

## COPROCESSING OF CELLULOSIC WASTE AND COAL

H. Jung, J. W. Tierney and I. Wender  
Chemical and Petroleum Engineering Department  
University of Pittsburgh  
Pittsburgh, PA 15261

### Introduction

Paper and other cellulosic wastes constitute more than half of landfill volumes. These materials could be a significant energy source<sup>1</sup>; it is the object of this work to find ways of converting these huge volumes of waste to liquid transportation fuels.

It is well known, of course, that coal can be converted to liquid fuels. There are a number of ways of achieving this. A major route from coal to liquid fuels is by direct liquefaction in the presence of hydrogen or hydrogen donor solvents. Experiments have also demonstrated that cellulosic materials and biomass can be converted to oil in the same way<sup>2,3</sup>. However, there has been little or no work on the coprocessing of coal and these wastes. We call this route A.

Another way to converting coal to liquids is via the so-called COSTEAM process which involves the treatment of coal with carbon monoxide or synthesis gas ( $\text{CO} + \text{H}_2$ ) in the presence of water and an alkali compound as catalyst<sup>4,5,6</sup>. Again, it has been demonstrated that cellulosic wastes can be converted to liquids in the same manner<sup>7,8</sup>. However, as far as we know, there has been no work on coprocessing coals with these wastes via the COSTEAM process, which works particularly well with low rank coals such as lignite and subbituminous coals. Most of our coprocessing experiments are being carried out with cellulosic wastes and these coals. We call this route B.

### Experimental

#### *Route A (hydrogen and/or hydrogen donor solvents with a molybdenum catalyst)*

Wyodak subbituminous coal, obtained from the Argonne Coal Sample Bank, and ordinary copy paper (6.7% moisture and 7.2% ash) were used in this study. Three grams (either coal, paper or a mixture of both), slurried with 12 g of tetralin and 5000 ppm of  $\text{Mo}(\text{CO})_6$  plus 10,000 ppm of sulfur, were charged in a horizontally shaken 45cc microautoclave with an initial hydrogen pressure of 1000 psig. The reactions were carried out at two different temperatures (325°C and 400°C) for one hour with reaction pressures of about 1800 psig and 2300 psig, respectively.

The nonvolatile products were recovered with THF and then filtered through a cellulose thimble. The filtered materials (THF insolubles) were then extracted with boiling THF. The conversion to THF-solubles was calculated from THF insolubles on an maf basis. THF was removed by rotary evaporation and the product was fractionated into pentane-solubles (oil) and pentane-insolubles (asphaltenes). Since, in the case of  $\text{H}_2$ -tetralin runs, pentane-solubles include the tetralin, some of which reacted during the reaction and some was lost during the product analysis, only asphaltenes were accurately measured. As a result, the oil and gas fraction was calculated by subtracting the recovered asphaltenes from the total converted. Gases were collected and analyzed by a GC equipped with a Porapak Q column and a 5A molecular sieve

column using a carrier gas with the composition of 8.5% H<sub>2</sub> and 91.5% He.

#### *Route B (CO and H<sub>2</sub>O with an alkali catalyst)*

Severe mass transfer limitations were experienced in a microautoclave for CO-H<sub>2</sub>O runs so that reactions in CO-H<sub>2</sub>O environments were carried out in a 300cc autoclave. A total of 8 g of reactants mixed with 24 g of water and 1.02 g of Na<sub>2</sub>CO<sub>3</sub> were used with 580 psig (cold) of CO. The reactor was heated to 400°C in about 50 minutes and was held for one hour while stirring at 1400 rpm. Due to the significant amount of water, pressures up to 4200 psig were registered. The reactor was then cooled to below 200°C in 10 minutes. Figure 1 shows a typical history of the temperature and pressure during a run in a CO-H<sub>2</sub>O environment.

The same product analysis procedure was employed in Route B runs, except that oil fractions and gas fractions could be measured because the pentane solubles were free of tetralin. The oils were directly calculated from pentane solubles and the gas fraction by subtracting the oils from the oil and gas fraction which was determined from the asphaltene content.

### Results and Discussion

#### *Route A (H<sub>2</sub>-tetralin system)*

Table 1 lists the results at 400°C using a molybdenum catalyst with added sulfur. As expected, conversion of the paper is almost complete. It has been reported that only 90% of a caustic type of lignin was converted under similar conditions with no added catalyst<sup>9</sup>. The conversion of paper yielded only about 10% of high molecular weight asphaltenes with a large yield of oil and gas. Wyodak coal is also converted in high yield but with significant amounts of asphaltenes. Since conversions and yields of oil and gas are very high for paper, the conversion and yield of coal in the coprocessing runs were calculated with the assumption that addition of coal has no influence on paper conversion. As shown in Table 1, the conversion of coal was increased to 91.7% when the 33 wt% of paper was coprocessed, up from 86% of conversion when coal was reacted alone. However, the yield of oil and gas remained unchanged. Addition of paper evidently increased the conversion of coal. Increase in the amount of paper to 50 wt% in the coprocessing does not seem to increase this effect.

It has been proposed that the thermal depolymerization of lignin forms phenoxy radicals, which then cause scission of carbon-carbon bonds in coal<sup>9</sup>. Cellulose in paper can also form phenoxy radicals which may assist the liquefaction of coal in our coprocessing runs. It has also been hypothesized that, at temperatures as high as 400°C, phenoxy radicals polymerize or recombine so that their enhancing effect is minimal<sup>9</sup>. This may help explain the finding that the same oil and gas yield of coal was obtained in the coprocessing as that of coal alone.

Reactions were carried out at a lower temperature (325°C) and the results are listed in Table 2. Even at the lower temperature, paper gave high conversion (88.9%) and high oil and gas yields (77.2%). However, there was a decrease in conversion of coal when the reaction temperature was decreased to 325°C. Both the coal conversion and the yield of oil and gas from the coprocessing run are almost same as those from coal alone at 325°C, suggesting that the effect of paper is small at 325°C. This result is surprising since a synergistic effect of lignin during lignin-coal coprocessing is reported to be the most pronounced in this temperature range<sup>9</sup>.

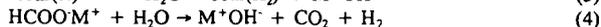
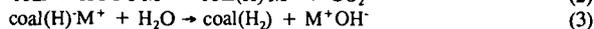
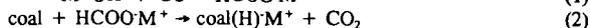
### Route B (CO-H<sub>2</sub>O system)

The results of runs in CO-H<sub>2</sub>O environments with Na<sub>2</sub>CO<sub>3</sub> catalysts at 400°C are summarized in Table 3. The paper conversion was almost as high as that in the H<sub>2</sub>-tetralin case. However, the product contains more high molecular weight asphaltenes. The same trend is observed for the coal only run in COSTEAM. As stated earlier, there were severe mass transfer limitations in a microautoclave when reactions were carried out in a CO-H<sub>2</sub>O environment. For example, the conversion of coal in a microautoclave at 400°C was about 32% in a CO-H<sub>2</sub>O environment while that in a 300cc autoclave with stirring was 84%.

