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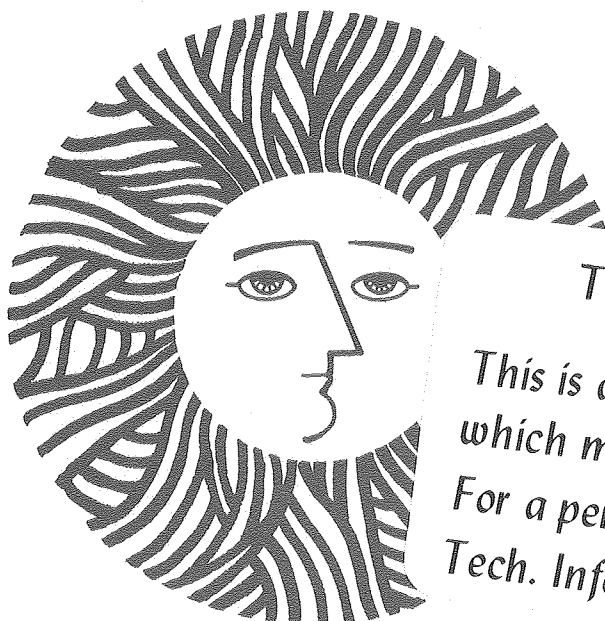
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TITRATION OF ACIDS AND ANIONS IN AQUEOUS PRODUCT AND FEED SLURRIES

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LIQUEFACTION OF DOUGLAS FIR WOOD SLURRIES

TITRATION OF ACIDS AND ANIONS IN AQUEOUS PRODUCT AND FEED SLURRIES

Summary

After hydrolytic pretreatment, wood slurries contain substantial amounts of organic acids. Additional acids are produced during the liquefaction step whether or not there is prehydrolysis. The acids have pH's in the range of about 3 to 5 and are easily titrated potentiometrically with sodium hydroxide. Anions present in neutralized slurry or in aqueous product can be titrated with hydrogen chloride solution with appropriate corrections for sulfate if present, and for excess titrant at the low pH of the endpoint.

Typical aqueous product at low liquefaction severities is about 0.4N in organic acids plus their anions. Evaporation of samples of neutralized water and weight of the sodium salts remaining indicate an average equivalent weight of acid as (very approximately) 90. When aqueous product is recycled to the prehydrolysis step and thence to liquefaction, only a portion of the acid/anion content is decomposed. As a result, the concentration increases substantially.

While simple carboxylic acids — especially acetic — are formed, there must be substantial amounts of more complex acids.

Titration curves indicate acids with a range of pK's from 3.0 or less to 5.0 or more. The lower pK's could come from hydroxy or keto acids or from the first ionization of particular dicarboxylic acids. Many of the acids formed must be quite volatile, since a high percentage is lost by the common procedure of drying overnight in an oven. One typical titration curve can be reproduced accurately by assuming the acids present are a 62/38 mixture of acids with average pK equal to that of acetic acid (4.76) and stronger acids with average pK $\sim$ 3.5. These observations are in the process of being verified by GC and GCMS tests on extracts of water samples including identification of major individual compounds.

A work-up procedure for aqueous samples, applicable to CEU, PDU or batch samples, is recommended.

A. Introduction

There is long experience that organic acids are formed during liquefaction of Douglas Fir. Even though neutralized or even somewhat alkaline slurries are fed, product water is normally acidic. In PDU run TR-10, for example, the major aqueous effluent had a pH of about four and the overhead aqueous condensate was just above three. There does not appear to be quantitative information on the amount of acid present or the anions formed by reaction with the sodium carbonate from the slurry. This report covers a preliminary effort to fill the gap.

