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BENCH-SCALE STUDIES OF BIOMASS LIQUEFACTION WITH PRIOR HYDROLYSIS

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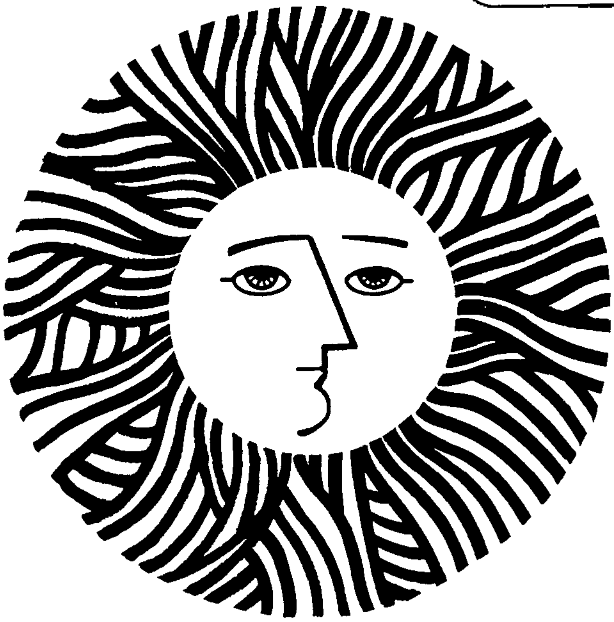

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DISCLAIMER

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BENCH-SCALE STUDIES OF BIOMASS LIQUEFACTION WITH PRIOR HYDROLYSIS

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BENCH-SCALE STUDIES OF BIOMASS LIQUEFACTION WITH PRIOR HYDROLYSIS

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OBJECTIVES

This study dealt with biomass liquefaction, and, in particular, with the so-called LBL process. The objectives were (1) to find trends in operating conditions that would improve the yield and quality of the oil produced from biomass, and (2) to explore the chemical feasibility of technically sound options to modify the LBL process that could improve the economics of the process to a great extent. Recycle of the spent synthesis gas (after scrubbing excess CO_2 from it) and recycle of a significant portion of the aqueous phase emerging from the liquefaction reactor were the recognized options for process modification.

SUMMARY AND CONCLUSIONS

The liquefaction experiments were conducted batchwise using autoclaves. The oils produced in batch experiments were poor in quality, i.e., they solidified at room temperature and contained excessive amounts of acetone insoluble material, compared to oils produced in flow mode at the biomass liquefaction test facility at Albany, Oregon and in the process evaluation unit of LBL.

Possible causes of the differences in the quality and yields of oils are differences in the synthesis gas pressure initially imposed, and the rate of heating to the reaction temperature during which irreversible reactions can take place, as well as differences in gas/liquid contacting.

It is not likely that the results obtained batchwise in autoclaves will permit researchers to zero in on the optimum conditions to be imposed in flow systems, unless some radical modifications are made in the design and operation of autoclaves.

An initial gas phase containing 36% CO_2 and 64% H_2 was found to be as effective (for liquefaction) as a CO_2-free synthesis gas containing 60% CO and 40% H_2.[16] This finding, within the limitations of the batch experimental mode, is significant in several respects. 1) It is contrary to conclusions drawn by many researchers that CO is essential to liquefy biomass with Na_2CO_3 as a catalyst. 2) It indicates that it is not essential to scrub carbon dioxide ever present in gasification products. With H_2 as the primary reactant readout supplied as an optimum partial presence, a savings in synthesis gas cost may outweigh an incremental expense of operating at higher total pressure. The maximum synthesis gas utilized was found to be less than 0.2 g mols/100 g wood liquefied, compared to 0.7 assumed in the cost studies of the process. Whereas this finding is encouraging insofar as the economics of the process is concerned, any translation of the current results into flow systems would be hazardous.

Studies of the recycle of the aqueous phase of the liquefaction products for hydrolysis revealed or confirmed the following: 1) Organic acids are produced both in the course of hydrolysis and liquefaction (a confirmation). 2) The sodium salts of the organic acids present in the hydrolyzed slurry do not seem to undergo much decomposition in the liquefaction stage, and become more concentrated on recycle. This observation may not be valid under more severe liquefaction conditions. 3) Similarly the organic acids present in the aqueous phase of the liquefied slurry are not decomposed to any significant degree, when recycled, in the hydrolysis step.