It should also be pointed out that the amount of oil (pentane solubles) can be quantitatively measured in CO-H<sub>2</sub>O runs since no hydrogen-donor solvent was used. As can be seen in Table 3, most of the product from paper is gas, suggesting the reaction conditions are so severe that most of the liquid product formed light gaseous materials.

Addition of paper to coal provided only a slight increase in coal conversion (~1%). However, the coprocessing of paper with coal decreased the amount of asphaltenes to half of that produced from coal alone and almost doubled the amount of oils from coal. With the CO-H<sub>2</sub>O route, the coprocessing of paper and coal yielded higher quality products. It is also possible that coal may, to a certain extent, prevent liquid formed from paper from reacting further to form gases.

It has been proposed that the pathway for conversion in the CO-H<sub>2</sub>O system utilizing an alkali catalysts includes a formate intermediate<sup>4,5</sup>.



Both the formate ion and water supply hydrogen to coal radicals, while reactions (1) and (4) complete the water-gas shift reaction to generate gaseous hydrogen. Table 4 shows the results of gas analyses for the runs listed in Table 3. As can be seen, about 78% of the CO is converted by the water-gas shift reaction to form hydrogen and CO<sub>2</sub> with a small amount of light hydrocarbons.

Since our experiments were carried out in a batch mode, the system pressures at room temperature after reaction were higher than the initial pressure of pure CO (580 psig) due to the water-gas shift reaction (water is condensed at room temperature). From the gas composition data with the final pressure at room temperature, the total conversion of CO can be calculated and is listed in Table 4. The total conversion of CO includes conversion to supply H<sub>2</sub> to coal and a water-gas shift reaction conversion. The difference between the total moles of CO converted and the moles of hydrogen produced gives the moles of hydrogen consumed by the reactants (coal and paper). The moles of consumed hydrogen thus calculated are also listed in Table 4. As can be seen, the total conversions of CO are all about 78%, regardless of the type of reactants. However, more hydrogen is consumed for coal conversion than for paper conversion. An intermediate amount of hydrogen is consumed by the mixture of coal and paper. According to the reaction pathway proposed, one mole of CO<sub>2</sub> should be produced for every mole of CO converted. However, the amount of CO<sub>2</sub> produced is less than the amount of CO converted. Even when the water-gas shift reaction was carried out in the absence of the reactants, the amount of CO<sub>2</sub> produced was smaller than H<sub>2</sub>, suggesting that a significant amount of CO<sub>2</sub> is

dissolved in the aqueous phase. In the paper runs, larger amounts of CO<sub>2</sub> were produced than from coal runs, suggesting that a large portion of gas produced from paper is CO<sub>2</sub>.

#### Summary

Based on an exploratory study of coprocessing of paper and subbituminous Wyodak coal, the following conclusions were drawn. A possible desirable effect of paper in coprocessing was observed in both the H<sub>2</sub>/tetralin/Mo system and the CO/H<sub>2</sub>O/alkali system at 400°C. More specifically, the conversion of coal was increased due to the addition of paper in the H<sub>2</sub>/tetralin/Mo system, but the quality of the product seems to be unchanged. However, very little increase in coal conversion was observed when coprocessing in the CO/H<sub>2</sub>O/alkali system, while the product quality of coal was significantly improved (more oil and less asphaltenes). No effect of paper was observed at 325°C in the H<sub>2</sub>/tetralin/Mo system.

#### Acknowledgements

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**Table 1.** Liquefaction in the H<sub>2</sub>/tetralin/Mo system at 400°C for 1 hour.

Reactant	Conversion (%)	Asphaltenes (%)	Oil and Gas (%)
paper	98.6	10.2	88.4
coal	86.0	39.9	46.1
coal (50%) + paper (50%)	91.7 <sup>a</sup>	44.0 <sup>a</sup>	47.7 <sup>a</sup>
coal (67%) + paper (33%)	91.7 <sup>a</sup>	46.0 <sup>a</sup>	45.7 <sup>a</sup>

a: conversion and yield with respect to coal.

**Table 2.** Liquefaction results in H<sub>2</sub>/tetralin/Mo system at 325°C.

Reactant	Conversion (%)	Asphaltenes (%)	Oil and Gas (%)
paper	88.9	11.7	77.2
coal	35.9	21.6	14.3
coal (67%) + paper (33%)	37.7 <sup>a</sup>	25.3 <sup>a</sup>	12.4 <sup>a</sup>

a: conversion and yield with respect to coal.

**Table 3.** Liquefaction results in the CO/H<sub>2</sub>O/Na<sub>2</sub>CO<sub>3</sub> system at 400°C for 1 hour.

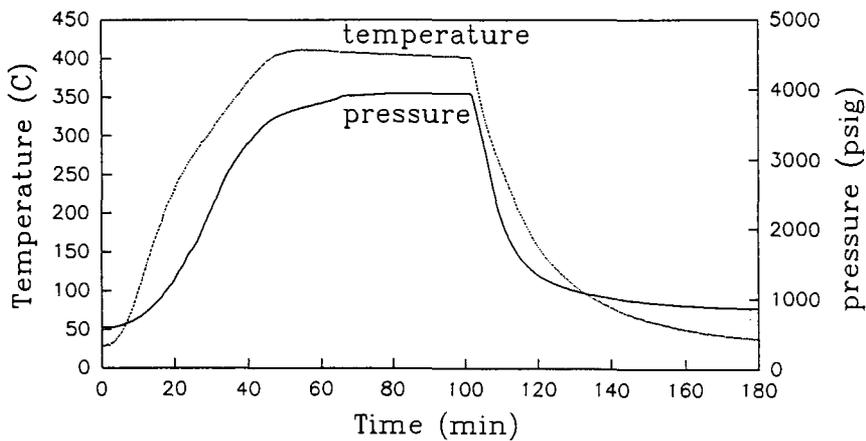
Reactant	Conversion	Asphaltenes	Oil and Gas	Oil	Gas
paper	96.6	15.2	81.4	7.0	74.4
coal	84.2	42.8	41.4	15.1	26.4
coal(50%) + paper(50%)	85.3 <sup>a</sup>	22.9 <sup>a</sup>	62.4 <sup>a</sup>	38.1 <sup>a</sup>	24.3 <sup>a</sup>

a: conversion and yield with respect to coal.

