimize the shift reaction but give high conversions of cellulose to oil. Figure 3 shows the progress of conversion of cellulose with time for a relatively low water-to-cellulose ratio. A feed ratio of water:cellulose:catalyst of 80:40:2 with an initial carbon monoxide pressure of 600 psi was used. The reaction temperature was 350° C, but about 80 minutes was needed to reach this temperature in the autoclave. Nearly 60 percent of the conversion occurred before the system reached 350° C, and the conversion approached a limit of about 78 percent after the reaction was in progress at 350° C for 45 minutes.

The extent of water-gas shift concurrent with the conversion reaction is also shown in figure 3. A steep rise in the extent of the water-gas shift reaction accompanied with increased formation of hydrogen and carbon dioxide was observed in the period between 15 to 45 minutes after the reactor reached 350° C. The inference is that the conversion reaction is faster than the shift reaction. Thus, the preferred operating technique would be to use short reaction residence times with a small sacrifice in cellulose conversion, while gaining a greater reduction in wasteful shift of carbon monoxide to carbon dioxide. Future continuous unit operations should not suffer from long reactant heat-up times, and consequently will permit a better definition of preferred conditions.

Effect of Vehicle and Solvent

Although equal weights of cellulose and water may be converted to oil in good yields, the presence of additional liquid(s) may improve the process considerably. The major liquid that probably will be used commercially is water. The effect of water on the conversion was discussed above; here, let us examine its other roles in converting organic wastes to oil, as well as the role of various additive liquids.

Water is involved in many ways in this reaction. First, most substrates contain large amounts of moisture. Second, since most organic wastes are highly oxygenated, water is formed merely by heating them to reaction temperature; so it is a reaction product. Third, water, as formed in the substrate during the reaction, or simply added to the reaction mixture, is a mechanical vehicle for facilitating mixing of reactants and preventing condensations to chars by diluting the reaction intermediates.

Water is also a solvent of sorts. It is true that most substrates are not soluble in water under normal conditions, but solvation can occur between the hydroxyl groups of the substrate and water. It is an excellent medium for intermediate hydrolysis of cellulose and other high-molecular-weight carbohydrates to water-soluble sugars. The primary reactions in the conversion to oil likely involve formation of low-molecular-weight, water-soluble compounds such as glucose or pyruvic acid. In addition, alkaline catalysts are water soluble, thus facilitating their dispersion throughout the reaction vessel in readily available form.

Finally, but importantly, water is a reactant. The hydrogen added to the substrate comes from water, which consumes carbon monoxide by reacting with it to form carbon dioxide and hydrogen.

Nevertheless, there are reasons for trying to replace part of the water with other vehicles or solvents. An excess of water accentuates removal of carbon monoxide. Also the vapor pressure of water is high as operating conditions approach the critical temperature of 375° C. Steam pressures become excessive at higher temperatures, depending on the quantity of water present.

At temperatures above 350° C, only a few solvents meet the requirements of stability, low vapor pressure, solvent action, and low-to-moderate cost. One of these solvents is anthracene oil, a byproduct of coal-tar refining. Other excellent solvents are high-boiling heterocyclic bases such as isoquinoline and alkylpyridines. These latter compounds are not only excellent solvents of high stability, but also powerful catalysts for reactions leading to cellulose liquefaction. High conversions can be obtained by using smaller amounts of isoquinoline than of anthracene oil. Because of their cost, however, it will be necessary to recover the heterocyclic bases for recycling.

The effectiveness of anthracene oil and isoquinoline in liquefying white pine wood chips at 380° C is shown in table 5. When either anthracene oil or isoquinoline replaced part of the water, the operating pressure was considerably lowered.

TABLE 5. - Effect of solvent on operating pressure and cellulose conversion

(40 g soft pine, 1,200 psig initial CO pressure, 380° C)

Water, ml	Solvent, ml		Time, min	Operating pressure, psig	Conversion, percent	Oil yield, percent
	Anthracene oil	Isoquinoline				
40	-	-	15	5,850	73	22
20	40	-	15	4,300	95	51
20	40	-	120	4,300	96.5	53
20	-	5	15	4,200	98	57

Catalysts

Water-soluble alkaline compounds, such as sodium carbonate, are effective catalysts (table 6); conversion of over 90 percent and oil yields of 45 to 50 percent are attainable with these catalysts. Generally, hydroxides, carbonates, bicarbonates, and formates of the alkali metal and alkaline earth groups are effective catalysts. At process conditions, these materials probably exist as a mixture of carbonates, bicarbonates, and formates as they undergo conversion from one form to the other.

