

Gasification of Agricultural Residues (Biomass): Influence of Inorganic Constituents

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Four different biomass samples are included in this study, viz., sphagnum peat, wheat straw, sugar beet pulp, and potato pulp. They were chosen to represent a wide range of plant origin and inorganic content. This paper represents a preliminary investigation of an approach based on pyrolysis of biomass to produce volatile products and chars, followed by gasification of the chars. The particular interest lies in the investigation of the influence of the indigenous metal ions on the rate of gasification. Carbon dioxide has been used for the gasification, and the biomass was analyzed for nine metals, uronic acids (which are implicated in the binding of inorganic counterions), protein, and Klason lignin. The highest individual metal ion content was 13 964 ppm of potassium in potato pulp, and the gasification rates, under constant conditions, covered up to a 20-fold range, with char from potato pulp being the most readily gasified and char from peat the most resistant. The correlation of gasification rates with content of the major metal ions (alkali metals and alkaline earths) was poor. However, a high level of correlation was observed when wheat straw was omitted. It is speculated that the latter biomass may be anomalous with respect to the other three because of its high silica content.

Thermochemical conversion of biomass continues to be a topic of active research. The predominant approaches involve either pyrolysis to oils (with or without hydrogenation), i.e., liquifaction, or alternatively direct gasification of the biomass to combustible gases. These two approaches involve "overlapping" chemistry. The production of pyrolysis oils also generates chars, which are potential substrates for the approach described in this paper. Direct gasification involves complex chemistry, and the gases produced may include both primary pyrolysis products and also secondary reaction products, e.g., from reaction of pyrolysis water with char to produce water gas. One of the major disadvantages of direct gasification is the inevitable simultaneous production of tars, phenols, and acids, which must normally be removed by washing the gases before they are used for combustion. The composition of the gases is also complex (even after washing), and hence they have limited use for synthesis purposes. We have adopted the approach that in some circumstances the optimum route for utilization of biomass may be to pyrolyze at moderate temperatures to produce volatile pyrolysis products plus char and then separately to gasify the char, e.g., with CO₂ to CO or with H₂O to CO + H₂. The gasification products from chars are clean and have higher value as synthesis gases (e.g., for methanol).

We have previously described the catalytic influence of metals and metal ions on pyrolysis (DeGroot and Shafizadeh, 1984a) and on gasification of biomass chars (DeGroot and Shafizadeh, 1984b; DeGroot and Richards, 1988a). These effects have been studied by addition of salts to wood (DeGroot and Shafizadeh, 1984b) and also by systematic variation of the indigenous metal ions in wood from which chars are then produced (DeGroot and Richards, 1988a). In the latter studies the metal ions are held as counterions to the uronic acid constituents

of the cell wall and can be controlled by standard ion-exchange procedures (DeGroot, 1985). On the basis of this background, we have embarked on a systematic study of gasification of chars from biomass. We propose to select a wide range of biomass materials, where possible of low or negative economic value, in which the metal ion content is high. It is anticipated that chars from such substrates may often gasify rapidly (and hence at low cost) and that an ultimate correlation of the nature and amount of metal ions with char gasification rates may throw further light on mechanisms of catalysis of carbon gasification. The morphology and chemical nature of the various biomass sources will differ widely, in addition to the variation in metal ion content, but our present expectation, based on prior studies of wood and cellulose, is that the latter aspect will be dominant in its influence on char gasification rate.

EXPERIMENTAL SECTION

Biomass Samples: Preparation and Analyses. The peat sample of the sphagnum/woody type was a commercial gardening peat. Wheat straw was from winter wheat, and the sugar beet and potato pulps were gifts from the Sugar Co. (Malmo, Sweden) and Starkelsen (Kristianstad, Sweden), respectively. The air-dried samples were milled in a Cyclotec mill (Tecator AB, Hoganas, Sweden) to pass a 0.5-mm screen. From this, a 20-40-mesh fraction, which represented the major part of the milled materials, was used for the experiments without any other treatment.