**Table 4.** Gas compositions after 1 hour of run in CO/H<sub>2</sub>O/Na<sub>2</sub>CO<sub>3</sub> system at 400°C (initial pressure of CO=580 psig).

reactant	final pressure (psig)	CO	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>6</sub>	CO conversion (%)	H <sub>2</sub> consumption (mole)
paper	950	14.2	37.8	47.1	0.9	0.1	77.1	0.078
coal	863	14.9	37.5	46.3	1.4	0.3	78.0	0.113
coal + paper	913	13.5	38.2	47.0	1.3	0.3	78.5	0.090

Figure 1. Typical heating and cooling for coal conversion (Route B).



## VOLATILE FATTY ACIDS PRODUCTION BY ANAEROBIC FERMENTATION OF URBAN ORGANIC WASTES

C. Sans, J. Mata-Alvarez  
Department of Chemical Engineering  
University of Barcelona, E-08028.  
F. Cecchi, P. Pavan.  
University of Venice, I-30123.

### KEYWORDS

Volatile fatty acids, methyl ethyl esters, organic fraction of the municipal solid waste

### ABSTRACT

During six months of experimentation, a plug-flow system without recirculation was employed to study the volatile fatty acids (VFA) production by means of anaerobic fermentation of urban organic wastes. Results showed an important VFA production at mesophilic range of temperature (37°C). Particularly, VFA concentration in the outlet sludge went from 11.8 g/L at 2 days of retention time up to 23.1 g/L at 6 days of retention time.

### INTRODUCTION

One of the biotechnologies developed in the last years to utilize municipal solid wastes (MSW) for useful energy and materials recovery is the anaerobic digestion. Particularly, the anaerobic fermentation of the organic fraction of the municipal solid wastes (OFMSW) mainly to acetic, propionic, butyric and valeric acids has been studied. The volatile fatty acids obtained can be recovered and used to produce methyl or ethyl esters which, considering their elevate octane number (between 103-118), could be advantageously used as additive for gasoline (D'Addario et al., 1992). An alternative possibility would be the production of biogas in a second step of the anaerobic digestion. The resulting sludge from the fermentation could be converted in an optimal soil amendment after a composting step. All these possibilities makes the alternative particularly interesting.

The main studies described in the literature about the steps for the production of esters from MSW are the ones made by Antonopoulos in the U.S.A and D'Addario and co-workers in Italy (Antonopoulos and Wene, 1989; D'Addario et al., 1992). However, further research is necessary in order to study the feasibility of the process.

This work shows and discusses the results obtained using the OFMSW to produce volatile fatty acids in a tubular pilot-scale reactor at mesophilic temperature. The influence of operational parameters, such as hydraulic and solid retention time and organic loading rate, on the hydrolytic-acidogenic phase of the anaerobic digestion has also been investigated.

## MATERIALS AND METHODS

### Experimental device

The research was carried out with a pilot-plant, located in the experimental facilities of the University of Venice in Treviso (Italy). The plant can be divided in two sections. In the first section, the substrate is introduced into a 80 liters tubular reactor from the feed tank by an archimedean screw. The retention time of the sludge in the reactor can be controlled changing the turn of the screw. In the second section, the sludge coming out from the reactor goes to a separation area where part of the liquid phase is separated from the outlet sludge. VFA will be extracted from the liquid phase. The concentrated sludge can be partially recycled to the feed tank by a recycling archimedean screw and partially discharged.

### Substrate

The substrate used for the experimentation was a mixture of the OFMSW coming from the mechanical selection plant of San Giorgio di Nogaro (Udine, Italy), and source sorted OFMSW coming from the food market of the city of Treviso (Italy). Tables 1 and 2 show the most important characteristics of both types of refuses. Initially, the substrates were mixed in a way to obtain a feed substrate with a total solids (TS) content around 20 % and a total volatile solids (TVS) content around 60 % TS, adding water for diluting purposes when necessary. The feeding mixture was prepared three times a week and kept in the feeding tank. The archimedean screw carried the substrate daily inside the digester at the desired loading rate, by controlling the time and rate of running of the screw, which determined the hydraulic retention time.

### Analytical methods

The digestion process was monitored following the analytical procedure according to the Standard Methods for the examination of water and wastewater (1985). Total volatile fatty acids (TVFA) were carefully monitored in the feed, in the outlet sludge and in each valve of the reactor, when possible. TVFA were determined by a gas-chromatographic method (Chromatograph Vega serie 6000 Carlo Erba). Conditions of this analysis were: Capillary column type Nukol, length 15 m, internal diameter 0.53 mm; Injector temperature, 200°C; Detector -flame ionization- temperature, 220°C; Air pressure 120 kPa, H<sub>2</sub> pressure 70 kPa; Temperature program (isotherm): 106°C; Duration, 6 minutes; Carrier pressure 30 kPa.

## RESULTS AND DISCUSSION

During six months of continuous operation, the acidogenic process was studied at different working conditions in the mesophilic ( $37 \pm 2^\circ\text{C}$ ) range of temperature. Table 3 shows the operational parameters and results obtained in the 4 different mesophilic periods experimented.

The start-up of the digester was performed at mesophilic temperature for almost one month. During the first period (period 1), solid recirculation was operated, in a way to work with a solid retention time (SRT) > hydraulic retention time (HRT). But, due to different technical problems

mainly at the separation and recirculation stage, the complete control of the solids retention time was not possible, although it can be considered close to 8 days. Taking into account the difficulties found during the first period of operation it was decided to eliminate solid recirculation system in the next periods experimented. Hydraulic and solid retention times studied were 2, 4 and 6 days (periods 2, 3 and 4, respectively). The screw of the reactor operated discontinuously. This particularity and the obliquial disposal of the digester caused separation of the liquid phase back to the feed box and desiccation of the sludge inside de digester. Thus, in order to avoid these problems, the reactor position was changed and placed horizontally during period 4 and for the rest of the periods studied. The influence of reactor design on the results during this period were sufficiently important to present them separately (period 4.1: obliquial reactor; period 4.2: horizontal reactor, see Table 3).

Figure 1 shows the VFA production with retention time of periods 1-4. The TVFA concentration in the outlet sludge obtained when working at  $SRT > HRT = 2$  days, that is, with solid recirculation (period 1) was 19.5 g/L. This concentration is quite superior compared with the one obtained in period 2 (mean value 11.8 g/L, see Table 3), when working at  $SRT = HRT = 2$  days without solid recirculation. The solid recirculation implied the presence of acidogenic inoculum in the feeding mixture which increased bacterial activity and substrate degradation in the reactor. Another result that supports this conclusion is the higher ammonia concentration in the outlet sludge of period 1, compared with period 2 (360.3 mg/L and 101.3 mg/L, respectively). This indicates a major protein mass degradation in the working conditions of the first period. The TVFA concentration obtained in period 3 ( $HRT = SRT = 4$  days) increased respect period 2 (18.3 g/L and 11.8 g/L, respectively), which could indicate that retention time of 2 days (period 2) was not enough for an optimal degree of substrate degradation. This hypothesis is confirmed by the acid concentration reached in period 4.2 ( $HRT = SRT = 6$  days), when correction in digester disposal was already done. There were obtained 23.1 g/L of volatile fatty acids in the outlet sludge, which determine the increasing profile of VFA production with retention times (see Figure 1). The optimal bacterial activity in period 4.2 was also reflected in the ammonia concentration, which was higher when acid concentration was maximum (486.7 mg/L in the digester sludge of period 4.2).