Because of the large amount of carboxylic acids and their anions, which must be acidified and reneutralized in successive hydrolysis/liquefaction steps, it does not appear economic to recycle water in the unmodified LBL process. Modifications which might make recycle feasible include: (1) Developing operating conditions for liquefaction offsetting the adverse effects of low pH (3 to 4); (2) Developing a prehydrolysis process operating at less acid conditions, i.e. at pH 2.5 to 4 or at alkaline conditions; or (3) replacing the sodium carbonate now used for alkalization with less expensive calcium carbonate or perhaps using lime in a sodium carbonate recovery step as in the paper industry's alkaline pulping process.

INTRODUCTION

This study primarily concerned the chemical aspects of converting biomass into oil. In particular it dealt with the LBL biomass liquefaction process.

In the LBL process wood chips or other biomass forms are first prehydrolyzed under mild conditions (180°C, 131 psig, pH = 1.7 to 2.0) using 23 parts biomass (dry basis), 77 parts water, and 500 to 750 ppm sulfuric acid. The prehydrolyzed slurry, when subjected to wet grinding (using pulp refiners), becomes pumpable, i.e., can be injected into high pressure vessels (> 2000 psig) by means of commercially available positive displacement pumps. Upon addition of 6 parts of sodium carbonate per 100 parts biomass prehydrolyzed, the slurry and synthesis gas are injected into a reaction vessel maintained at 3000 psig and 350°C and given a residence time of about 45 minutes. Using this process, with variations imposed by equipment limitations, about 10 barrels of oil have been obtained at the biomass liquefaction process development unit (PDU) of the Department of Energy, located at Albany, Oregon.

Although the chemical feasibility of the process became established quickly at Albany, it has not been possible to conduct a sufficient number of test runs there to zero in on the optimum operating conditions which influence both the yield and quality of the oil produced. Thus the determination of the influence of the operating conditions on the liquefaction reactions was left to bench scale experiments.

Several institutions were commissioned by DOE to make a technical and economic feasibility analysis of the LBL process and a companion process (PERC) for which the Albany facility was designed and built. Such analyses involved much guesswork regarding the yield and quality of the oil that could be produced under optimum conditions (synthesis gas utilization, effluent water treatment, etc.), but they nevertheless shed considerable light on the areas that would be critical to process economics. For example, it was assumed that 335 lbs water had to be heated to about 350°C per 100 lb dry wood charged.[1] If, under adverse conditions it becomes necessary to evaporate the effluent water, it would require about 60 lbs of additional wood to supply the needed heat. It was also assumed that 1.40 lb moles of synthesis gas (50% CO, 50% H_2) would be needed for the liquefaction of 100 lb wood, which in turn, would require gasification of about 76 lbs of wood (dry basis). The costs of these ancillary unit-operations constituted a considerable portion of the projected cost of the crude oil produced from wood (> $48.00/bbl). These considerations played an important role in the design of experiments conducted in the course of this study.

EXPERIMENTAL APPROACH

The experimental approach adopted was much the same as others used by researchers dealing with direct liquefaction of coal or biomass. Perhaps the less common feature was the use of the cooling coils of the autoclave for heating as well. The modification made is illustrated in Figure 1. The silicone oil used was stable below 400°C and had a vapor pressure of about 20 psig at that temperature. It was recirculated, using a centrifugal pump through the heaters followed by a cooler before being returned to the reservoir. After loading the autoclave, the heater bank was stabilized to bring the temperature of the oil exiting the fifth heater to the desired level, e.g. 380-400°C, while the oil was being circulated without going

