# PRODUCTION OF FURFURAL BY DILUTE-ACID HYDROLYSIS OF WOOD: METHODS FOR CALCULATING FURFURAL YIELD

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#### ABSTRACT

The production of furfural via dilute-acid hydrolysis of lignocellulosic materials has been under study for many years. Furfural yield values have been reported to be 40–60% of the theoretical value in closed systems and 50–80% when furfural is rapidly removed from the reaction medium. Furfural yield calculations are simple in batch systems since the mass of wood charged is known. However, when continuous units are used, these calculations become difficult because the mass flow of material that is fed to the reactor is often unknown, or not measurable. To overcome this problem, two estimating methods have been developed: 1) an experimental approach based on output streams mass balance and assuming that input = output, and 2) a mathematical methodology leading to the estimation of feed mass flow. Results obtained by means of these methods have been compared with precise values resulting from complete mass balances. To validate the different computing methods proposed, experiments were carried out in a process development unit. The operating conditions within the tubular reactor were:  $H_2SO_4$  concentration: 0.6%; slurry consistency: 6.0–6.6%; reaction temperature: 200–230 C; residence time: 95–105 sec. Results have shown that calculations based on output streams are incorrect. However, those obtained by mathematical estimation are relatively accurate and require short periods of experimental manipulations.

*Keywords:* Furfural yield, estimating methods, continuous unit, steam heating, mass balance, thermal balance, yield divergence.

#### INTRODUCTION

Finite world reserves of petroleum have generated great interest in the development of physico-chemical processes for the production of chemicals and fuels. Many forms of lignocellulosic biomass, such as agricultural and forest-processing residues as well as hardwood trees, are overproduced and underutilized. The hemicellulose contained in these raw materials can be hydrolyzed easily, using mineral acids, to produce xylose and arabinose, which yield furfural on further hydrolytic attack. Moreover, it has been reported that furfural might arise from anhydroglucose units present in cellulose by means of an oxidation-decarboxylation-hydrolysis sequence (Garves 1981). Because of the ether nature of the furan ring, furfural is destroyed by dilute acids, thus producing formic acid and black resin (Sain et al.

Wood and Fiber Science, 25(1), 1993, pp. 91-102 © 1993 by the Society of Wood Science and Technology 1982). On the other hand, cellulose is simultaneously hydrolyzed to produce glucose, but at a lower rate than hemicellulose. Glucose is converted to levoglucosan via thermally activated reactions, and 5-hydroxymethylfurfural (HMF) by further hydrolytic action. The final decomposition products from glucose in an acidic medium are levulinic acid and formic acid (McKibbins et al. 1962).

Furfural was discovered by Dobereiner as early as 1832 when he was trying to synthesize formic acid from sugar by means of the catalytic action of  $H_2SO_4$  and  $MnO_2$ . It was only about a century later, in 1920, that the first systematic research was conducted in order to produce furfural from corn cobs. In 1922, Quaker Oats undertook the industrial production of furfural from oat husks (Crönert et al. 1972). Over the past fifty years, research has been carried out to better understand the chemical reactions involved in the overall process and to improve furfural yields. However, these studies were up against important difficulties, such as the heterogeneous nature of the reactions, the chemical and structural complexity of raw materials, the importance of side reactions in addition to the large number of parameters that had to be considered to conduct systematic work.

When continuous units are used, furfural yield calculations become difficult to make because the mass flow of material that is fed to the reactor is often unknown or not measurable. The main objective of the present study consists of proposing two methods for estimating the mass flow of wood fed to the reactor, thus allowing furfural yields to be determined. The results thus obtained are validated by comparing them to absolute values derived from complete mass balances. Moreover, this paper presents an extensive bibliographic study on furfural yields obtained under different operating conditions and operational modes using various lignocellulosic raw materials in order to define maximum yields that can be reached.

#### EXPERIMENTAL

### Raw material

The raw material used in the experiments was a mixed hardwood sawdust. The mixture was ground and screened, and only the smallest particle size fraction (<0.25 mm) was used. It should be noted that since grinding is a physical pretreatment that enhances the accessibility to the lignocellulosic complex, the glycosidic bonds become more accessible to hydrolytic action. The hardwood sawdust contained 20.5% of pentosans, as determined by standard methods from extractive-free wood (Browning 1963).