Figure 2 shows the yields obtained in the different mesophilic periods studied. Important yields were obtained when solid recycling was applied (period 1): yield expressed in percentage of TVFA produced per TS of the feeding mixture reached 9.3 % and in percentage of TVS reached almost 15 %, which can be considered an optimal result, taking into account the high organic loading rate operated (66.9 kgTVS/m<sup>3</sup>d) and the kind of substrate utilized for the digestion. When there was no solid recycle (periods 2, 3 and 4.2) yields increased with increasing retention time (see Figure 2). Maximum values were obtained at 6 days of retention time and those were 7.8% TS, 13.9% TVS and 12.1% TCOD.

TVFA concentration obtained in the sludge samples from the first valve of the tubular reactor where quite high for the four mesophilic periods: the concentration increased with retention time from 9 g/L in period 2 up to 13.4 g/L in period 4.2. This is because acidogenic bacteria are fast-growing bacteria, with minimum doubling times around 30 minutes (Mosey, 1983) and are capable of fermenting the soluble fraction of the organic refuse to produce a mixture of VFA in a short interval of time. Maximal VFA concentration in the first valve was obtained in period 1, when solid recycling was operated (17.8 g/L), that is, with acidogenic inoculum in the feeding mixture.

The stability parameters -pH and alkalinity- were always within the optimal ranges: pH in the reactor varied between 4.77 (period 2) and 5.97 (period 4.1) but mean value never reached values that could inhibit the acidogenic process, that is, pH values below 4.5 (Zoetemeyer et al., 1982).  $\Delta$ TA in the outlet sludge kept always quite high and between 11.6 and 19.5 gCaCO<sub>3</sub>/l, as well as ammonia concentration (between 81.2 mg/L and 486.7 mg/L, see Table 3), so the system was always optimally selfbuffered.

### CONCLUSIONS

This work shows that the acidogenic fermentation of the organic fraction of the municipal solid waste in a tubular reactor and at pilot scale level, is an optimal process for the obtention of volatile fatty acids. These fatty acids are the raw material of valuable products, like methyl-ethyl esters or alkane.

In mesophilic conditions, the production of VFA increased with the retention time up to a production of 23.1 g/L for 6 days of retention time. No inoculation of the substrate was necessary as VFA concentration was already important at short retention time (first valve of the tubular reactor). The yields obtained can be considered as optimal (15% expressed as TVFA, % TVS fed), considering the high values of loading rates employed (66.9 KgSV/m<sup>3</sup>d) and the mixture of urban wastes utilized as substrate for the digestion. The acidogenic process, in the working conditions studied, is stable, considering the parameters pH, alkalinity and ammonia. Furthermore, the ammonia concentration in the reactor sludge has revealed as a good indicator of the bacterial activity.

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Table 1: Main characteristics of the OFMSW coming from the mechanical selecting plant of San Giorgio di Nogaro (Italy).

PARAMETERS	AVER.	MAX.	MIN.	STD	SAMPL.
TS, g/Kg	647.2	832.4	472.2	89.3	45
TVS, g/Kg	300.8	487.5	212.4	65.1	33
TVS, % ST	45.4	62.4	35.8	6.9	33
TCOD, % ST	51	76	23	15	22
TKN, % ST	1.36	1.79	1.06	0.22	22
P, % ST	1.41	1.82	1.02	0.30	10
TC, % ST	22.05	26.80	18.94	2.78	6

Table 2: Main characteristics of the source-sorted OFMSW coming from the market of the city of Treviso (Italy).

PARAMETERS	AVER.	MAX.	MIN.	STD	SAMPL.
TS, g/Kg	163.9	353.3	69.42	58.5	115
TVS, g/Kg	153.6	568.3	54.7	82.5	88
TVS, % ST	90.0	95.3	52.8	16.8	87
TCOD, % ST	112	133	84	64	44
TKN, % ST	2.07	3.07	1.21	6.39	45
P, % ST	2.57	5.45	0.82	6.26	43
TC, % ST	43.21	48.80	34.25	15.16	19

Table 3: Working conditions and averaged results obtained at steady state conditions in the 5 periods studied at mesophilic conditions.

PERIOD	1	2	3	4.1	4.2
HRT, d	1.8	1.9	3.8	4.9	4.6
SRT, d	-	2.0	4.0	6.0	6.0
OLR, KgSV/m <sup>3</sup> d	66.9	85.2	42.3	33.9	38.5
Feed:					
TS, g/Kg	198.5	248.3	244.9	285.9	285.5
TVS, g/Kg	122.2	159.0	159.2	155.7	160.4
STS, g/Kg	32.7	38.6	35.2	34.2	34.6
SVS, g/Kg	27.2	32.9	27.9	27.8	28.7
TCOD, gO <sub>2</sub> /Kg	188.0	199.5	192.7	179.5	196.7
SCOD, gO <sub>2</sub> /Kg	33.7	41.7	37.9	30.9	32.1
pH	5.92	6.11	6.19	6.39	6.06
ΔTA, gCaCO <sub>3</sub> /l	2.9	4.0	2.9	3.4	3.6
TVFA, mg/L	2902	2645	7651	4722	4361
Sample valve 1:					
STS, g/Kg	27.7	61.2	64.3	38.9	55.3
SVS, g/Kg	20.2	42.7	47.3	27.8	36.6
pH	5.33	4.77	5.68	5.21	5.69
ΔTA, gCaCO <sub>3</sub> /L	10.7	12.3	9.0	9.0	13.0
NH <sub>4</sub> -N, mg/L	223.4	40.6	177.6	49.0	100.7
TVFA, mg/L	17822	9061	12782	7375	13372
Sample exit reactor:					
TS, g/Kg	230.4	255.2	304.0	419.5	303.6
TVS, g/Kg	125.5	153.9	188.2	214.5	152.7
STS, g/Kg	24.1	58.4	71.4	45.3	36.5
SVS, g/Kg	17.0	40.6	48.5	29.3	25.0
TCOD, gO <sub>2</sub> /Kg	161.2	212.6	237.9	247.8	214.8
SCOD, gO <sub>2</sub> /Kg	22.1	39.8	52.6	28.6	38.8
pH	5.57	5.08	4.98	5.97	5.72
ΔTA, gCaCO <sub>3</sub> /L	11.6	14.7	17.2	16.2	19.5
NH <sub>4</sub> -N, mg/L	360.3	101.3	81.2	255.4	486.7
TVFA, mg/L	19524	11780	18265	13000	23110