There has been some question about the role of carbon dioxide formed by decomposition and/or reduction of wood. CO_2 reacts with carbonate or hydroxyl ion to form bicarbonate ion. The pH at various CO_2 and carbonate levels is as follows:

<u>Level</u>	<u>pH</u>
0.1M Na_2CO_3	12
0.05M Na_2CO_3 /0.05M	
NaHCO_3 (or other 1:1 mixtures)	10.3
0.1M NaHCO_3	8.2
0.05M NaHCO_3 , 0.05M	
CO_2	6.4
0.04M CO_2	4

Note that a saturated solution of CO_2 at one atmosphere partial pressure and 20°C is about 0.04M.

If the aqueous phase at the beginning of a liquefaction run is 0.5M in Na_2CO_3 ($\sim 5\%$), CO_2 , evolved from wood, will react to form bicarbonate -- at least as the reactor is cooled. When half a mole of CO_2 per liter of water has reacted the pH will be a little over 8 at room temperature. Additional CO_2 will be absorbed, reducing the pH further, but the solubility of CO_2 at room temperature and one atmosphere is only about 0.04M. The resulting pH will be about seven, but can be more or less depending on the partial pressure in the reactor and the rate of approach to equilibrium at ambient conditions in the pH meter. Carbon dioxide must be at least one of the acids causing the pH variations noted by Battelle (1) (their figure 1).

(1) Quarterly Technical Report "Bench Scale Research in Biomass Liquefaction in Support of the Albany, Oregon Experimental Facility, AN-05-15-89018, Oct.-Dec. 1980, Pacific Northwest Laboratory, Richland, Washington."

However, as stronger organic acids are formed, they react with carbonate and bicarbonate to evolve CO_2 and form their anions. Thus, at pH's below about 5 to 6, we expect to find no significant amount of carbonate or bicarbonate remaining. At higher pH's bicarbonate should be expected and allowed for.

With all the LBL process water samples we have looked at to date, the initial pH and titration behavior show that organic acids are present and the carbonate and bicarbonate ions have been destroyed.

B. Experimental

Solutions of sodium hydroxide (0.2M and 1.0M) and hydrochloric acid (1.0M) were prepared from DILUT-IT Ampoules (J.T. Baker Co.) and also checked against reagent grade anhydrous sodium carbonate. Titrations were carried out with an Orion Model 701A pH meter standardized against standard buffer solutions.

C. Results

Table I gives all the titration results on aqueous products obtained to date.

Discussion

The data given in Table I show that some organic acids are formed in the prehydrolysis step. These are normally neutralized with Na_2CO_3 , so that the resulting slurries at pH's ~ 8.0 contain carboxylate ions ($\sim 0.12\text{N}$ in titration (3) and bicarbonate ion ($\sim 0.06\text{N}$ according to titrations (1) and (4)). In any case, part of the carboxylic acid product is formed during the prehydrolysis step.

Considerably more organic acid is formed at the liquefaction stage. The product appears as both partially ionized acid and as anion corresponding to the sodium bicarbonate present in the slurry, so that the product water is a carboxylate/carboxylic acid buffer. While phenols as well as carboxylic acids are formed, they are probably not acidic enough to be converted in the present titrations. In Albany PDU run 10, for example, the organic acid plus anion content of the product water is roughly triple (0.35N) that of slurry ($\sim 0.12\text{N}$).

Other single-pass product waters from LBL autoclave runs have anion plus acid contents from 0.36N (run RA-20) to 0.58N (run RA-24). The results of the series RA-20 to RA-24 show that the content decreases with increasing severity. The order of increasing severity is:

Run	Time/Temperature		Equivalent/hg.
24	0 min	330°C	0.58
42	0 "	340°C	0.52
23	30 "	330°C	0.44
18	0 "	360°C	0.43
22	60 "	330°C	0.41
20	30 "	360°C	0.36

Differences among these three not really significant.

Run 42, although carried out without prehydrolysis, fits at a reasonable point in this sequence. This suggests that if acids are not formed in a prehydrolysis, equivalent amounts are formed during liquefaction. Substantial amounts of carboxylic acids can therefore be found in the PERC process product.