The data in table 6 show that the alkali carbonates are more effective catalysts than stannous chloride or ferrous sulfate, which are acidic catalysts often used to hydrogenate coal. The ammonium cation (NH_4^+) is similar chemically to the alkali metal cations, and it is no surprise that ammonium hydroxide also gave high conversions of cellulose; but the oil formed in the presence of NH_4OH had a high nitrogen content, and this is a disadvantage.

TABLE 6. - Effect of various catalysts on cellulose conversion

(20 g filter paper, 40 ml water, 1,500 psig initial CO pressure,[1] 350° C)

Catalyst	Weight, g	Time, min	Conversion, percent
-	-	120	63
$FeSO_4$	1	120	69
K_2CO_3	.2	120	80
Na_2CO_3	.2	15	78
Na_2CO_3	.2	120	81
Na_2CO_3	1	120	96
[2] NH_4OH	1	120	73
[2] NH_4OH	10	120	96
$SnCl_2$	1	120	77

[1] Operating pressure about 4,800 psig.
[2] A 30-percent aqueous solution of NH_3.

The alkaline salts may serve several purposes:

1. In the presence of carbon monoxide, they are converted to formates which are reducing agents and transfer hydrogen to the oxygenated or unsaturated compounds, and then are regenerated in situ. In other words, they serve as homogeneous catalysts for converting solid wastes to oil.

2. Alkali carbonates are catalysts for the water-gas shift reaction.

3. Alkaline materials are catalysts for many known organic rearrangements and disproportionations that yield materials containing less oxygen than the original carbohydrates.

4. Alkaline salts may neutralize organic acids formed in the system. Without neutralization, these acids could promote charring.

Much more work is required before the mechanism of catalytic action by alkali salts is clear. But the postulation that formates are intermediates is consistent with these facts.

1. Formates have been identified in the aqueous solution obtained from cellulose treatment.

2. Formates are intermediates in water-gas shift reactions catalyzed by a number of salts.

3. Formates may be synthesized in good yield by treating alkali carbonates with carbon monoxide and water under conditions of the waste conversion reaction.

4. Cellulose can be converted to oil in the absence of carbon monoxide, by heating with large amounts of sodium formate and water.

The hydrogen atom in the alkali formate (HCOONa) is probably transferred to the substrate during the conversion to oil. The water-gas shift reaction in the presence of alkali carbonates probably proceeds via formation and decomposition of the alkali formates:

$$Na_2CO_3 + H_2O + 2CO \rightarrow 2H\text{-}\overset{\overset{O}{\|}}{C}\text{-}ONa + CO_2$$

$$2H\text{-}\overset{\overset{O}{\|}}{C}\text{-}ONa \rightarrow H_2 + CO + Na_2CO_3$$

$$\text{Net reaction:} \quad H_2O + CO \rightleftarrows H_2 + CO_2$$

Catalysts for converting cellulose to oil are more effective at low temperatures (250° C) than at higher temperatures.[13] Aqueous solutions of 2 to 5 percent sodium carbonate or bicarbonate brought about good conversions of cellulose to bitumen at 250° C. Because of the large quantities of catalyst solution used in operating at this temperature, the solution would be recycled.

Table 7 shows the results of eight successive autoclave runs on newsprint with recycling of the aqueous phase containing the catalyst. The oil yield on the first run is usually low because part of the cellulose hydrolysis products remains in the aqueous solution. Thereafter, an equilibrium concentration of soluble carbohydrates and carbohydrate derivatives is reached so that, in effect, all the hydrolyzed cellulose appears converted to bitumen, water, and carbon dioxide. After a few cycles, there was a decrease in conversion. However, the conversion could be returned to the 90-percent level by increasing the reaction time. Reduction of the carbon monoxide pressure, however, caused a considerable drop in conversion.

TABLE 7. - Effect of recycle catalyst solution on cellulose conversion

(250° C, 50 g newsprint, 10 g $NaHCO_3$, 200 ml of recycle solution)

Run	Initial CO pressure, psig	Time, min	Oil yield, percent	Conversion, percent
[1]1.....	800	15	40	91
[2]2.....	700	15	54	92
3.....	700	15	43	82
4.....	700	15	44	88
5.....	700	15	46	84
6.....	700	60	53	91
7.....	400	60	41	78
8.....	400	60	40	78

[1]200 ml water added.