#### Process development unit (PDU)

The acid hydrolysis experiments were performed in a process development unit (Fig. 1) located at the Université de Sherbrooke (Canada). This PDU is composed of the following elements:

a) Feed vessel.—In order to achieve a complete mass balance, the feed vessel was charged with a precise quantity of wood of known moisture content (approximately 5%). Water was added to obtain initial consistencies of about 10%.

b) Recirculation value. — The aqueous slurry in the feed vessel (R1) was recirculated through a homogenization valve (V1) ( $\Delta P_{max} = 7.0$ MPa) to mix the wood in order to obtain a homogeneous slurry. This operation also caused a certain wood solubilization, decreasing the viscosity and thus improving the slurry pumpability.

c) Steam injector. — The slurry was heated by direct injection of live steam (S1) produced in an electric boiler (R3). The desired temperature was attained almost instantaneously, which proved to be an advantage over the typical long preheating periods necessary in electrically-heated batch reactors. However, steam injection diluted the wood slurry. The evaluation of steam flow rate was necessary to achieve mass balances calculations as well as to estimate the actual slurry concentration at the beginning of the hydrolytic treatment. Slurry consistency dropped from 9.4% to 6.0– 6.6% after steam injection.

d) Shear valve. — The heated slurry was rapidly pumped at high pressure (18–20 MPa) by a piston pump (P2) and then was discharged through a homogenizing valve (V2) to moderate pressure (3.5 MPa). Remark: controlled sudden expansion through an orifice induces structural changes (i.e., defibration/defibrillation) in the lignocellulosic matrix.

d) Acid injection system. – Sulfuric acid (9–10% wt/wt) was pumped (P5) at approximately 60 ml/min. This provided a concentration of 0.6% wt/wt in the slurry entering the tubular reactor.

e) Tubular reactor. — The reactor was a stainless steel coil (inner diameter = 1.0 cm, thickness = 1.1 mm, length = 17.2 m). Residence time (98–104 sec) varied with reaction temperature (200–230 C) because of changes in



FIG. 1. Flowsheet of the process development unit (PDU).

steam flow rate and slurry specific volume. During this period, chemical reactions, mainly acid hydrolysis, resulted in the partial solubilization of wood and subsequent dehydration reactions leading to the formation of furfural. Turbulent regime characterized the flow of the wood slurry through the tubular reactor.

f) Base injection system. —An aqueous NaOH solution (8–9% wt/wt) was pumped (P6) at about 50 ml/min at the outlet of the tubular reactor in order to neutralize the acidic slurry. This addition instantaneously stopped the hydrolytic reactions.

g) Expansion vessel. — The slurry was expanded to atmospheric pressure through a homogenization valve (V3). This flash vaporization was carried out: 1) to cool down the slurry rapidly; and 2) to separate volatile products in the vapor phase, which were condensed using a cooling coil. Apart from water, the condensate contained acetic acid, formic acid, methanol, terpenes, furfural, and HMF. Among the noncondensable gases, there was probably carbon dioxide resulting from a thermally activated decarboxylation reaction. In order to avoid losses of volatile products, the condensate from the cooling tower was absorbed in cold water.

Before beginning an experiment, the whole system was thermally stabilized by pumping water (P4). When the prescribed values of physico-chemical properties, such as temperature and pH were reached, the source of water was switched off and the slurry was admitted to the system.

The treated slurry was finally filtered and the resulting filtrate kept for further analysis. It was very important to clean the system properly between two trials using hot acid and alkaline reagents. This operation was required in order to dissolve solid build-up on reactor walls. If this operation were not performed, the residence time would have varied from one experiment to the other. In addition, washing was necessary to achieve correct integral mass balances. More details about the process development unit are available elsewhere (Carrasco 1988; Abatzoglou et al. 1990).

The process development unit was connected to a data acquisition system taking readings at intervals of 10 sec. The most important measured variables recorded were: pressure and temperature at pumps P1 and P2 as well as pressure and temperature in the tubular reactor. Control of the PDU was achieved via PID and on/off controllers.

### Product analysis

High Performance Liquid Chromatography (HPLC) was used for the quantitative determination of soluble products in the condensate and filtrate. This technique was chosen for routine analysis because of its rapidity of execution compared to silvlation and GC analysis. Reproducibility tests appeared to be satisfactory (<3-9%). The chromatograph had a BioRad HPX-87P column equipped with a Gilson #302 pump and a Rheodyne 9125 injection system. A BioRad protection column retained the ions present in the sample. The integration of peaks was achieved by means of an HP-3392A integrator. The following substances were detected and quantified in the filtrate: monosaccharides (glucose, mannose, xylose, and arabinose) and dehydration products (levoglucosan, 5-hydroxy-methylfurfural, and furfural). No oligomers were detected. Only small peaks remained unidentified. The condensate contained mainly furfural (methanol was also identified, but its quantitative determination was difficult because of its high volatility). Sorbitol was used as internal standard.