Since the heat-up time to reach the above temperatures is roughly one half-hour, it is obviously equivalent to much less than 30 minutes at temperature — perhaps about 10 minutes. The above results suggest, therefore, that most of the acids formed will survive being recycled at the same low severity. Waters from runs 36 and 38 (water recycled) show build-up to above 0.8N. A detailed calculation of the ratio of recycle water to total water in the product is necessary to estimate how much recycle acid was destroyed.

The indication that water effluents in a recycle system will contain 0.8 to 0.9 equivalents/kg of acid plus anion allows us to estimate the amount of sulfuric acid and subsequent sodium carbonate needed in each run. For example:

Assume 1000 kg wood (dry basis), 1000 kg fresh water (probably as water content of wet wood chips) and 2500 kg recycle water, 0.7N anion, 0.15N acids. Equivalent sulfuric acid needed is $2500 \cdot 0.7 + 3500 \cdot 0.14^* = 1800$ g equivalents or 88 kg (100% H_2SO_4 basis). The amount of Na_2CO_3 to neutralize to pH ~ 8 is the amount equivalent to the sulfuric acid (1800 g equivalents) plus the amount equivalent to the recycled acid ($2500 \cdot 0.15$ or 375 equivalents) plus the amount equivalent to the organic acids generated in hydrolysis ($3500 \cdot 0.12N$ or 420 equivalents). this is a total of 2595 equivalents. Because of the weakness of sodium bicarbonate as a base, we find one mol of sodium carbonate solution constitutes effectively only 1.60 equivalents in this titration rather than two. Thus we need $2595/1.60 = 1622$ mols or 172 kg dry carbonate — roughly 17% of the dry weight of the wood.

* Calculated excess normality of sulfuric acid required for a pH of 1.7.

Figure 1 illustrates titration of prehydrolyzed wood slurry with 0.2N NaOH and 0.1M Na_2CO_3 . Figure 2 shows titration of an aqueous product with NaOH and back titration with HCL to low pH. The latter curve is compared to calculated curves assuming all acid has $\text{pK}_a = 4.76$ (e.g. acetic acid) and acid is a mixture of weak acid ($\text{pK}_a = 4.76$) and stronger acid ($\text{pK}_a = 3.0$). The latter calculated curve happens to fit the data well.

The shape of the titration curves (figure 2) strongly suggests that the aqueous product is indeed a mixture of acids with various $\text{pK}'\text{s}$, probably ranging from 3 or less to 5 or more.

At this point, it is not possible to give a very precise estimate of the average molecular weight or equivalent weight of the acids. By evaporation of neutralized acids from autoclave run RA-33, and weights of the sodium salts, we made an estimate of 92 for the equivalent weight. Acetic acid has $\text{MW} = \text{EW} = 60$ and butyric 88. Levulinic has $\text{MW} = \text{EW} = 116$. Adipic acid has $\text{MW} = 146$, $\text{EW} = \text{MW}/2 = 73$. All these plus many other carboxylic acids are present, so that an average equivalent weight around 90 is certainly plausible.

While simple carboxylic acids — especially acetic — are formed, there must be substantial amounts of more complex acids.

A work-up procedure for aqueous samples, applicable to PEU, PDU or batch samples, follows.

Suggested procedure for Routine Analysis

1. Titrate 20 g sample of aqueous product with 1N standard NaOH to endpoint (pH 7.5-8.0). Transfer quantitatively to continuous extractor.
2. Extract non-acid components from above sample with appropriate solvent (e.g. chloroform). Recover aqueous layer quantitatively in separatory funnel.
3. Titrate total sample with 1N HCL to $\text{pH} = 1.7$. correct titer for (a) excess HCL necessary to give end pH in final volume $[\text{INVERSELOG}(-\text{pH}) \cdot (\text{Final Volume Sample})/\text{NHCL}]$; and (b) sulfate content, if any, of sample.

$$\frac{\text{INVLOG}_{10}(-\text{pH})}{0.012} \div \left(1 + \text{INVLOG}_{10}(-\text{pH})\right) \cdot (\text{Mols } \text{SO}_4^{=}) \div (\text{Kilograms Original Sample}) \cdot (\text{Grams Original Sample}).$$

4. a. (Optional) Transfer quantitatively to continuous extractor and extract organic acids with appropriate solvent (e.g. ether).
- b. (Optional) If original pH was high enough that bicarbonate ion is indicated, stir for a short period, then back titrate with NaOH to endpoint (pH 7.5-8). Difference between HCL titer and NaOH titer measures bicarbonate content.