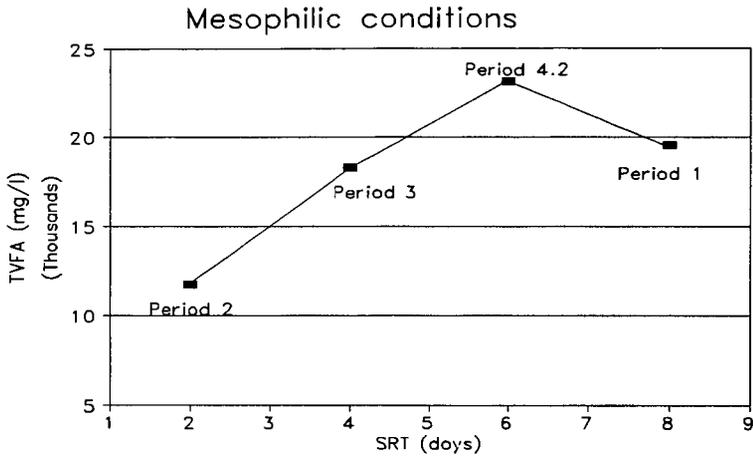


Figure 1: Variation of TVFA production in the outlet sludge with solid retention time in mesophilic conditions.

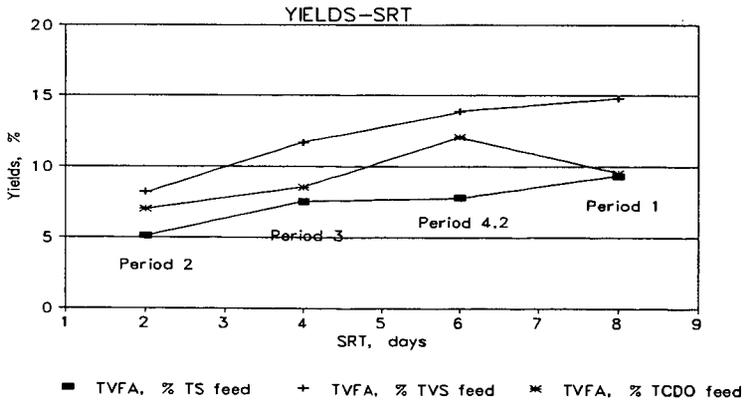


Figure 2: Yields obtained in the four mesophilic periods studied.

## THE COPROCESSING OF FOSSIL FUELS AND BIOMASS FOR CO<sub>2</sub> EMISSION REDUCTION IN THE TRANSPORTATION SECTOR

Meyer Steinberg  
Brookhaven National Laboratory, Upton, NY 11973

### INTRODUCTION

Research is underway to evaluate the Hydrocarb process for conversion of carbonaceous raw material to clean carbon and methanol products. These products are valuable in the market either as fuel or as chemical commodities. As fuel, methanol and carbon can be used economically, either independently or in slurry form, in efficient heat engines (turbines and internal combustion engines) for both mobile and stationary single and combined cycle power plants. When considering CO<sub>2</sub> emission control in the utilization of fossil fuels, the coprocessing of those fossil fuels with biomass (which may include, wood, municipal solid waste and sewage sludge) is a viable mitigation approach. By coprocessing both types of feedstock to produce methanol and carbon while sequestering all or part of the carbon a significant net CO<sub>2</sub> reduction is achieved if the methanol is substituted for petroleum fuels in the transportation sector. Biomass removes CO<sub>2</sub> from the atmosphere by photosynthesis and is thus a prime feedstock for mitigation of CO<sub>2</sub> emission from mobile sources. Since the availability of biomass will, in most cases, determine the amount of petroleum that can be displaced, it is essential to obtain maximum yield in the conversion process.

#### Basic Hydrocarb Process

The basic Hydrocarb Process would use carbonaceous feedstock or combination of feedstocks to produce, in addition to pure carbon, the coproducts, hydrogen, methane or methanol. The process which combines 3 basic steps; (1) a hydropropylyzer (HPR) in which the carbonaceous material is hydrogasified with a recycled hydrogen-rich gas to form a methane-rich gas (2) a methane pyrolyzer (MPR) in which methane is decomposed to carbon and hydrogen and (3) a methanol synthesis reactor (MSR) in which the CO is catalytically combined with hydrogen to form methanol (MeOH or CH<sub>3</sub>OH) and the remaining hydrogen-rich gas is recycled to the first step (HPR). The principal distinguishing features of the process are that the hydropropylysis is an exothermic reaction which does not require internal heating, the methane pyrolysis is an endothermic process which does require heating and the recycled hydrogen-rich gas conserves the energy balance in the process.

#### Process Simulation Computer Model

A Hydrocarb process simulation computer model was developed based on well-known thermodynamic data taking into account equilibrium among the gaseous species CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O and carbon in the solid phase. This detailed model allows the complete determination of the mass and energy balances around each reactor and around the entire process for various feedstock types and for various pressure and temperature conditions in each of the reactors. From numerous computer runs we cite here only two configurations which are most relevant to CO<sub>2</sub> emissions reduction. In one configuration we obtain a net zero CO<sub>2</sub> emission and in the other configuration we maximize the production and utilization of methanol as transportation fuel and substantially reduce CO<sub>2</sub> emission although not to zero.

### Hydrocarb Methanol as an Alternative Transportation Fuel

An analysis can also be made with respect to CO<sub>2</sub> emissions when considering methanol displacing gasoline as a transportation fuel. About 30% of the U.S. anthropogenic CO<sub>2</sub> emission comes from the transportation sector which is about equal to emissions from stationary sources. EPA has estimated that 1.54 gallons of methanol can displace 1 gallon of gasoline in automobiles on a mileage per unit energy basis. Gasoline emits 9 Kg CO<sub>2</sub> per gallon. For maximum Hydrocarb methanol production configuration, the CO<sub>2</sub> emitted is 4 Kg CO<sub>2</sub> per gallon of gasoline displaced. There is thus a 55% reduction in CO<sub>2</sub> emission by the use of Hydrocarb methanol in displacing gasoline. Hydrocarb methanol can yield from 80% to 130% greater reduction in CO<sub>2</sub> emission than the other conventional biomass gasification plant for methanol production.

### Cost Estimates

The following is a summary of the conclusions of a preliminary economic study of alternate fuel options. The preliminary capital cost estimate was determined based on a comparative analysis with a Texaco Coal gasification process plant assuming that equal gas throughput through the gasifier will have the same capital cost when escalated to 1992 dollars. Credit was taken for elimination of the air separation plant and half credit for acid gas removal which are not needed in the Hydrocarb plant. A reasonable plant capacity handling 5000 dry metric tons of biomass per day (DMT/day) selected mainly by the deliverability and cost of biomass from an area of a fast rotational crop tree plantation (bundled willow). The economic parameters assumed for methanol production based on the maximum yield of methanol option and results in a production cost of \$0.405/gallon methanol.