Before analysis of the uronic acid anhydride and Klason lignin values, samples (3.000 g) were extracted in screw-capped glass tubes (100 mL) with 80% aqueous ethanol (3 × 75 mL; 15 min) at room temperature in an ultrasonic bath (a method proven to be an effective and lenient method for removal of both hydrophilic and lipophilic low molecular weight extractives). Each extraction was followed by centrifugation for 10 min and decantation of the supernatant, which was discarded. The uronic acid and Klason lignin contents were determined in the residue as previously described (Theander and Westerland, 1986) by a decarboxylation method and as a residue after removal of the polysaccharides by sulfuric acid treatment, respectively.

Metals were determined on the unextracted samples at the

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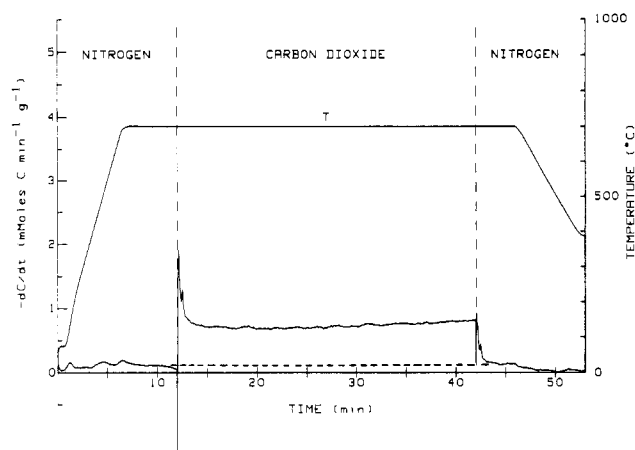


Figure 1. Reaction rate profile for the gasification of potato pulp char (HTT 750 °C) at 700 °C.

National Swedish Laboratory for Agricultural Chemistry (Uppsala, Sweden), using a Perkin-Elmer 5000 atomic absorption spectrometer after digestion in $\text{HNO}_3\text{-HClO}_4$ (7:3, v/v).

All values are on a dry-matter basis, determined by oven drying at 105 °C for 18 h. Ash and crude protein (% N \times 6.25) were determined on the unextracted samples (AOAC, 1975).

Chars from Biomass Samples. Chars were prepared by carbonization of the biomass samples at five selected heat treatment temperatures (HTT), viz., 600, 700, 750, 800, and 900 °C. A porcelain boat containing 200–400 mg of the sample was introduced into a preheated (± 2 °C control) horizontal tube furnace purged with flowing nitrogen (40 mL min^{-1}). Traces of oxygen were removed from the nitrogen stream by passing it through a high-capacity oxy-trap (Alltech Associates). The sample was heated for 10 min, and the boat containing char was then pulled into a water-cooled tube at the upstream end of the furnace tube, where it was cooled to ca. 15 °C under nitrogen before being exposed to the air. The char samples were stored in a desiccator purged with nitrogen.

Determination of Gasification Rates. Gasification was carried out in a gasification reactor/detector system that has been described in detail previously (DeGroot and Richards, 1988a). The char (3–5 mg) in the reactor was heated (e.g., at 700 ± 2 °C) under 20 mL min^{-1} flow of N_2 for 5 min and then gasified under 20 mL min^{-1} flow of CO_2 (Matheson, 99.99%) for 30 min. The effluent gases from the reactor were mixed with 10 mL min^{-1} air flow before entering a zirconium oxide oxygen detector maintained at 680–700 °C. The oxygen level of the air flow was reduced by the stoichiometric quantity of oxygen required for the combustion of combustible gases formed by pyrolysis or gasification of the sample. The oxygen concentration of the combined gas streams was monitored by the detector, and changes in oxygen concentration were related to the rate of production of combustible gases by a microcomputer-based data acquisition/control unit. The rate was expressed in terms of millimoles of carbon gasified per unit time per gram of char. For the purposes of this study, it was assumed that the only combustible gas produced was CO by the reaction $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$. The removal of 1 mol equiv of O_2 from the gas stream was therefore due to gasification of 1 mol equiv of carbon.

A representative gasification rate profile is shown in Figure 1. Some pyrolysis normally occurred during heating under N_2 prior to gasification. After the reactor temperature was stabilized and a base line (the dotted line in Figure 1) had been established to indicate the rate of pyrolytic gasification at this temperature, CO_2 was valved into the reactor and the rate of gasification increased sharply. The rate was monitored for 30 min, and then N_2 was valved into the reactor in place of CO_2 . The reactor was next cooled to 400 °C to establish a base line free of pyrolytic gasification. The total extent of gasification due to reaction with CO_2 was calculated by digital integration of the detector response above the pyrolysis base line. Blank correction was made on each sample run, and at least two experiments were performed with each char and the average values used.