[2]50 g newsprint added in this and each succeeding run.

[13]Work cited in footnote 7.

Although originally alkaline, the pH of the recycle aqueous phase drops to about 5 during use, probably because small amounts of soluble organic acids form. The gradual decrease in conversion rate with reuse of catalyst solution suggests that acidic compounds are accumulating and that eventually regeneration of the solution may be necessary. Regeneration should be possible by heating the solution to the temperature at which the acidic compounds are destroyed.

The most effective catalysts, however, for converting cellulosic materials to oil at 350° C are high-boiling heterocyclic nitrogen bases, such as isoquinoline, discussed in the section on vehicles. These dual-role catalyst-vehicles or solvents are particularly effective in promoting the efficiency of hydrogen utilization at high temperatures (table 8). Hydrogen utilization correlates well with conversion of carbohydrates to oil, and is a measure of catalyst effectiveness. Hydrogen utilization is defined arbitrarily as the hydrogen added to the cellulose divided by the hydrogen released. The hydrogen released is obtained from equivalency to the carbon dioxide content of the final gas. This figure is only an estimate because some carbon dioxide is liberated by the cellulose and some carbon dioxide is dissolved in the water in the system.

TABLE 8. - Efficiency of hydrogen utilization

(40 g soft pine, 1,200 psig initial CO pressure, 380° C for 15 min)

Catalyst	Water, ml	Conversion, percent	Final gas composition, volume-percent			Hydrogen utilization, percent
			H_2	CO	CO_2	
None.....	40	73	18	47	33	45
Isoquinoline, 5 g...	20	98	6.8	49	41	83

The soft pine used in the experiments of tables 5 and 8 contained some naturally occurring catalysts; addition of a few percent of sodium carbonate or potassium carbonate would increase conversion to about 90 percent, but would not increase hydrogen utilization. Isoquinoline usually effects carbohydrate conversions greater than 95 percent, and hydrogen utilization normally greater than 80 percent (table 8).

It is interesting to speculate on the reasons for the high effectiveness of nitrogen bases as catalysts. Like ammonia, they can form salts, such as isoquinoline formate, which may give up its formate hydrogen to the substrate more easily than the alkali formates. On the other hand, the alkali metal formates, having limited solubility in the organic phase, may decompose before they can donate all their hydrogen to cellulose fragments.

There is another intriguing possibility. Nitrogen bases have low reduction potentials and are excellent hydrogen transfer agents. Perhaps hydrogen adds to isoquinoline and the resulting hydroaromatic compound then donates this added hydrogen to the cellulose. The effectiveness of anthracene oil as a solvent may be due to its content of many heterocyclic nitrogen compounds.

Effect of Substrate

Water-soluble carbohydrates and carbohydrates that readily hydrolyze to water-soluble compounds (at mildly alkaline conditions) can be converted to a bitumen at 250° C.[14] Materials which have been converted to bitumen at 250° C include glucose, lactose, sucrose, corn stalks, newsprint, pine needles and twigs, and sewage sludge. Cellulose in some freshly cut trees and cellulosic materials with large amounts of lignin resist attack at 250° C, but they do react at higher temperatures.

Animal waste, once an essential fertilizer for successful farming, now creates a formidable disposal problem. The underlying reasons are two: expanded use of chemical fertilizers, estimated at more than 30 billion pounds in 1970; and the concentration of animal population (cattle, swine, and poultry) which produces annually some 2 billion tons of wastes.[15] Soils near concentrated animal populations receive heavy doses of manure, which through drainage contribute pollutants to surface waters. Transporting animal wastes long distances to where they could be used is not economical.

Bovine manure (a major animal waste) appears to be mostly cellulosic, yet the material is somewhat more resistant to conversion than cellulose itself; resistant lignins may be present. Bovine manure is not readily converted to oil at 250° C, but treatment with carbon monoxide and steam at 380° C and high pressure results in high conversions of bovine manure to oil. Because of the calcium, sodium, and potassium content of the manure, the addition of catalysts is not necessary. Compositions of bovine manure and product oil are shown in table 9.