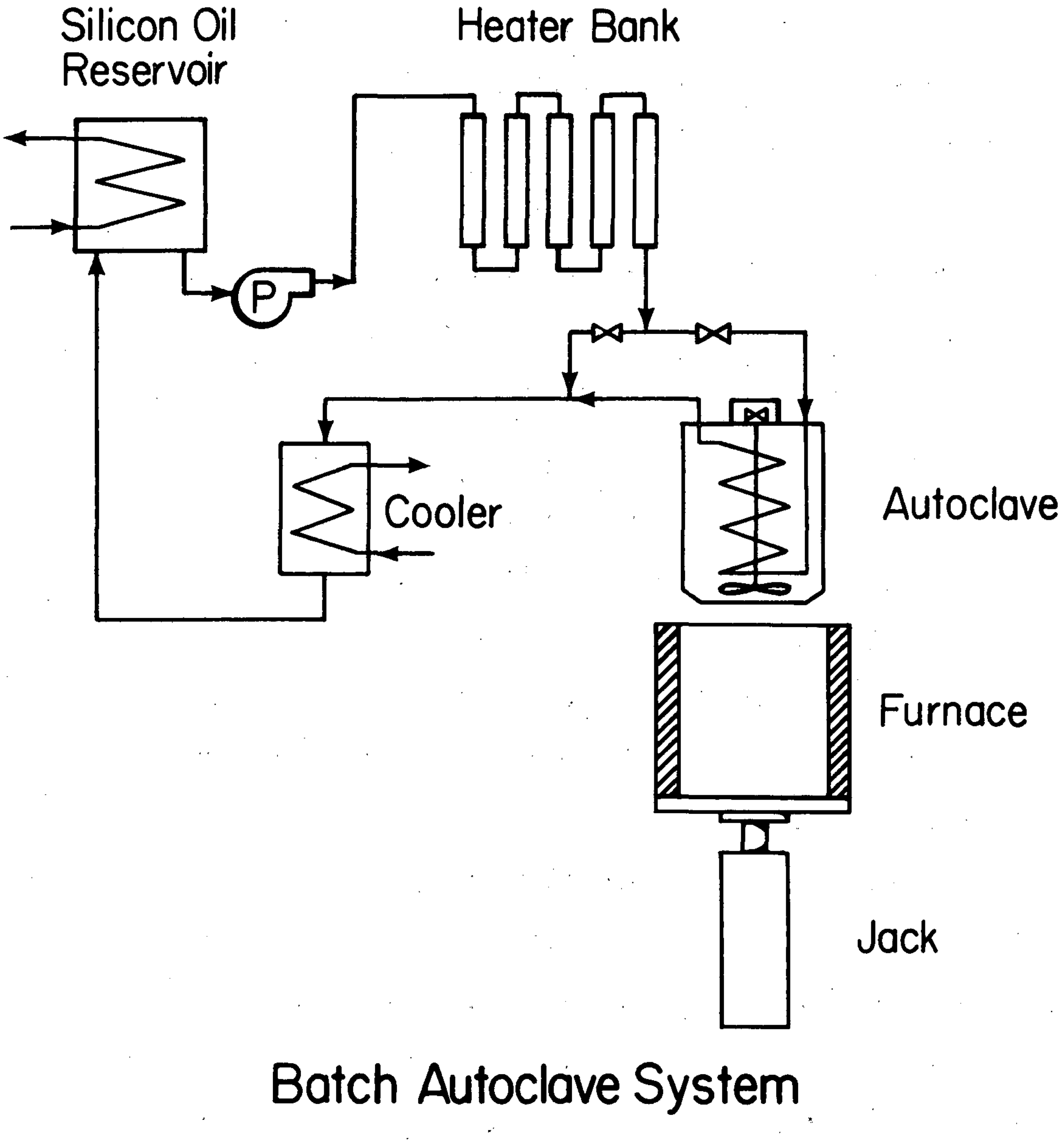

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Fig. 1. Schematic diagram of batch autoclave system.

through the autoclave coil. Simultaneously the temperature of the furnace of the autoclave was raised to about 600°C while being kept below the autoclave. When the desired conditions were attained, the hot oil was diverted through the autoclave coil and the furnace was raised to its proper position, zero time. Simultaneous internal and external heating minimized the thermal shock. Temperature and pressure readings were recorded at approximately 5-minute intervals. Once the desired temperature was reached, the current to the furnace was turned off and the desired temperataure was maintained by adjusting the current flow to the fifth heater only if it was desired to maintain that temperature for a fixed period of time. To terminate the reaction, the furnace was lowered and the current to the heater bank was turned off. A typical temperature-time relation for a liquefaction run in the 1-L autoclave is shown in Fig. 2. The autoclave contained a glass liner with 300 g hydrolyzed wood slurry. It is seen that the desired temperature of 340°C was reached within 30 minutes and the run was terminated 5 minutes later. The figure also shows that the cooling rate of the contents of the glass liner was about 10°C/min.