Solids content in slurries was determined by lyophilization. Since volatile products were removed using this technique, a correction had to be made to evaluate the total solids content. This method was preferred to the conventional vacuum-evaporation method since the latter was not able to remove water completely at low temperature. At higher temperatures, sugar degradation reactions could occur.

Sodium sulfate, formed by the neutralization of  $H_2SO_4$  and NaOH, was quantified by atomic absorption (Na<sup>+</sup>). Since this salt was found in large quantities, it was very important to evaluate accurately its content in order to make precise mass balances. The neutralization of  $H_2SO_4$  had to be carried out to obtain a pH = 3-4. At higher pH, sodium acetate and other organic salts were formed. At pH >7, NaOH was also found to be present. When the solution contained more than one salt, it was impossible to determine the total weight of salt since the molecular weights of the various salts were different.

### **RESULTS AND DISCUSSION**

An extensive bibliographic study was conducted in order to compile furfural yield results reported during the last forty years. Table 1 contains the best furfural yield values found in each work. Raw materials used were xylose; agricultural residues such as bagasse, rice husks, and corn stalks; black liquor; and hardwoods. The most frequently used acid was H<sub>2</sub>SO<sub>4</sub> at concentrations ranging from 0.08 to 5% wt/ wt. Slurry consistencies ranged between 5 and 20%. Reaction temperature generally varied between 150 and 250 C. Reaction times varied in a very large interval (30 sec-5 h) depending on the other operating conditions. Reactors used were either autoclaves (with or without continuous distillation of vapors formed) or continuous reactors, such as continuously stirred tank reactors (CSTR) or plug flow reactors (PFR). Processes were carried out under pressure or at atmospheric pressure. In certain cases, a co-catalyst was added (i.e., sea salt). Apart from the work of Sproull et al. (1985), all experiments were conducted with either continuous steam or water. Almost all hydrolyses were achieved in one single stage. In spite of these large intervals of operating conditions, furfural yield mostly ranged between 40-60% (percent of the theoretical) when furfural remained in the reacting medium and 50-80% when furfural was removed from the reactor (with either continuous steam or by transferring it into an organic phase in which there was no acid). These results indicate that furfural has to be separated from the acidic medium if high yields are hoped for. Industrial processes, like Quaker Oats, Savo-Rosenlew, and Agrifurane, provided yields of 49, 47, and 65%, respectively (Campana and Alves 1987). These results are in agreement with those obtained in laboratory experiments.