An equivalent gasoline price and incremental cost of gasoline displaced has also been calculated. The U.S. national average gasoline price toward the end of 1989 was \$1.12 per gallon. Taking into account methanol displacement, production cost, taxes, markups and distribution cost, the incremental cost of gasoline displaced is equal to \$1.01/gallon or 11¢/gallon less than the national average.

A further cost comparison was made with other biomass derived alcohol production processes. Comparing ethanol produced by acid and enzymatic hydrolysis, methanol produced by steam-oxygen gasification and ethanol produced by fermentation. Hydrocarb methanol for a 5000 DMT/day biomass plant costs from 50% to 75% less, on a lower heating value (LHV) basis, than the other ethanol or methanol processes as reported in the literature..

### **CONCLUSION**

The Hydrocarb process has the potential, if the development objectives are achieved, to produce alternative transportation fuel from indigenous resources at lower cost than any other biomass conversion process. Our comparisons suggest the resulting fuel can significantly displace gasoline at a competitive price while mitigating CO<sub>2</sub> emissions and reducing ozone and other toxics in urban atmospheres. This general conclusion could also apply to stationary power generation in peaking and combined cycle power generation plants.

## GAS RECOVERY AND UTILIZATION FROM MUNICIPAL SOLID WASTE LANDFILLS

Todd A. Potas  
RUST Environment & Infrastructure  
3033 Campus Drive, Suite 175  
Minneapolis, MN 55441  
(612) 551-1001

### INTRODUCTION

Landfill gas recovery and utilization can be a viable energy resource. This gas, which is composed mostly of methane, carbon dioxide and minor amounts of non-methane organic compounds (NMOCs), is generated by anaerobic degradation of the municipal solid waste (MSW) in place. Although landfills are required to place a clay cap over the MSW to contain the gas generated, as well as to minimize environmental exposure to any other biological and chemical hazards, the cap can be breached by many mechanisms, including; gas migration through and around the cap, leachate migration, rain water erosion and heavy equipment activities. Therefore, MSW gas will eventually migrate out of landfills and be emitted to the atmosphere. Air emissions of NMOCs and methane from landfills are of concern, as there are over 6000 active MSW landfills nationwide as of 1987 with the potential to emit annually over 283,000 tons of NMOCs and over 12 million tons of methane (1). In addition, there are over 32,000 closed solid waste disposal facilities in the United States, many of these facilities having received MSW (2).

Gas recovery systems installed at landfills have been proven to effectively capture high quality gas (greater than 500 Btu/cubic foot). New Source Performance Standards (NSPS) for new and existing MSW landfills have thus been proposed by the US Environmental Protection Agency which outline minimum control requirements for gas recovery and subsequent combustion or utilization of the NMOCs in the landfill gas. These rules are proposed as 40 CFR Parts 51, 52 and 60, Standards of Performance for New Stationary Sources and Guidelines for Control of Existing Sources: Municipal Solid Waste Landfills; Proposed Rule, Federal Register, May 30, 1991.

Landfills required to comply with this proposed rule will be any new or operating landfill with the potential to emit more than 167 tons of NMOCs/yr (150 Megagrams/year) and closed landfills that have accepted waste since November 8, 1987. Assuming an average gas generation potential of 230 cubic meters/megagram (7374 cubic feet/ton) and an average NMOC concentration of 8,000 ppm NMOC (as hexane) in the landfill gas, any landfill that has or is accepting over 50,000 tons of MSW/year (45,400 Megagrams/yr) or that has a total of 750,000 tons of MSW in place would be required to comply with the proposed rule (1). A landfill of this size will generate approximately 280,000 cubic feet of landfill gas per day or, assuming 500 Btu/cubic foot in the gas, 5.8 MMBtu/hr. Testing the actual NMOC concentrations and gas flow rate from the landfill to show that the landfill gas emissions are actually under the threshold is possible and the procedures to show this are also outlined in the NSPS.

Landfills of the size mentioned will be required to show that their emissions are below 167 tons/year threshold of NMOCs by source testing, or the minimum gas collection and combustion requirements of the pending NSPS, which is referred to as "Best Demonstrated Technology" (BDT) to control the NMOC emissions, must be implemented. BDT is the combination of an active gas collection system and a combustion device with 98% NMOC combustion efficiency. Figure 1 shows a diagram of a model landfill with an active gas collection system, an energy recovery unit and two types of combustion flares (open and enclosed) (3). The diagram also shows other necessary ancillary equipment for gas recovery and utilization, such as a slurry cut-off wall, a leachate collection system and perimeter vents. A landfill with the equipment illustrated would be expected to comply with the proposed NSPS.

## DISCUSSION

The minimum requirement for complying with the proposed rule in terms of simplicity of operation is an active gas collection system and an open flare. Candle flame type open flares are relatively inexpensive to install and operate. However, it is not possible to accurately sample air emissions from open flares. In addition, the open flare has no defined residence time at temperature and is aesthetically unpleasant due to the sight of the candle flame. Open flares are also difficult to control and can be subject to flame out during high winds. Therefore, it is difficult to predict the air emissions from open flares over an extended period of time, although the open flare is a dramatic improvement over venting landfill gas directly to the atmosphere.

Alternatively, enclosed flares; 1) provide for stack emissions measurement, 2) have a defined residence time, and 3) keep the flame hidden. This is due to the defined combustion chamber created by the stack of an enclosed flare. They also provide better mixing and temperature control in the combustion chamber, assuring more complete combustion. Therefore, the enclosed flare can be expected to perform with more dependability in keeping air emissions to a minimum than an open flare.

A deficiency of both types of flares is that they do not make use of the landfill gas as a fuel (energy) source. There are two major types of heat engine electrical generation systems that are capable of utilizing landfill gas for electrical power generation. The two types are reciprocating internal combustion engines and gas turbines. There are several advantages and disadvantages to each utilization option.

### Reciprocating Engines

Reciprocating engines are popular due to their flexibility, low capital cost, low gas pressure and small size (base units start at 0.8 MW (1200 HP)). It is easy to add and subtract units with variations in the landfill gas generation or the size of the collection system and they operate with low maintenance costs. In addition, when the reciprocating engines are operated at low operating pressure (12 - 30 psi), there is less gas compression condensate to handle and treat than if operating at high operating pressure (60 - 160 psi). The disadvantage of reciprocating engines are their relatively low combustion efficiencies as compared to turbines; 80% for internal combustion engines compared to 99+% for gas turbines. This results in low overall efficiencies for power generation and relatively higher air emissions for the same amount of gas combusted.