Figure 5 shows temperature-time relationships obtained during hydrolysis test-runs using 1-liter and 1-gallon autoclaves. Since it was felt desirable not to expose the wood to surfaces heated to temperatures in excess of 20°C of the desired final reaction temperature, it took about 30 minutes to reach 180°C whereas the same temperature could have been reached within 8 minutes if the silicone oil circulated were heated to 400°C. Figure 3 also shows the heating rates attained in a 1-gallon autoclave using the same internal heating system. It is seen that it took an excessively long period of time

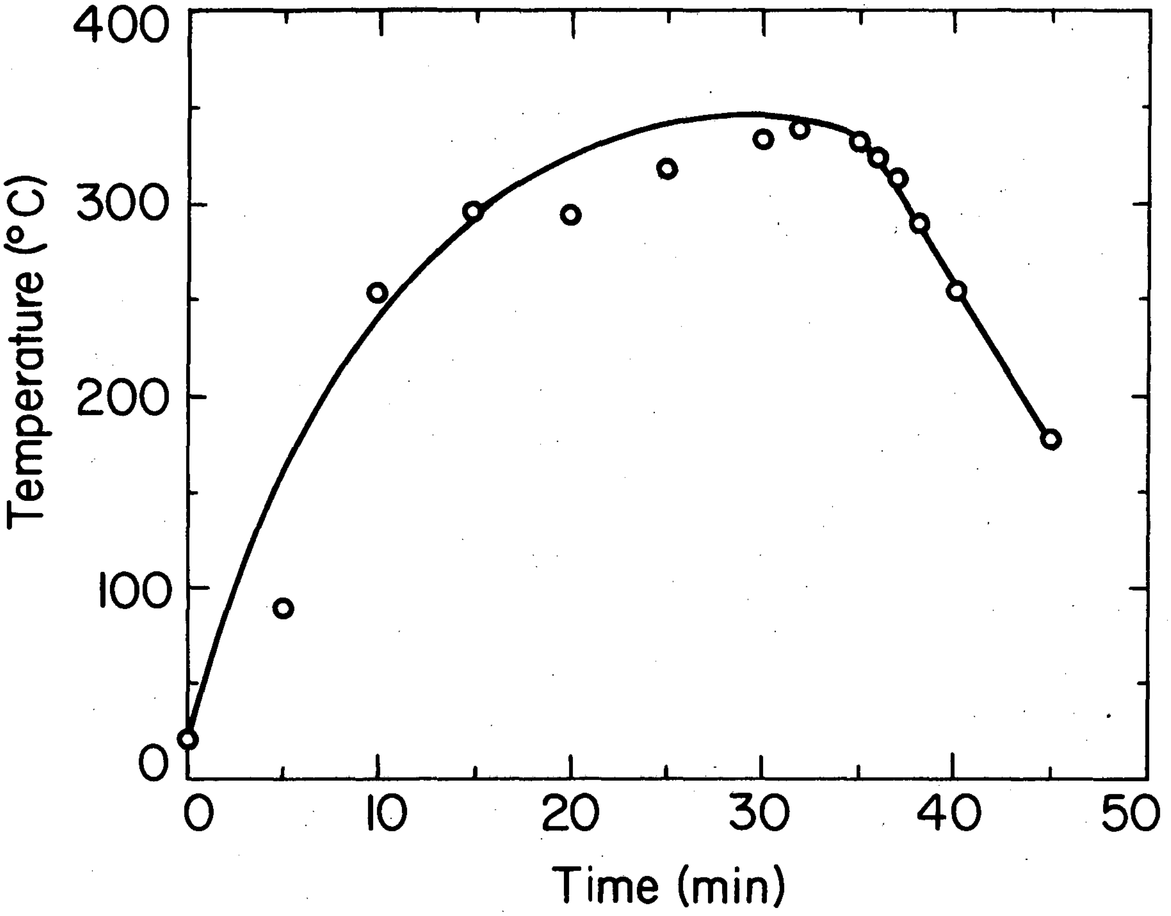

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Fig. 2. Heating and cooling rates achieved in 1-liter autoclave.