Furfural produced in the continuous unit de-

Raw material	Catalyst	Temp.	Time	Slurry concent.	Reactor	Yield (% of theor.)	Reference
Rice husk	CH <sub>3</sub> COOH, 0.5%	195 C	40 min		Autocl.	39%	Sharma and Sahgal 1983
Xylose	$H_2SO_4, 0.1 N$	300 C	1-2 sec	5% wt	PFR	6070%	Medeiros and Burnet 1983
Corn stalk		180 C	45 min	L/S = 8/1	Autocl.	6080%	Mital and Biswas 1977
Bagasse	$H_2SO_4, 0.5\%$	170 C	50 min	L/S = 16/1	Autocl.	41%	Nee and Yse 1975
Bagasse pith	$H_2SO_4, 0.5\%$	170 C	20 min	L/S = 13/1	Autocl.	54%	Nee and Yse 1975
Xylose	$H_2SO_4 + Salt$		2 h	2.5% wt	Autocl.	12-42%	Milov. and Corona 1971a
Bagasse	$H_2SO_4 + Salt$		5 h		Autocl.	55-82%	Milov. and Corona 1971a
Bagasse pith	H <sub>2</sub> SO <sub>4</sub> , 3%	150 C	1 h	L/S = 10/1	Autocl.	57%	Heikal et al. 1980
Bagasse	$H_2SO_4$ , 1.3%	170 C	45 min	L/S = 10/1	Autocl.	60%	Ramos 1972
Xylose	H <sub>2</sub> SO <sub>4</sub> , 4.5%	180 C	70 min	20% wt	CSTR	75%	Sproull et al. 1985
Rice straw	$H_2SO_4$ , 2%	130 C	2 h	L/S = 4/1	Autocl.	38%	Chawla et al. 1980
Rice straw	H <sub>2</sub> SO <sub>4</sub> , 1.6%	180 C	2 h	L/S = 4/1	Autocl.	41%	Bains et al. 1977
Corn stalk	H <sub>2</sub> SO <sub>4</sub> , 1.6%	180 C	2 h	L/S = 4/1	Autocl.	26%	Bains et al. 1977
Rice hull	$H_2SO_4$ , 0.5 M	185 C	2 h	L/S = 10/1	Autocl.	50%	Sharma and Sahgal 1982
Agricult. resid.	$H_2SO_4, 0.2-2\%$	150–250 C	30-200 sec	5–20% wt	PFR	63-76%	Campana and Alves 1987
Corn stalk	H <sub>2</sub> SO <sub>4</sub> , 8%	150 C	1 h	L/S = 10/1	Autocl.	60%	El-Shinnawy 1985
Black liquor	$H_2SO_4$			40% wt		30%	Maurice 1987
Bagasse	$H_2SO_4$	180 C	70 min	L/S = 1/0.3	Autocl.	69%	Milov. and Corona 1971b
Bagasse	CH <sub>3</sub> COOH, 1%	210 C	2 h			51%	Singh et al. 1984a
Bagasse	$H_2SO_4, 0.4\%$	200 C	115 min	L/S = 15/1	Autocl.	62%	Singh et al. 1984b
Rice hull	$H_2SO_4, 0.4\%$	200 C	115 min	L/S = 15/1	Autocl.	70%	Singh et al. 1984b
Hardwood	H <sub>2</sub> SO <sub>4</sub> , 0.4%	220–230 C	2 min	10% wt	PFR	52%	Abatzogiou et al. 1990
Hardwood	$H_2SO_4, 0.8\%$	220–230 C	2 min	10% wt	PFR	40-55%	Abatzoglou et al. 1990

 TABLE 1. Schematic review of maximum furfural yields obtained by acid hydrolysis of either xylose or lignocellulosic materials.

scribed in this work remained in the reactor once it was formed. Thus, expected furfural yields had to range, in the best conditions, from 40 to 60%. Some preliminary results showed that furfural yields were 70-80% (percent of the theoretical value) or higher when calculations were made by considering that solids output = solids input (this argument will be discussed later). Because of these suspicious results (when compared to those generally accepted in the literature), it was necessary to achieve complete mass balances in order to confirm or reject these values. Only two representative experiments were considered in this paper in order to analyze the different methods developed for calculating furfural yields and to discuss divergences observed when comparing them to the precise values obtained by means of an absolute method, which is based on the exact quantity of wood fed to the tubular reactor.

The operating conditions of two complete typical experiments are shown in Table 2. Residence time increased slightly as the reaction temperature increased because of the variation in the flow of steam injected as well as the change in slurry specific volume. These two temperature-dependent variables affected the total mass flow. The fluid dynamic regime of the slurry within the tubular reactor was turbulent (Re =  $1.2-1.4 \times 10^4$ , assuming that the slurry physical properties were those of water). Moreover, the length/diameter ratio was high (L/D = 1,720). Therefore, the tubular reactor behaves as a plug flow reactor, with all the fluid elements having the same residence time. Mass flow of condensate was 15 and 20% of the total mass flow at 200 and 230 C, respectively (equilibrium flash calculations, by considering the slurry as pure water, yielded 20 and 25% vapor fraction, respectively).

Furfural yield is commonly expressed as a percent of the theoretical value (i.e., g of furfural produced/100 g of potential furfural in wood fed). Thus, it is absolutely necessary to know the exact quantity of wood fed into the reactor to obtain precise results. However, installing stable flowmeters was often found not

**TABLE 2.** Operating conditions of the two typical diluteacid hydrolysis experiments chosen to test different methods for calculating furfural yield.