Table I. Analyses of Biomass Samples^a

	sphagnum peat	wheat straw	sugar beet pulp	potato pulp
uronic acid anhydride	5.2	2.4	16.0	11.7
Klason lignin	35.9	19.9	1.5	2.6
crude protein	3.6	3.0	10.8	5.0
ash yield	1.23	4.29	3.03	3.40
sodium	103.9	80.0	678.3	111.0
potassium	169.4	8000.7	5854.0	13964.5
magnesium	515.9	556.1	1393.8	508.6
calcium	770.0	2927.1	5668.1	795.3
manganese	12.8	18.3	47.1	4.2
iron	405.8	82.0	106.8	22.6
cobalt	<0.4	<0.5	<0.5	<0.5
nickel	<0.6	<0.7	<0.7	<0.7
copper	2.1	6.6	4.1	3.2

^a Units: Metals are reported as milligrams per kilogram and all other values as percent. All values are on a dry-matter basis.

Table II. Char Yields^a

	HTT, °C				
	600	700	750	800	900
sphagnum peat	25.5	22.3	21.1	19.5	17.6
wheat straw	21.2	19.3	18.6	18.0	15.7
sugar beet pulp	21.2	19.1	17.9	16.0	15.0
potato pulp	22.8	20.4	19.0	16.7	16.4

^a Units: Percent of biomass (dry ash-free basis), assuming no ash loss during pyrolysis; mean of two determinations.

RESULTS AND DISCUSSION

The four biomass samples were chosen to originate from a wide range of plant species and plant function; all of them are potentially available on a large scale and at relatively low cost, although the value of the sugar beet and potato pulps will be especially sensitive to the question of whether they find local use as animal feed. A range of chemical analyses is shown in Table I. The total ash contents do not correlate well with uronic acid content, and this probably indicates that in the sugar beet and potato pulps (especially the former) the uronic acid is present mostly as pectic substances in which some of the carboxyl groups are significantly esterified and hence do not bind metal ions. The Klason lignin of the peat will include humic compounds (Theander, 1983) and also acid-insoluble products from polyphenols. The peat sample used in the present study was of the sphagnum type, but with substantial contribution from woody sources. We have previously shown that sphagnum mosses and peat contain very low amounts of lignin (Theander, 1983). The major metal ion contents cover a very wide range. The high iron in peat presumably results from preferential binding of polyvalent iron from ground water during peat formation. The other three biomass samples all contain high calcium, which is likely to be present predominantly in cell wall material, and high potassium, which probably originates (with magnesium) in protoplasm. The wheat straw contains less total metal ions than the two pulps but gives a higher ash yield. This is because the straw contains significant silica.

The char yields from pyrolysis of the samples are shown in Table II for several different pyrolysis or heat treatment temperatures. There is little difference in char yields, despite the major differences in metal ion content (e.g., between peat and potato pulp). In previous studies in which inorganic salts were added to wood, the char yield was significantly increased, especially by the presence of alkali-metal salts (DeGroot and Shafizadeh, 1984b). However, it has also been shown that lignin and other poly-

Table III. Gasification and Pyrolysis of Chars^a

HTT, °C	sphagnum peat	wheat straw	sugar beet pulp	potato pulp
600	2.2 (11.4)	6.1 (9.0)	13.5 (9.0)	21.6 (9.5)
700	4.0 (6.4)	6.0 (4.7)	16.0 (6.9)	25.9 (6.0)
750	3.4 (6.8)	5.5 (4.6)	16.9 (3.6)	27.4 (4.7)
900	1.1 (3.1)	1.1 (0.5)	13.7 (1.7)	20.7 (2.3)

^a Conditions: Gasification in CO₂ at 700 °C for 30 min. The first value represents the percent of char gasified and the value in parentheses represents the percent weight loss by pyrolysis. All values are based on the ash-free content of char.