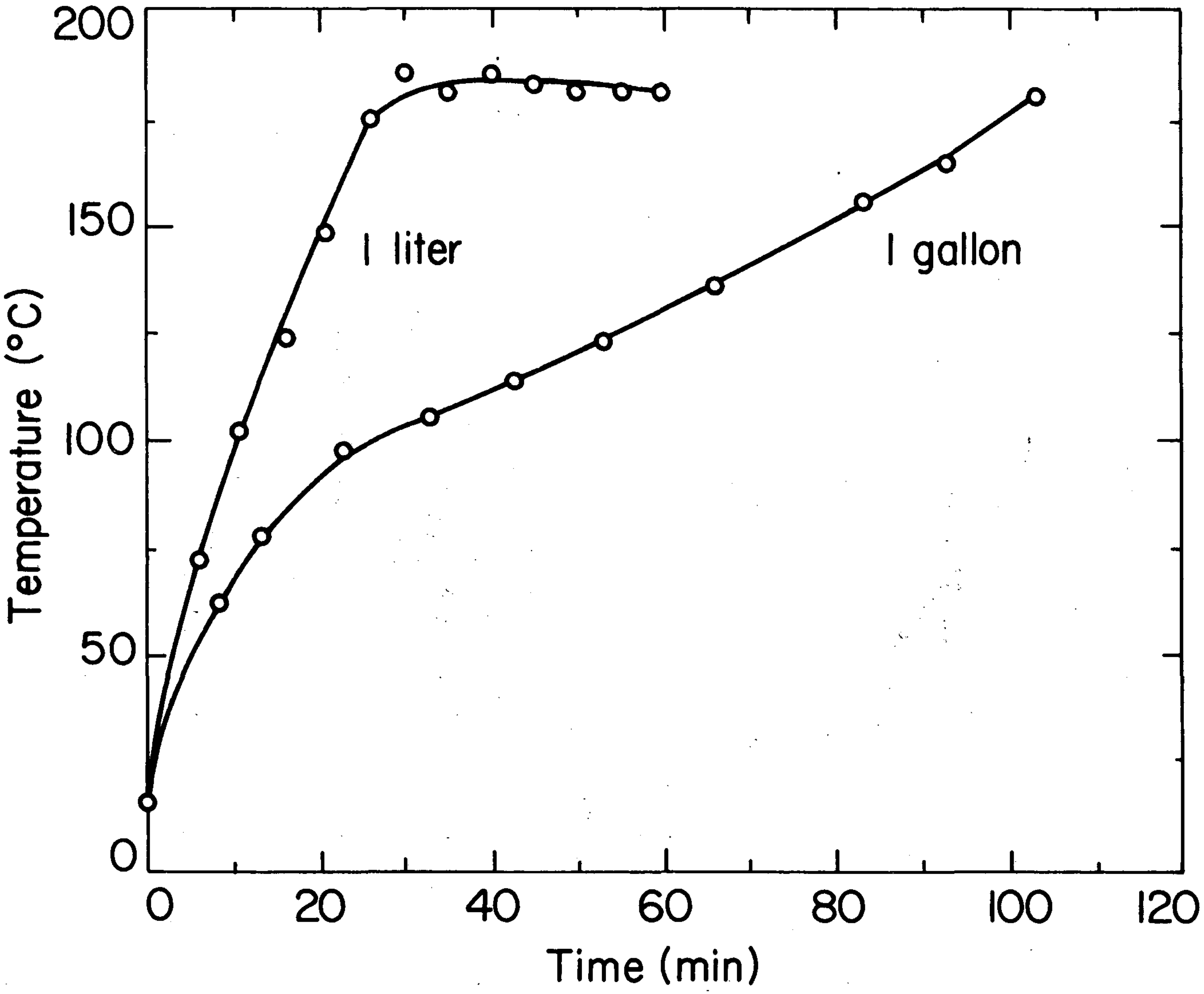

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Fig. 3. Heating rates during hydrolysis in 1-liter and 1-gallon autoclave.

to reach the desired final temperature. (The heating system was not designed for the larger autoclave.)

Figure 4 shows (circles) pressure as a function of temperature (a cross plot of data on temperature vs. time and pressure vs. time) obtained in a test run in which the autoclave was initially pressurized to 500 psig. Also plotted in the figure are steam pressure as a function of temperature and synthesis gas pressure as a function of temperature, calculated assuming that it was not reacted and behaved as an ideal gas. The curve that hugs the circles is the sum of the two solid lines below it. Beyond 300°C the observed pressures differ greatly from results of the idealized calculations.