·····	Exp. MB1	Exp. MB2
Wood consistency in the	9.4	9.1
feed vessel (% wt/wt)		
Pressure at the inlet of	$18.7 \pm 0.1$	$19.2 \pm 0.1$
shear valve (V2)		
(MPa)		
Pressure at the inlet of	3.4	3.4
tubular reactor (MPa)		
Mixing temperature	$200.2\pm0.8$	$225.9 \pm 0.9$
(slurry fed + steam)		
(°C)		
Reaction temperature	$200.2 \pm 0.5$	$230.3 \pm 0.5$
(°C)		
Residence time in the	98	104
tubular reactor (sec)		
Mass flow of treated	808.1	718.4
slurry (g/min)		
Mass flow of condensate	143.4	179.5
(g/min)		
Total mass flow (g/min)	951.5	897.9
9.2% H <sub>2</sub> SO <sub>4</sub> mass flow	62	62
(g/min)		
H <sub>2</sub> SO <sub>4</sub> concentration in	0.6	0.6
the reactor (% wt/wt)		
8.8% NaOH mass flow	52	52
(g/min)		

to be technically viable in most of PDUs due to high pressure, geometrical constraints, pumping oscillations, etc. In order to solve this problem, three alternatives can be considered. Two are based on integral mass balances while the third one is based on a combination of differential mass balance and thermal balance.

### Complete integral mass balance (MBI)

The exact amount of wood that went through the system is achieved by calculating the difference between the mass of wood initially put into the feed vessel and the mass of wood remaining in it after the experiment. The latter was measured by lyophilization in order to take into consideration solids as well as substances solubilized during the recirculating action through the homogenization valve V1 (see Fig. 1). It is obvious that this technique is tedious and costly because of long time manip-

		Glucose (mg)	Xylose (mg)	Arabinose (mg)	Mannose (mg)	Levogluvosan (mg)	HMF (mg)	Furfural (mg)
Filtrate from the treated slurry (A)	200 C 230 C	4,622 (4,160) 6,435 (5,791)	14,568 (12,820) 2,070 (1,821)	1,185 (1,043) 594 (523)	2,402 (2,161) 1,005 (905)	360 (360) 1,927 (1,927)	367 (521) 3,998 (5,681)	1,266 (1,741) 2,795 (3,844)
Filtrate from the PDU washing (B)*	200 C 230 C	1,536 (1,383) 2,534 (2,281)	4,414 (3,885) 0	00	00	0 273 (273)	0 1,144 (1,625)	585 (804) 3,805 (5,233)
Condensate (C)	200 C 230 C	00	0 0	0 0	0 0	00	0 0	1,268 (1,743) 6,314 (8,682)
Total (A + B + C)	200 C 230 C	6,158 (5,543) 8,969 (8,072)	18,982 (16,705) 2,070 (1,821)	1,185 (1,043) 594 (523)	2,402 (2,161) 1,005 (905)	360 (360) 2,200 (2,200)	367 (521) 5,142 (7,306)	3,119 (4,288) 12,914 (17,759)
* This filtrate was obtained	from the slurry	recovered by washing th	ie PDU (excluding the feed	I vessel) at the end of t	he experiment. Values	between brackets corres	pond to equivalent we	ght of wood.

**TABLE 3.** Quantitative determination by HPLC of soluble products present in condensate and filtrates (output streams)

ulations (i.e., washing of feed vessel, filtration, and drying of large samples). However, this method leads to precise furfural yield values and will serve as reference for comparison purposes. The percent of theoretical furfural yield was calculated as the ratio between the weight of furfural produced and the weight of potential furfural fed. The furfural produced comes from three streams: condensate, filtrate from treated slurry, and filtrate from slurry recovered by washing the PDU. Quantitative determination of furfural in these solutions was achieved by HPLC (see Table 3). The potential furfural fed was evaluated by multiplying the weight of wood fed by two coefficients: 0.205 (pentosan content in wood) and 0.727 (weight conversion factor from pentosan to furfural).

# Integral mass balance based on output streams (MBO)

This method consists of taking small samples within the whole condensate, treated slurry, and slurry recovered by washing the PDU. The MBO method assumes that soluble substances and insoluble residue in output streams are equal to those in input streams (i.e., wood fed). However, weight corrections are needed for the output streams in order to take into consideration the gain or loss of weight due to hydration/dehydration reactions (i.e., addition/removal of water molecules) for all the identified soluble solids (sugars and levoglucosan), furfural and HMF. By means of molecular weights, it is possible to find out the weight of wood generating a given weight of soluble substances, such as sugars (xylose, arabinose, glucose, and other hexoses) and dehydration products (furfural, levoglucosan, and 5-hydroxymethylfurfural).