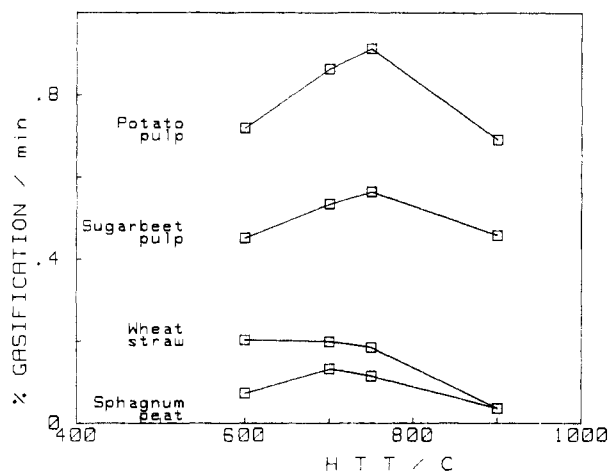


Figure 2. Effect of HTT on the rate of gasification of biomass chars at 700 °C.

phenols pyrolyze to char in much higher yield than polysaccharides (Sadakata et al., 1987). In Table II therefore we probably see a high char yield from peat because of the high polyphenol and humus content (showing as lignin in Table I) and high char yields from the other three samples due to influence of high inorganic content on polysaccharide pyrolysis to char. The decrease in char yield as HTT increases from 600 to 900 °C is about 25%, which obviously represents a reduction in yield of material for gasification. In any economic assessment of these processes, however, the optimum HTT would depend on several factors. The rate of gasification is dependent on HTT (see below), and also at lower HTT's, we see more production of pyrolysis products during gasification, which could be either an advantage or a disadvantage, depending on the ultimate use of the gasification products.

Table III shows the extent of pyrolysis and of gasification of chars prepared from the four biomass samples at different HTT's and gasified for 30 min at 700 °C. Char from a pure cellulose (Whatman CF11) showed no significant gasification rate at this temperature. Unless the pyrolysis temperature is significantly higher than the gasification temperature, a part of the weight loss is due to pyrolysis and part to gasification, and these two effects are determined and reported separately by methods described in detail earlier (DeGroot and Richards, 1988a) and briefly described in the Experimental Section. A pyrolysis-gasification profile for char from potato pulp is shown in Figure 1. In the peat and straw samples with HTT 600 °C and gasification at 700 °C, the pyrolysis exceeds gasification, but with the two pulp samples the gasification is so rapid that it exceeds pyrolysis under all of the conditions studied. It is evident that there is an optimum HTT for maximum gasification, and this effect is illustrated in Figure 2 for rate of gasification at 700 °C plotted against HTT. The maximum is most marked with the most reactive chars and occurs at

Table IV. Correlation Coefficients (r) for Metal Ion Content (Millimoles/100 g of Char) versus Char Gasification Rate at 700 °C (HTT 700 °C)

	all four biomass samples plus cellulose	wheat straw omitted
K + Ca	0.8289	0.9742
K + Ca + Na	0.8298	0.9610
K + Ca + Mg	0.8233	0.9549
K + Ca + Na + Mg	0.8204	0.9390

about 750 °C HTT. Similar effects have been noted previously for wood chars (DeGroot and Richards, 1988b). The type of char most reactive to gasification at all HTT values is that from potato pulp. The simplest interpretation is that this effect is associated with the very high potassium content of the potato pulp. The char from sugar beet pulp, however, is only slightly less reactive, while containing much less potassium and much more calcium. Evidently then, both potassium and calcium are catalyzing the gasification. There is no indication that the high iron content of the peat results in significant catalysis of char gasification, despite the fact that iron has been shown to exhibit high initial catalytic activity in previous studies (DeGroot and Shafizadeh, 1984b).

We have made a preliminary attempt to correlate char gasification rates with various groupings of metal ion contents in the chars from the four biomass types, and the resultant correlation coefficients are shown in Table IV, including char from pure cellulose with total metal ion content less than 100 ppm and zero gasification rate. This table shows correlations only for char of HTT 700 °C, but similar correlations were also obtained for HTT ranging from 600 to 900 °C. These values show that a tentative approach to correlation can best be achieved by including all of the major alkali- and alkaline-earth-metal components and only three of the four biomass samples, i.e., by excluding chars from the wheat straw. The first effect is to be expected, since salts of these metal ions have been shown to catalyze gasification (DeGroot and Shafizadeh, 1984b). Our preliminary explanation of the second effect is that the char from wheat straw is less reactive to gasification than would be expected from its metal ion content because some of the potassium becomes "deactivated" as a catalyst by reaction with silica during pyrolysis [cf. Kuhn and Plogann (1983)]. The very tentative conclusion therefore is that the chars from the three biomass samples other than wheat straw show some correlation of total content of alkali and alkaline-earth metals, but we intend to pursue the question of this type of correlation and the effects of silica over a much wider range of biomass materials in the future.