Due to the malfunction of the automatic temperature device (applied to the current fed into heater No. 5), the control was done manually. The desire for standardization of a series of test runs (e.g., to reach the final temperature in 30 minutes) while varying other conditions (e.g., final temperature, impeller, stirring speed) necessitated changes either in the hot oil recirculation rate and/or its temperature. As a result, seemingly minor impositions and minor remedies resulted in fluctuations in the temperature-time profiles. Figure 5 shows the ranges of the recorded slurry temperatures at 5-minute intervals when it was desired to reach 340°C within 35 minutes and cool immediately. Figure 5 shows that the temperature reached within 10 minutes ranged from about 150°C to 270°C. From the point of view of heater design modifications in the future, Figure 5 provides an idea about the heating rates that can be attained in 1-liter autoclaves.

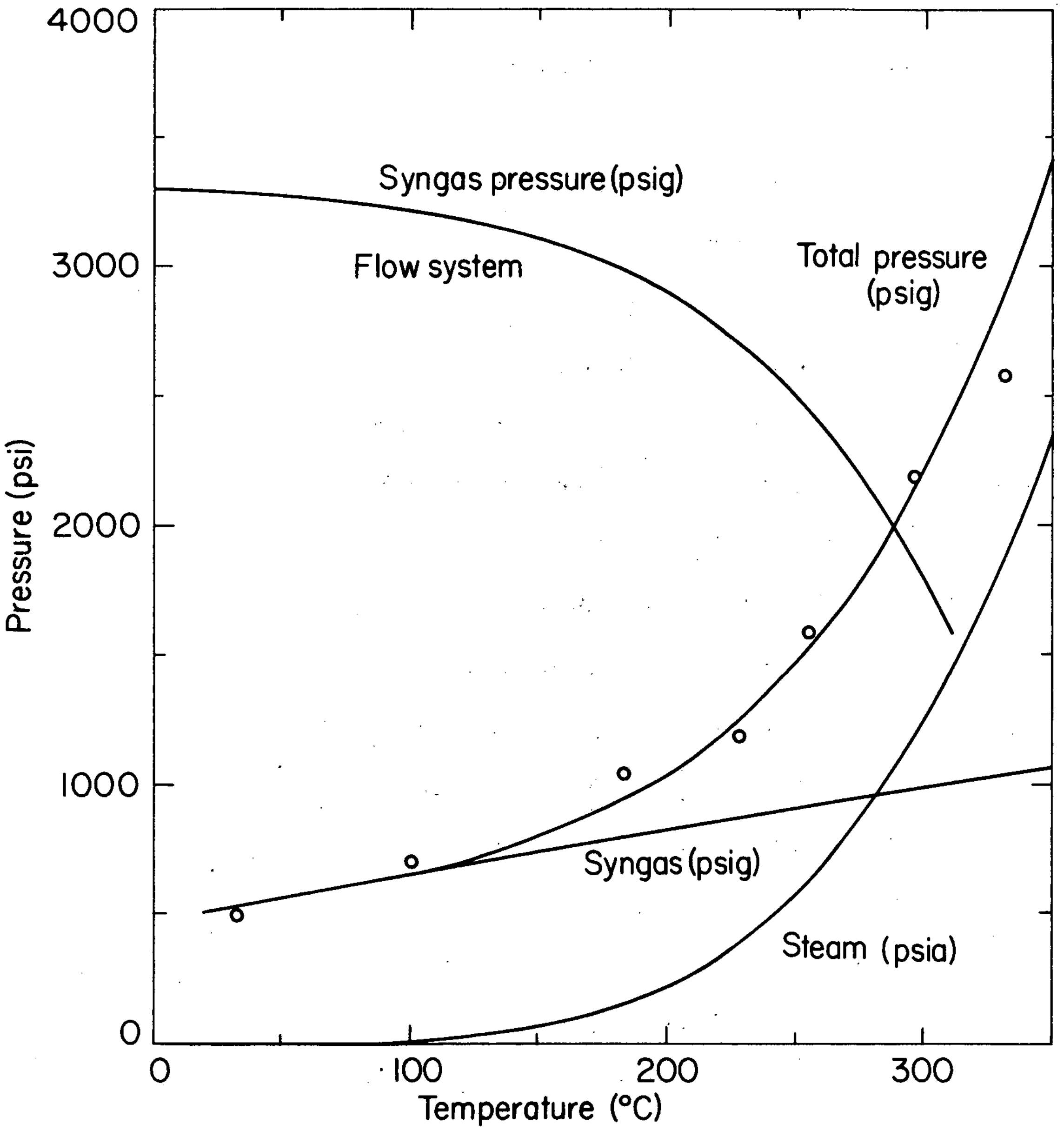

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Fig. 4. Observed (circles) and calculated pressures in 1-liter autoclave as a function of temperature.