TABLE 9. - Composition of bovine wastes and product oil

(100 g manure, 40 g water, 1,200 psig initial CO pressure, 6,000 psig operating pressure, 20 min at 380° C)

Constituent	Composition of manure, percent		Composition of oil,[1] percent
	As used	Dry, ash-free basis	
Carbon.....	20.5	52.2	78.6
Hydrogen.....	2.5	6.4	9.5
Nitrogen.....	1.3	3.3	4.2
Sulfur.....	.5	1.2	.37
Oxygen.....	14.5	36.9	7.3
Ash.....	15.1	-	-
Water.....	45.5	-	-

[1]Conversion 99 percent, oil yield 47 percent.

CONTINUOUS UNIT INVESTIGATIONS

To date, preliminary continuous experiments have been conducted with solutions of sucrose, a typical carbohydrate, to avoid initially the

[14]Work cited in footnote 7.
[15]Work cited in footnote 4.

mechanical problems encountered in pumping solids or slurries at high pressure. The experimental approach will be extended to study conversion of starch and micronized cellulose (paper) to oil to provide background data on these typical materials found in waste. Concurrently, a special slurry feed pump is being tested for high-pressure operations; when proven dependable, it will be added to the continuous unit to feed slurried refuse after the preliminary study of typical ingredients is completed.

Experiments in the continuous bench-scale unit have been made at 350° and 380° C, and significant oil yields were obtained. Operability and oil production have been demonstrated at total pressures (carbon monoxide and steam) of 4,000, 3,000, and 2,000 psig. Sucrose feed concentrations were 33 and 50 percent. Sodium carbonate, added as catalyst, ranged from about 1.5 to 5 percent of the solution.

Table 10 lists the conditions and results for a preliminary continuous run. The oil yield is fairly good, considering that 50 percent is the theoretical maximum for sucrose. Products from other runs are now being processed and analyzed. Reactor modifications to improve both carbon monoxide retention in the reactor and the gas-liquid contact area will be tested to accelerate the reaction of carbon monoxide with organic materials. This would improve oil yield per reactor volume, an important plant design consideration.

TABLE 10. - Continuous unit operating conditions

Test conditions:	
Feed composition:	
H_2O.....percent..	64
Sucrose.....do..	31.5
Na_2CO_3.....do..	4.5
Feed density.....g/ml..	1.15
Temperature.....° C..	350
Pressure (H_2O + CO).....psig..	4,000
Liquid feed rate.....ml/hr..	90
Gas feed rate.....scf/hr..	2.0
Residence time.....hr..	1.0
Duration.....hr..	7
Gross run results:	
Oil collected.....g..	75
Oil yield from sucrose.....percent..	33

The product from the continuous runs is generally a brownish-black oil at room temperature. Even though its density is only slightly less than that of the water layer, the oil is separated by centrifugation at room temperature. The oil produced at 350° C had an elemental composition of 75.2 percent C, 9.1 percent H, and 15.7 percent O (by difference); its heating value is 15,200 Btu per pound. The oil produced at 380° C contained 77.7 percent C, 9.4 percent H, and 12.9 percent O.

Mass, infrared, and ultraviolet spectrometric examination of the oil produced at 350° C and 4,000 psig indicated that the oil is almost entirely aliphatic with ether linkages and carbonyl and hydroxyl groups present. Much of the material appeared to exist in cyclic structures. Nuclear magnetic resonance examination showed that most of the hydrogens in the product were in methylene or methyl groups; a large proportion of these groups were alpha or beta to a carbonyl group or to an unsaturated carbon atom. About 4 percent of the hydrogen was "unsaturated" hydrogen--probably on olefinic (rather than aromatic) carbon atoms; another 3 percent of the hydrogen occurred in the form of -OH groups. There was no indication of aldehydic hydrogen ($-\overset{H}{C}=O$).

The results of a simulated distillation by gas-liquid chromatography are as follows:

Percent distilled (distillate wt/original wt)	Temperature, ° C
0.5	[1]42
5.0	85
10.0	133
20.0	188
30.0	236
40.0	281
50.0	327
60.0	384
70.0	488

[1]Initial bp.

CONCLUSIONS

A significant part of the energy demand of the Nation can be obtained on a renewable basis by converting nearly every kind of organic solid waste to a low-sulfur oil by treatment under pressure with carbon monoxide and water. Methods for lowering carbon monoxide consumption and for operating at lower pressures have been found; these offer the potential of low processing costs for converting cellulosic wastes to oil. While the effects of temperature, pressure, and water on this process have been explored, more work is required to find optimum conditions for the conversion. A continuous unit has operated successfully, and preliminary results have been obtained on the conversion of sucrose to oil.

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