G.C. Analyses to be performed

- Alkaline aqueous sample before extraction
- (Optional) Extract of alkaline sample
- Acidified aqueous sample
- (Optional) Original sample before titration
- (Optional) Acidified extract.

Above should be carried out with recorded size of sample (e.g. 5 μ L), taken from measured weight or volume of sample at point sampled. Other optional analyses include GCMS and HPLC on any of the above or on derivatives.

Typical Calculation

20.05g Sample - initial pH 4.7 requires 4.23 ml 1N NaOH to bring to pH = 7.9. After extraction of neutrals, residual sample requires 4.15 ml 1N HCL to bring to 4.7 and total of 18.44 ML to bring to pH = 1.7. Volume of sample estimated to be 57 ML. From ratio 4.15/4.23 estimate ~ 2% of sample was lost in transfers and sampling for GC. "Free" acids are calculated as

$$\frac{4.231 \text{ 1.ON}}{20.05} = 0.211 \text{ Equiv/Kg}$$

Correction of HCL titer calculated to be $\frac{\text{INVLOG}(-1.7) \cdot 57}{1.0} = 1.14 \text{ ML}$

(For 1.7 pH, INVLOG (-1.7) = 0.0200.)

From preparation of sample it is known to have had a total of 26g H₂SO₄ added/1000g aqueous layer or 0.265 mols/Kg. Sulfate correction is

$$\frac{0.0200}{0.012} (1 + \frac{0.200}{0.012}) \cdot 0.265 \cdot 20.05 = 3.32 \text{ ML.}$$

Net HCL titer is then 18.44 - 1.14 - 3.32 or 13.98 ML and total of free acids and anions per kg is $\frac{13.98 \times 1.02}{20.05} = 0.711 \text{ equiv/kg.}$

The density of the effluent water is found to be 1.042 g/ML. Therefore the normality of total acid and anion is $0.711 \cdot 1.042 = 0.741$.

<u>Summary</u>	<u>Equiv/kg</u>	<u>Equiv . Liter</u>
Free Acid	0.211	0.220
Acid + Anion	0.711	0.741
Anion by diff.	0.500	0.522

FIGURE 1
 Titration of Wood Slurries after Prehydrolysis with Sodium Hydroxide and with
 sodium Carbonate.