Xylose or arabinose ( $M_w = 150.1 \text{ g/mol}$ )  $\rightarrow$  Pentosan (Mw = 132.1 g/mol) Furfural ( $M_w = 96.1 \text{ g/mol}$ )  $\rightarrow$  Pentosan (M<sub>w</sub> = 132.1 g/mol) Glucose or mannose ( $M_w = 180.2 \text{ g/mol}$ )  $\rightarrow$  Hexosan (M<sub>w</sub> = 162.1 g/mol) Levoglucosan ( $M_w = 162.1 \text{ g/mol}$ )  $\rightarrow$  Hexosan (M<sub>w</sub> = 162.1 g/mol)

HMF ( $M_w = 126.1 \text{ g/mol}$ )  $\rightarrow$  Hexosan ( $M_w = 162.1 \text{ g/mol}$ )

From this reaction scheme, it is easy to evaluate the weight of soluble product resulting from a given weight of polymer in wood. For example, 100 mg of xylose are produced from 88 mg of xylan or 100 mg of HMF originates from 128.5 mg of hexosan.

Quantitative determination of all soluble products was achieved by HPLC (see Table 3). No oligomers were present. Unidentified peaks were only at the trace level. Complete integral mass balances are depicted in Table 4 for experiments having lasted approximately 220– 225 sec.

The percent of theoretical furfural yield was calculated as the ratio between the weight of furfural produced and the weight of potential furfural fed. The furfural produced comes, as previously indicated, from three streams: condensate, filtrate from treated slurry, and filtrate from slurry recovered by washing the PDU. The potential furfural fed has to be evaluated from the weight of wood fed, as indicated in the previous section. Since the weight of wood fed is unknown, the MBO approach is based on the following hypothesis: input = output, so that the weight of wood fed is calculated from the weight (expressed in terms of weight of wood) of insoluble and soluble products contained in output streams:

- Condensate, which contains only furfural and HMF.
- Treated slurry. Two samples were taken: one was lyophilized and the other filtered. The residue obtained by lyophilization contains insoluble solids, soluble solids (sugars and levoglucosan) as well as sodic salt. From the filtered sample, it was possible to quantify the soluble products (sugars and levoglucosan), which allows correcting the lyophilized residue by adding/subtracting the weight due to hydration/dehydration reactions. On the other hand, the filtrate contains the salt obtained by neutralization with NaOH. This amount has to be subtracted from the lyophilized residue. Finally, the fil-

TABLE 4.	Complete integral mass balance (MBI): Fur
fural yields	s obtained from an absolute method.

	Exp. MB1 (T, = 200 C)	Exp. MB2 (T, = 230 C)
Wood put into the feed		
vessel		
w <sub>o</sub> (g)	328.2	329.9
Wood remaining in the feed		
vessel at the end of		
experiment		
w <sub>r</sub> (g)	141.6	151.8
Wood actually fed		
w <sub>f</sub> (g)	186.6	178.1
Potential furfural		
$\mathbf{F}_{t}$ (g)	27.8	26.5
Furfural produced		
F <sub>p</sub> (g)	3.1	12.9
% of theoretical furfural yield		
$(F_p/F_t)$	11.1	48.7

trate contains also furfural and HMF, which has to be added to the lyophilized residue after weight conversion to equivalent wood.
Slurry recovered by washing the PDU. The

same experimental procedure as for the treated slurry was applied.

This technique (MBO) requires less time manipulations than the method based on complete mass balance (MBI), but as will be discussed later, leads to erroneous furfural yield results. Integral mass balances following the MBO approach are detailed in Table 5.

## Differential mass balance in conjunction with thermal balance (MBT)

The objective of this approach is to mathematically evaluate the mass flow of slurry fed. A thermal balance on the steam injector (i.e., sensible heat is transferred to the slurry fed by steam condensation) gives the following equation:

$$\dot{m}_{f}x \int_{T_{0}}^{T_{m}} C_{p_{wood}} dT +$$

$$+ \dot{m}_{f}(1 - x) \int_{T_{0}}^{T_{m}} C_{p_{water}} dT = \dot{m}_{s}\lambda \quad (1)$$