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Registry No. Na, 7440-23-5; K, 7440-09-7; Mg, 7439-95-4; Ca, 7440-70-2; Klason lignin, 8068-04-0; manganese, 7439-96-5; iron, 7439-89-6; cobalt, 7440-48-4; nickel, 7440-02-0; copper, 7440-50-8.

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Bioaccumulation of Cinmethylin in Bluegill Sunfish

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Technical cinmethylin and Cinch 7EC herbicide showed low toxicity against various aquatic organisms. The bioaccumulation potential of [¹⁴C]cinmethylin in the bluegill sunfish under a dynamic flow-through system at a constant concentration of 0.1 mg/L was examined. A rapid uptake of radioactivity was observed. Tissue residues plateaued after 3 days, and the mean tissue residues after 28 days of exposure were 35, 12, and 58 μg/g (ppm) for the whole fish, fillet, and viscera, respectively. The corresponding bioconcentration factors for the above tissues were 360, 120, and 600, respectively. Greater than 99% of the tissue residues was eliminated from the exposed fish after the 14-day depuration period. In addition to [¹⁴C]cinmethylin, major metabolites isolated from the treated fish were α-carboxycinmethylin and 8-hydroxy-α-carboxycinmethylin. *o*-Toluic acid and α-hydroxycinmethylin were observed as minor components.

Cinmethylin [7-oxabicyclo[2.2.1]heptane, 1-methyl-4-(1-methylethyl)-2-[(2-methylphenyl)methoxy]-, *exo*-] (1) is the active ingredient of Cinch 7EC herbicide. The *exo* diastereomer of this compound exhibited broad-spectrum preemergent herbicidal activity against various grassy weeds in soybeans, peanuts, and cotton (Peterson et al., 1983). Technical cinmethylin and Cinch 7EC herbicide showed low toxicity against various aquatic organisms (Table I). In order to assess its potential impact to the environment, the bioaccumulation potential of cinmethylin in the bluegill sunfish was examined. Major objectives of this report are to describe (1) the accumulation and depuration rates of [¹⁴C]cinmethylin residues in the fish and (2) characterization and identification of significant tissue residues.

EXPERIMENTAL SECTION

Test Materials and Reference Standards. Radiolabeled [*phenyl*-¹⁴C]cinmethylin and appropriate reference standards were synthesized at Shell's Biological Science Research Center, Modesto, CA (Lee et al., 1986). Chemical structures of these compounds are presented in Figure 1. The specific activity and

radiochemical purity of the test material were 56.4 μCi/mg and greater than 98%, respectively.

Test System. The in-life portion of the study was conducted by Analytical Bio-Chemistry Laboratories, Inc. The bioaccumulation of [¹⁴C]cinmethylin in the bluegill sunfish was conducted in 100-L glass aquaria containing 70 L of water. Test aquaria (one control and one treated) were immersed in a water bath and held at 22 ± 1 °C through the use of submersible heating elements.

A proportional diluter system described by Mount and Brungs (1967), with modifications of McAllister et al. (1972), was used for the intermittent introduction of [¹⁴C]cinmethylin in water into the test aquarium. The final specific activity of the ¹⁴C test material was 0.57 μCi/mg by the appropriate dilution of the ¹⁴C stock solution with unlabeled cinmethylin. Aerated well water (pH 8.2, dissolved oxygen 9.3 ppm) was delivered to the glass aquaria at a rate sufficient for six volume changes in 24 h. The diluter system delivered a nominal concentration of 0.1 mg/L cinmethylin.

Before the uptake portion of this study was initiated, the test solution was allowed to flow through the test aquaria for a 24-h equilibration period. The test concentration was confirmed by radioanalysis before the test fish were introduced. The uptake phase was initiated by transferring groups of 110 fish each to the control and treated aquaria. These fish were observed initially and every 24 h during the exposure period for mortality and adverse behavior. Water and fish were sampled at various time intervals throughout the uptake period.

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