## Gas Turbines

Gas turbines have the advantage of being highly efficient systems for electrical power generation, which results in relatively low air emissions. However, these two advantages come at the expense of several disadvantages; high capital and operating cost, limited flexibility, larger base capacity and higher maintenance costs than reciprocating engines, and the creation of large amounts of gas condensate. The gas compression condensate must often be treated as a hazardous waste. In addition, the turbines need a dependable gas source to operate efficiently. Both types of systems, turbines and reciprocating engines, are most efficiently operated when a flare is used as a back-up and/or as a supplemental combustion source to respond to fluctuations in landfill gas generation.

## Air Emissions Comparison

The air emissions generated from the landfill operations are obviously of highest concern when the landfill gas is vented directly to the atmosphere. The addition of an active gas collection system and combustion control system of the types mentioned above relieve this concern dramatically. Once installed, the emissions from an active gas collection system itself are near non-existent due to the negative pressure maintained in the system and the relatively non-porous landfill cap. Only infrequent cases of gas well maintenance or isolated landfill gas pockets breaching the cap would likely cause any significant amount of emissions. Minor amounts of volatile organic compound (VOC) emissions are generated from condensate water collected from gas collection system pumps, exposed manholes and vents, water storage tanks and turbine or reciprocating engine compressors, as the water will contain a small percentage of soluble and insoluble VOCs.

A comparison of the emissions from the three combustion sources discussed, enclosed flares, reciprocating internal combustion engines and gas turbines, is shown in Table 1. Data for the table was generated from averaged actual compliance stack testing using the number of tests shown in the title block for each type of unit tested. The emissions data shown as referenced for each type of combustion system is from reference (3). Data has been included for both low pressure and high pressure reciprocating internal combustion engines. The enclosed flare data can be used to estimate the emissions for an untested open flare, assuming well-maintained operation and temperature control.

There are several points to note when comparing the emissions data for the landfill gas combustion units discussed.

- 1) The sulfur dioxide emissions for the turbines and the reciprocating engines were quite low, just as they are for natural gas combustion. This is expected as landfill gas is typically low in sulfur, usually below 200 ppm in total sulfur compounds. Sulfur dioxide was not measured in the test data shown for the enclosed flare. The reference information shows an average value of 0.006 lbs/MMBtu for flares, reciprocating engines or turbines.
- 2) Carbon monoxide (CO) emissions were found to be relatively high for the reciprocating engines and the enclosed flares, while being low for the gas turbines. This

can be an important consideration if the landfill is located in a metropolitan area which is non-attainment for CO. The turbine option is, therefore, a good possibility for many metropolitan areas of the United States.

3) Nitrogen oxides (NOx) emissions were higher for the reciprocating engines compared to the gas turbines and the enclosed flare. The reference data showed the same trend, although the NOx emissions for the actual reciprocating engine tests averaged over 3 times higher than for the reference data. It is unknown why this was the case.

4) The NSPS for new and existing MSW landfills has indicated that the VOC destruction efficiency for the flare, the reciprocating engine and the gas turbine is expected to be greater than 98%, if the systems are operating properly at appropriate operating temperatures. Note the low or not detected VOC emission values for the three combustion systems shown in Table 1.

5) In general, the actual test data matched the reference information quite well, especially the general trends of the data comparing the various sources. The largest deviation of the actual data from the reference data was the higher NOx and CO emissions for the reciprocating engines than shown in the referenced data. Consideration for the carbon monoxide emissions and nitrogen oxide emissions, which could be of major significance in metropolitan areas of non-attainment for CO and ozone must be taken into account concerning air quality compliance issues.

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**TABLE 1  
EMISSIONS DATA FOR LANDFILL GAS COMBUSTION AND UTILIZATION SYSTEMS**

<b>3.8 MW TURBINES (44 MMBtu/hr) (2 turbines tested - 6 tests conducted)</b>				
	<b>NOX</b>	<b>SO2</b>	<b>CO</b>	<b>VOC</b>
Average	0.098	0.015	0.006	0.008
Maximum	0.118	0.035	0.010	0.009
Minimum	0.044	0.00	0.004	0.005
Gas Turbine* Reference Data	0.053	0.006	0.025	NA
<b>1200 HP High Pressure Reciprocating Engines (9.3 MMBtu/hr) (1 engine tested - 4 tests conducted)</b>				
	<b>NOX</b>	<b>SO2</b>	<b>CO</b>	<b>VOC</b>
Average	0.536	0.013	0.704	0.098
Maximum	0.763	0.018	0.818	0.111
Minimum	0.361	0.007	0.552	0.082
<b>1200 HP Low Pressure Reciprocating Engines (9.3 MMBtu/hr) (6 engines tested - 19 tests conducted)</b>				
	<b>NOX</b>	<b>SO2</b>	<b>CO</b>	<b>VOC</b>
Average	0.734	0.073	0.519	0.060
Maximum	0.936	0.204	0.685	0.075
Minimum	0.429	0.008	0.236	0.050
Internal Combustion* Reference Data	0.222	0.006	0.518	NA
<b>78 MBtu/Hr Enclosed Flare (2 flare tested - 6 tests conducted)</b>				
	<b>NOX</b>	<b>SO2</b>	<b>CO</b>	<b>VOC</b>
Average	0.019	NM	0.089	ND
Maximum	0.020	NM	0.106	ND
Minimum	0.017	NM	0.059	ND
Enclosed Flare* Reference Data	0.01	0.006	0.116	NA

**NOTES:**

ND - Not Detected    NM - Not Measured    NA - Not Available

All Data is Listed as Lbs/MMBtu

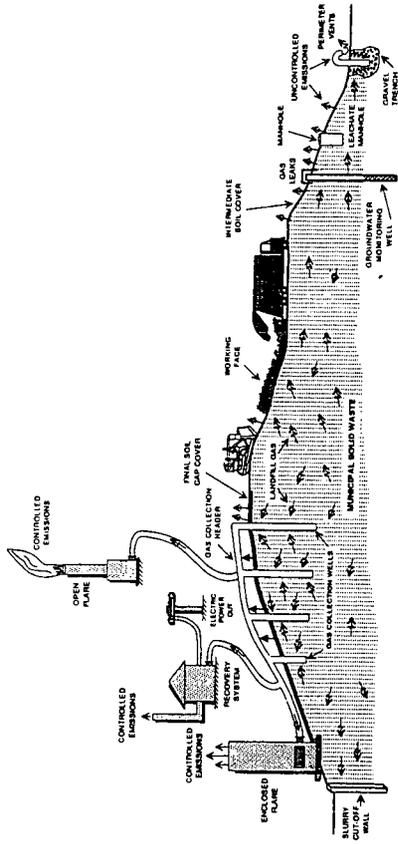
VOC Data listed as Total Hydrocarbon Emissions

\*Reference: Air Pollution Engineering Manual, AWMA, 1992.

Calculations assume 1 Ft<sup>3</sup> of LFG = 500 Btu. Assumed efficiency for turbine was 43%.