			Exp. MB1 (T, = 200 C)					Exp. M) (T, = 23(	B2 0 C)	
	Treated	slurry	PDU washi	Bu	Condensate	Treated	lurry	PDU w	Ishing	Condensate
	+	I	+		+	+		+	1	+
Solids after lyophilization (g)	120.18		78.58			96.03	02.20	101.64	L1 0L	
Salt (Na <sub>2</sub> SO <sub>4</sub> ) (g) Volatiles (g) <sup>1</sup> (Furfural + HMF)	2.26	25.00	0.80	0.27	1.74	9.53	00.02	6.86	11.61	8.68
Weight loss due to dehydration react. (g) <sup>2</sup>		2.59		0.68			1.06		0.25	
Total of solids and soluble								211	76	
products excluding salt (g)			125.02						0/.	
Potential furfural F, (g)			18.64					17	.25	
% of theoretical furfural yield			16.7					74	×.	
<ul> <li>Expressed as equivalent wood weight.</li> <li><sup>2</sup> Weight of soluble solids (gluc. + mann. + le</li> </ul>	svogl. + xyl. + ar	ab.) – equiva	lent weight of woo	d generatin	ig these substances.					

where:

Cp	=	heat capacity
m <sub>f</sub>	=	mass flow of slurry fed
m,	=	mass flow of steam injected
T <sub>o</sub>	=	initial slurry temperature
T <sub>m</sub>	=	slurry temperature after mixing with
		steam
х	=	slurry consistency (wt/wt)
		· · · ·

 $\lambda$  = evaporation heat of water

A differential mass balance on the entire PDU (see Fig. 1) enables the singling out of steam mass flow as follows:

$$\dot{m}_{s} = \dot{m}_{t} - \dot{m}_{a} - \dot{m}_{b} - \dot{m}_{f}$$
 (2)

where:

 $m_t = \text{total mass flow} = m_v \text{(condensate mass flow)} + m_i \text{(treated slurry mass flow)}$  $m_a = \text{acid mass flow}$ 

 $m_a = base mass flow$ 

From these two equations, the mass flow of slurry fed is expressed by the following equation:

$$\dot{m}_{f} = \frac{\dot{m}_{t} - \dot{m}_{a} - \dot{m}_{b}}{1 + \frac{1}{\lambda} \left( x \int_{T_{0}}^{T_{m}} C_{p_{wood}} dT + (1 - x) \int_{T_{0}}^{T_{m}} C_{p_{water}} dT \right)}$$
(3)

with:

$$C_{p_{water}}\left(\frac{J}{g^{\circ}C}\right) = 4.185$$
(4)

$$C_{p_{wood}}\left(\frac{J}{g^{\circ}C}\right) = 1.113 + 4.85 \times 10^{-3} T(^{\circ}C)$$
 (5)

$$\lambda\left(\frac{J}{g}\right) = 2775.7 - 4.1872T(^{\circ}C)$$
 (6)

Once the mass flow of the slurry fed is known, furfural yield calculations follow readily (Table 6).

At 200 C, the furfural yield is 11.1% of the theoretical value, as obtained by rigorous complete mass balance based on input stream (MBI). The values determined by using two

estimating methods are 16.7% (mass balance based on output streams, MBO) and 9.6% (differential mass balance with thermal balance. MBT). Therefore, the MBO method provides a value 45% higher than the real one, whereas the MBT method leads to a value only 14% lower. At 230 C, the real value is 48.7%, and the estimated values are 74.8% using the MBO method (i.e., 54% higher than the expected value) and 41.4% with the MBT method (15% lower). Consequently, furfural yield results deriving from integral mass balance based on output streams are not acceptable. This is due to the following fact: the total weight of solids and soluble products in all the product streams are significantly less than the weight of solids fed to the reactor. It implies a net weight loss in the system. Tables 4 and 5 confirm this assertion. At 200 C, only 125.0 g are found in the output stream from 186.6 g actually fed (i.e., weight loss of 33%). At 230 C, 115.8 g are retrieved in products compared to 178.1 g of wood fed. Several reasons may be considered in order to explain the weight loss:

- Thermal decomposition reactions leading to the formation of noncondensable gases. Carrasco et al. (1987) reported the production of 2-3% of CO<sub>2</sub> when pretreating wood in autohydrolytic conditions.
- Extractive content. Some of these substances are volatile and must be found in the condensate.
- Organic acids. Acetic acid and uronic acids, formed by thermally-activated reactions, can reach 8–10% in hardwoods.
- Degradation reactions of furfural and 5-hydroxymethylfurfural. The opening of a furan ring in acidic conditions leads to the formation of levulinic acid and formic acid (McKibbins et al. 1962).
- Products deriving from lignin. The hydrolytic action can be responsible for the scission of certain groups attached to aromatic rings, thus increasing volatiles. On the other hand, acid-catalyzed condensation reactions lead to the formation of dehydration products, thus providing a weight loss.