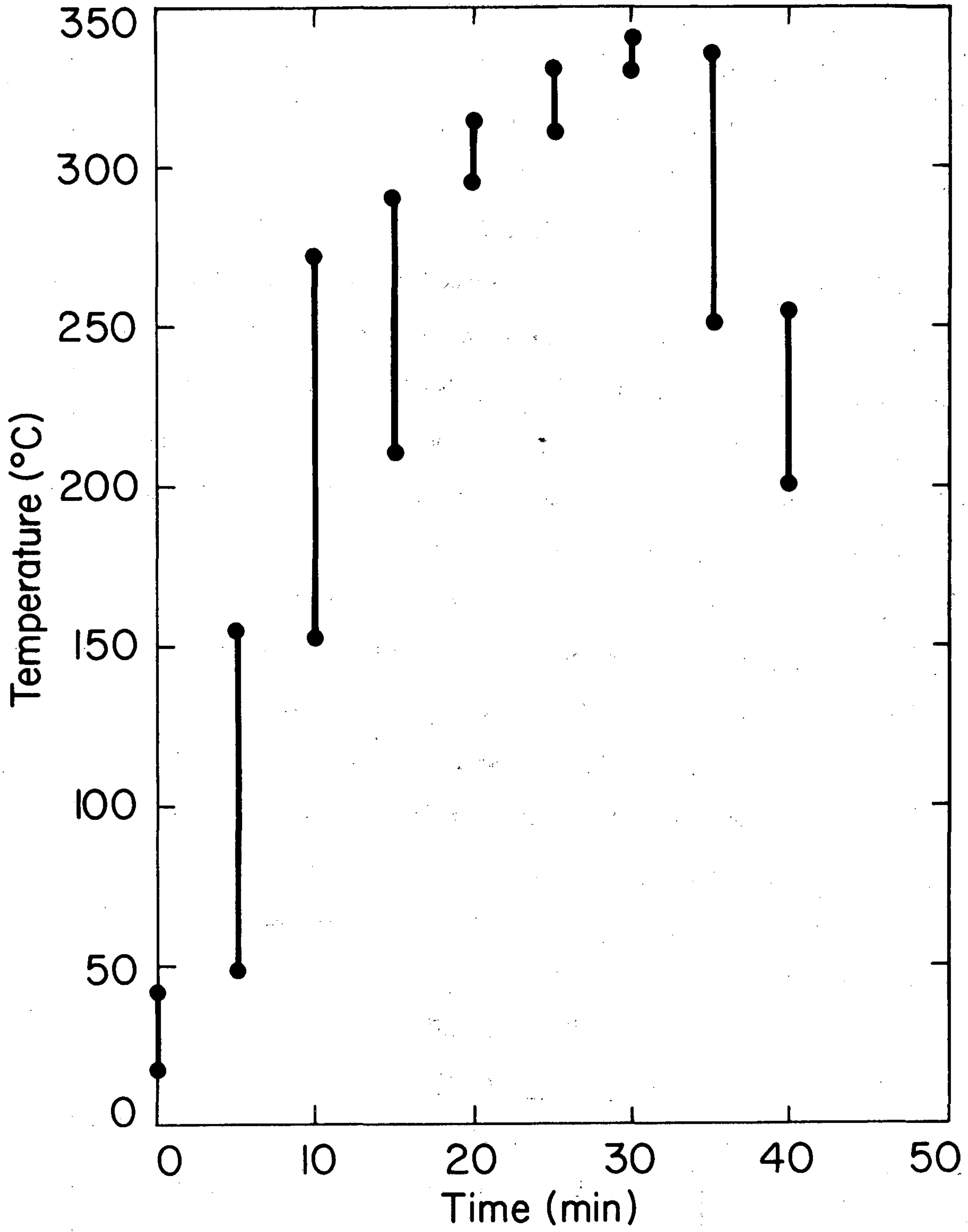

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Fig. 5. Ranges of observed temperature in 1-liter autoclave at 5-min intervals.