Assumed efficiency for reciprocating engines was 32%.

**FIGURE 1**  
**DIAGRAM OF A MSW LANDFILL WITH GAS COLLECTION AND RECOVERY SYSTEMS**



## USE OF WASTES FOR FUELS AND CHEMICALS

Robert Clyde  
Clyde Engineering, POB 740644  
New Orleans, LA 70174

**KEYWORDS:** Soil, Fungi, Toxic metals

### INTRODUCTION

Fibers from old cardboard boxes have high surface area for immobilization of cells which can degrade spilled fuels and produce other chemicals. When Celite is entrapped in the fibers, even more area is provided. A device for supplying oxygen quickly to cells is described.

### SOILS AND LAGOONS

Shulman (1) describes how the military has contaminated soils in many parts of the world with jet fuel and TNT. Wood preserving sites have also contaminated soils with chlorinated compounds. These toxic materials are getting into drinking water. White rot fungus degrades these toxic materials but it needs air to grow. When grown on sawdust and buried, it doesn't do a good job for lack of air even when tilled once a week, but when grown on old cardboard boxes, air is entrapped in the corrugations. Landfills consist of 12% cardboard boxes (2) so these are readily available. White rot fungus is sensitive to larger amounts of TNT (3) but on the inside of the corrugations it is protected. The boxes can also be weighted and put into lagoons. A device for putting fungi on boxes is shown in Fig. 2

Supplying air or oxygen for growing fungi is a problem because of low solubility (about 10 ppm). When holes are put in the valleys (Fig.1) of the corrugations and rotated in a half full device, liquid is carried up into the vapor space and falls down through the holes. Mass transfer to droplets is 10-15 times that to a flat surface (4). A US patent (5) covers cells on rotating fibers.

### TAXOL FOR CANCER

Taxol can be obtained from the bark of a yew tree but this kills the tree which grows very slowly. Scientists in Montana (6) have found a fungus that produces taxol. In the same article, the National Cancer INstitute has said it has "tremendous implications" for taxol production and Prof. Demain from MIT has said a problem would be to supply oxygen. A device as described in the previous section would supply oxygen much faster. Many women die of breast cancer and taxol is effective against other cancers too.

## TOXIC METALS

Lead and six valent chromium are very toxic. Over 100 cities exceed the limit of 15 ppb of lead. When Zymomonas mobilis was grown on Tyvek fiber from DuPont, it removed lead and chromium in a few seconds. A control with nutrient but no Zymomonas did nothing. Large amounts of metals were removed and small amounts also (21 ppb to 3). Lead was analyzed with a Hitachi Z-8100 polarized Zeeman atomic absorption spectrometer with a graphite furnace. A lab corrugator has been made from an old washing machine wringer so other fibers can be corrugated. Patent 4,530,763 describes uranium removal. For valuable metals like silver, brushes between the discs remove the cells as in patent 4,600,694.

## ETHANOL

Old cars and trucks still use leaded gasoline but ethanol has high octane and doesn't need lead. Old newspapers can be hydrolyzed to sugar and the sugar fermented to ethanol in 10-15 minutes as described by Clyde (7). Wayman (8) describes this as "remarkable." Bringi and Dale (9) put yeast on a single fiberglass disc and got "high rates of mass transfer...at low agitator speeds." They rotated at 90 rpm but we have found that 20-30 works well so less power is used for agitation. Ingram (10) puts the Zymomonas gene into E.coli so cellulose can be fermented. E.coli grows on fibers too. Old newspapers can be alternated with plastic (similar to the grooves in the ceiling below fluorescent lights) as in Fig. 2. There are health problems with MTBE. It gets into the blood.

## CALCIUM MAGNESIUM ACETATE

Salt causes much damage to roads and bridges. CMA can be made with Clostridium on rotating fibers (11). Mathews makes calcium magnesium propionate (12)

## COAL

Beer at MIT (13) sprays CMA into burning coal to remove most of the sulfur. Clostridium also converts syn gas to chemicals.

## RICE HULLS

Rice hulls are wasted but can be used for growing cells to degrade chemicals or produce chemicals.

## LACTIC ACID

Fast food containers are filling up landfills. Lactic acid can be made with a rotary biological contactor half full with air in the top. Polymers of lactic acid are biodegradable.

## OTHER APPLICATIONS

Pseudomonas putida grows on fibers as in example 6 of patent 4,530,763. At a meeting of the American Society of Microbiol. in New Orleans, Jackson (talk Q216) degraded toluene, Frackman removed cadmium (Q78) and Babu degraded cyanide (Q312). When an RBC with circular discs is rotated and a light shone in the top, the light hits a thin moving film as in patent 4,446,236. In other photo reactors, colored solution blocks the light. Titania can be entrapped in the fibers. Drops are also made from polyurethane foam as in patent 4,333,893. Scientists at Tufts University gave talk 151c at the Miami AIChE meeting describing putting nutrient down between small polyester discs in a zig zag fashion as in Fig. 3 and a well known company in New Jersey does the same. When cells are immobilized on rotating discs, however, the nutrient makes a large circle before going through holes to the next disc as in Fig.4.

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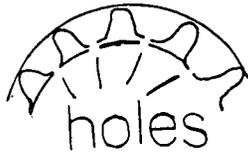


Fig.1

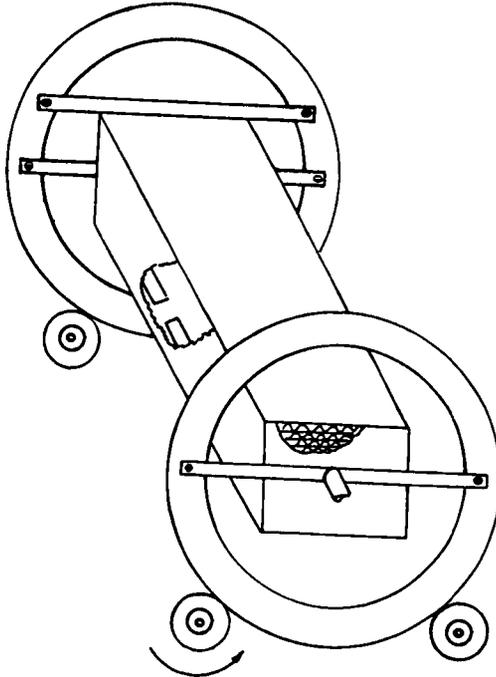


Fig.2

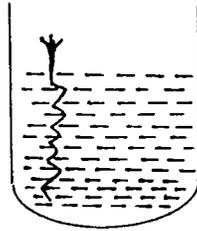


Fig. 3

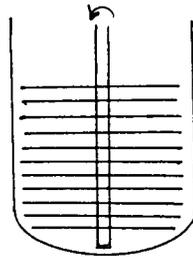


Fig. 4