**TABLE 6.** Differential mass balance in conjunction with thermal balance (MBT): Furfural yields obtained from a mathematical estimating method.

	Exp. MB1 (T. =	Exp. MB2 (T. =
	200 C)	230 C)
Mass flow of treated slurry		
(g/min)	808.1	718.4
Mass flow of condensate		
(g/min)	143.4	179.5
Total mass flow		
(g/min)	951.5	897.9
Mass flow of slurry fed		
(g/min)	635.4	563.4
Mass flow of steam		
(g/min)	202.1	220.5
Steam consumption (g of steam/		
100 g of slurry fed)	31.8	39.1
Mass flow of potential furfural		
(g/min)	8.90	7.90
Mass flow of furfural produced		
(g/min)	0.85	3.27
% of theoretical furfural yield	9.6	41.4

• A solid build-up on the tubular reactor walls, due to recondensation reactions between intermediate products formed during dehydration reactions and furfural, HMF or solubilized lignin fragments. Abatzoglou et al. (1990) reported that solid build-up can reach 16-48% of the total wood fed. In the present work, solids build-up remaining in reactor walls was minimized by thoroughly washing the reactor at the end of the experiment until the stream collected appeared to be clear. The liquor recovered was added to output streams for mass balance calculation purposes. Consequently, the weight difference between input (i.e., wood fed) and output (i.e., soluble products and insoluble solids) streams was due to insoluble sticky material remaining within the reactor after washing, noncondensable gases and mainly to unidentified soluble substances in output streams. However, even if a solid build-up cannot explain the difference between output and input weights, their formation is the major cause of the drop in furfural yields.

A sophisticated and extensive analytical procedure is required to find out missing ma-

terials in output streams when the MBO method is used to calculate furfural yields. However, the evaluation of furfural yield by the MBT method appears to be very simple and relatively accurate. Furfural yield is slightly underestimated, thus providing a conservative criterion. The mass flow of slurry fed is slightly overevaluated, which in turn implies that steam mass flow is lower than the actual value, the difference being probably accounted for by heat losses and uncondensed steam.

#### CONCLUSIONS

Studies on furfural production were conducted over the past forty years by using various raw materials and different operating conditions. The most representative substrates were xylose, agricultural residues (i.e., bagasse, corn stalks), black liquor, and hardwoods. The processing conditions varied over very large ranges and characteristic values were as follows:  $H_2SO_4$  concentration = 0.08–5%; slurry consistency = 5-20%; reaction temperature = 150-250 C; reaction time = 30 sec-5 h; pressure: atmospheric or higher; reactor: batch, PFR or CSTR; operation mode: with or without continuous steam distillation. In spite of these large ranges of operating conditions, furfural vield was in most of the cases 40-60% (percent of the theoretical) when furfural remained in the reacting medium, and 50-80% when furfural was removed from the reactor. These results clearly indicate that furfural must be separated from the acidic medium to reach high reaction selectivity. This can be achieved by either steam distillation or two-phase reaction (i.e., furfural transferred from an aqueous phase to either a vapor phase or an organic liquid phase).

The quantity of wood fed to the reactor has to be known to calculate furfural yields. However, it is often difficult to measure the mass flow of slurry fed to continuous units. In such a case, a complete integral mass balance is required to accurately evaluate furfural yield. To avoid these tedious and costly experimental manipulations, two different estimating methods were developed:

1) Experimental approach (MBO). - Insoluble solids and soluble products in output streams were evaluated and assumed equal to solids fed to the reactor. Experimental results showed net weight losses equivalent to 30-35% of wood fed to the reactor. These losses were mainly due to unidentified gases and soluble products. The expected solid build-up on reactor walls was minimized by washing the reactor. The liquor obtained was added to output streams. Unidentified products could have been noncondensable gases, volatile extractives, organic acids, degradation products, and small molecules deriving from lignin. Consequently, the output = input assumption required an extensive analytical identification and quantitative determination within the output streams to be satisfied. This approach was thus unacceptable. In this work, it was shown that the application of the MBO method leads to furfural yields 45-55% higher than real values obtained by complete integral mass balance.

2) Mathematical approach (MBT). — This approach consists of singling out the mass flow of slurry fed from two equations: i) differential mass balance around the entire PDU; ii) thermal balance at steam injector. This method avoids experimental manipulations. The results obtained indicated that estimated values are only 15% lower than real values, thus providing a simple, rapid and conservative way to evaluate furfural yields.

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