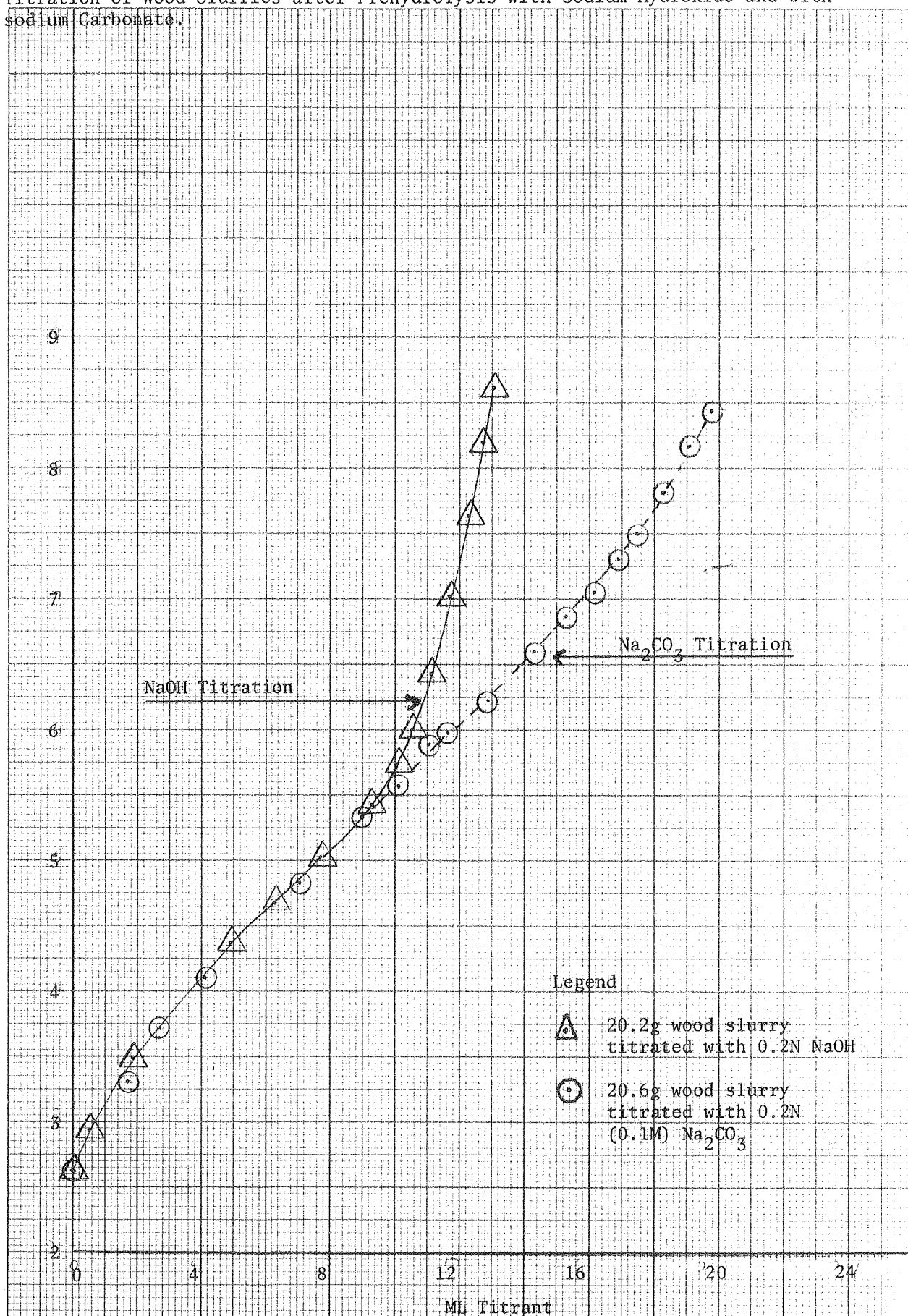


FIGURE 2
TITRATION OF PROCESS WATER

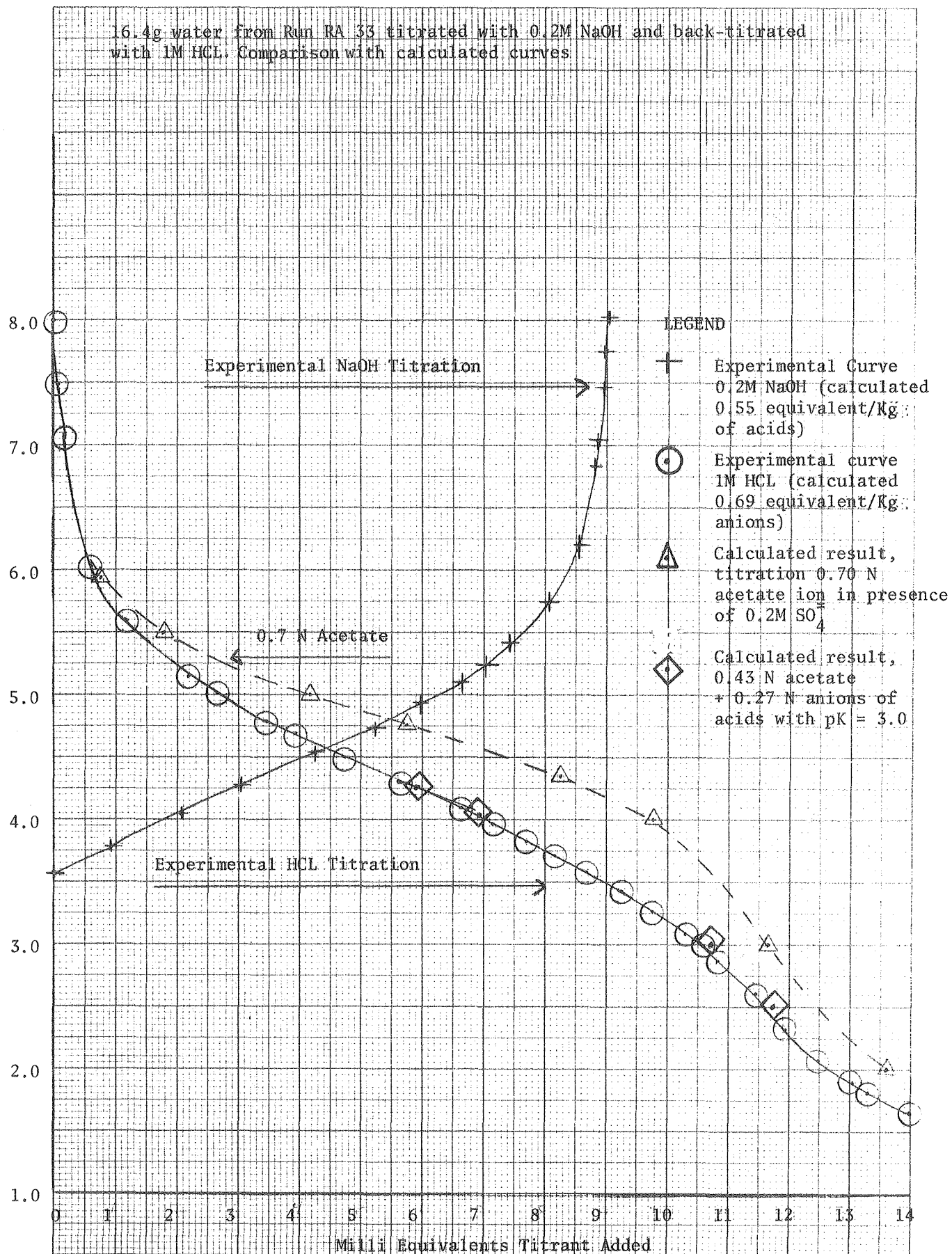


TABLE I
ORGANIC ACID AND ANION CONTENT OF PREHYDROLYZED WOOD SLURRIES

SAMPLE	INITIAL pH	EQUIVALENTS PER KILOGRAM SLURRY			COMMENTS
		ACIDS	ANIONS	TOTAL	
1. Slurry prepared at Albany, 1979, neutralized with Na_2CO_3 - 21% solids	7.9	--	0.19	0.19	"Anions" = carboxylates plus bicarbonate + ~ 0.01 Equiv H_2SO_4
2. Slurry prepared at Albany, Nov. 1980 - 21% solids	8.7	--	0.22	0.22	"Anions" = carboxylates (plus some bicarbonate)
3. Unneutralized slurry prepared at LBL from wood flour - 30% solids	2.6	0.12	--	0.12	Mostly carboxylic acids; less than 0.01 equivalent sulfuric acid
4. Same, titrated to pH = 7.9 with 0.1M Na_2CO_3	2.6	0.17*	--	0.17	At pH's above about 5.5, Na_2CO_3 acts as mono-basic alkali, forming HCO_3^- , not CO_2
5. Same, Titrated to pH = 8.7 with 0.1M Na_2CO_3	2.6	0.20*	--	0.20	
6. Slurry prepared at LBL from wood flour and recycled water with 3g Na_2CO_3 /100g wood added after hydrolysis	3.75	0.50	0.24	0.74	

* The higher values here than in titration (3), are only indicative of the weakness of bicarbonate as a base. 0.12 Equivalent/kg is the correct answer. See also reverse titration (1) and (2).

TABLE II
ORGANIC ACID AND ANION CONTENTS OF AQUEOUS PRODUCTS FROM WOOD SLURRY LIQUEFACTION

SAMPLE	INITIAL pH	EQUIVALENTS PER KILOGRAM			COMMENTS
		ACIDS	ANIONS	TOTAL	
Albany - TR-10-105 LBL Condensate Water	3.48	0.0495	--	0.0495	pH higher than at end of run because of storage in metal cans.
Albany TR-10-104 LBL Aqueous Effluent	4.12	0.17 1N	0.17	0.350	TR-104 is about 3.2 wt % acid plus anion.
LBL - RA 18 - 360°C, 0 minutes	4.92	0.138	0.29	0.43	Weighing sodium salts by evaporation from neutralized sample gave equivalent weight of acid as 90.
RA-18 repeat run	4.58	0.179	not run	--	
LBL RA-20 (360° - 60 min)	5.03	.099	(0.23 est.)	0.313	In these titrations, "0.23 est." means that amount of anion was calculated from quantity of sodium carbonate used in making original slurry. In others, anions titrated with 1M HCL
	4.89	0.116	0.24	0.36	
LBL RA-22 (330° - 60 min)	4.73	0.18	(0.23 est.)	0.41	
	4.62	0.173	0.24	0.41	
LBL RA-23 (330° - 30 min)	4.58	0.21	(0.23 est.)	0.44	
	4.49	0.199	(0.23 est.)	0.44	
LBL RA - 24 (330° 0 min.)	4.04	0.33	(0.23 est.)	0.56	
	3.98	0.315	0.26	0.58	
RA-42 Wood flour plus water containing Na ₂ CO ₃ . No prehydrolysis. Water is 1.3% Na ₂ CO ₃ = 0.24N base (340° 10 min)	3.79	0.308	0.217	0.525	Good endpoint because of absence of sulfate. Average pK from curve

TABLE II (continued)

SAMPLE	INITIAL pH	EQUIVALENTS PER KILOGRAM			COMMENTS
		Acids	Anions	Total	
LBL RA-33. (4th pass recycle water 340°C, 0 minutes). Slurries incompletely neutralized before liquefaction.	(1)3.60	0.539	0.168	0.71	Sample ⁽¹⁾ evaporated to dryness after neutralization. Wt. sodium salts removed (less estimated weight Na ₂ SO ₄) indicates acid/anion equivalent wt. of about 92.
	(2)3.56	0.549	0.141	0.69	
LBL RA-33. Same as above, but dried overnight in oven without neutralization (7.1% solids found) then re-dissolved and titrated.	3.88	0.149	0.175	0.32	Compared to previous titrations, shows drying overnight lost 72% of free acids. Wt. % dry sample indicates equivalent weight of remainder ~ 100.
LBL RA-36. 3rd pass water product slurries neutralized before liquefaction	5.13	0.170	0.67	0.84	Correction made for large content of Na ₂ SO ₄ .
LBL RA-36. Same titrated after addition of excess BaCl ₂ to precipitate SO ₄ .	4.52	0.172	0.70	0.87	Presence of large amount of BaCl ₂ affects reading of glass electrode. Titration curve obtained looks better, but result is not necessarily more accurate.
LBL RA-38. Autoclave series partial water recycle.	5.09	0.140	0.68	0.82	
LBL RA-39. Next sample run.	5.00	0.089	0.48	0.57	
LBL RA-40. Levulinic acid (1.3% in the water) used in pre-hydrolysis. No Na ₂ CO ₃ added.	2.46	0.642	0.00	0.642	Levulinic acid is a major peak in GC after liquefaction. Feed water 0.11 M levulinic. Average pK of product water from curve inflection ~ 4.4.