The separation procedure adopted in this study was developed by Seth et al.[21] (see Fig. 7 of Ref. 2). In this study it was simplified to a considerable degree. Centrifuging of the liquor to recover oil was omitted. Acetone solubles were not treated any further, nor were the acetone insolubles.

RESULTS

The summary of the data collected is appended. Data collected for a liquefaction test-run included the source, amount and the pH of the slurry utilized; amount of additives (Na_2CO_3, or $Ca(OH)_2$ in two runs) and the change in pH; composition and pressure of the synthesis gas imposed; temperature and pressure recorded at 5-minute intervals; yields of acetone solubles, residue and aqueous phase, composition of acetone solubles and residue (if sent for analysis); pH of the aqueous phase, and the fraction of the materials dissolved in it; and residual gas pressure and its composition. Data concerning a hydrolysis test-run included the amount of the wood flour used, the source of aqueous phase added, its pH, amount of the sulfuric acid added; temperature of hydrolysis as a function of time, and the amount and pH of the resultant slurry. In a few test runs the changes in the pH of the slurry and aqueous phase have been recorded as a function of the amounts of Na_2CO_3 (or $Ca(OH)_2$) and H_2SO_4 added.

DISCUSSION OF RESULTS

Reproducibility and Time-Temperature Effects

Eight runs were conducted in this phase of the study, three runs (No. 16-18) being devoted to reproducibility of the results. The yields of acetone solubles in the three runs cited were 28%, 31%, and 28%, respectively, and insoluble material, 17%, 18%, and 17%. The results obtained are remarkably close. However, the molar ratios of the synthesis gas (CO + H_2) present in the autoclave at the end of the runs to that initially charged were anomalous, i.e., 0.96, 0.99 and 1.07, respectively, two runs suggesting very little synthesis gas utilization and one, No. 18, indicating its generation. The molar CO/H_2 ratios in the spent gas were not very reproducible, i.e., 1.22, 1.46 and 1.19 for Run No's 16, 17 and 18, respectively, as compared to 1.5 in the initial gas charged. The lower CO/H_2 values in the spent gas is attributed to water-gas shift reaction. Since synthesis gas consumption and the composition of the spent gas are important factors in the process economics, the lack of reproducibility observed was not encouraging. For this reason, it was decided to monitor the yield and composition of the spent gas in every run regardless of the objective of the test run.

Table 1 shows the results of two sets of test runs designed to determine the influence of reaction temperature and residence time. A comparison of the results of three runs conducted at 360°C indicates close results in the yield of acetone and water soluble material. The sharp drop in solid residue yield as a result of the increase in residence time from 30 to 60 minutes is questionable. It is not reflected in the yields of acetone and water soluble material nor by the amount of synthesis gas utilized, and is not confirmed by the three runs at 330°C.

Table 1

Influence of Temperature and Time

Run No.	17	20	21	22	23	24
Final T, °C	360	360	360	330	330	330
Holdup time, min.	0	30	60	60	30	0
Acetone solubles %[2]	31	27	30	32	38	37
%C	75.7	79.0	80.8	76.3	76.0	72.6
%H	7.0	7.3	7.7	7.2	7.0	6.4
%O	17.3	13.7	11.5	16.5	17.0	21.0
Calorific value[3]	14,200	15,000	15,700	14,400	14,200	13,100
Acetone insolubles,%	18	18	10	17	18	15
Water solubles, %[4]	10	8	8	8	7	NA
Spent gas P, psig	680	770	764	709	590	530
%CO	22.3	17.0	8.5	12.6	77.9	43.3
$\%H_2$	51.1	42.2	45.8	43.6	5.4	29.5
$\%CO_2$	26.6	40.8	45.8	43.3	16.7	25.0
Syngas utilized,%[5]	1	10	18	20	NA	21

[1] In these runs 300 g Albany slurry and synthesis gas (60% Co, 40% H_2) at P = 500 psig (21°C) were used.

[2] These values appear low, possibly due to a loss of volatiles.

[3] Based on chemical analysis, c.f. references 3 and 4.

[4] Solids remaining after evaporation of water. To account for volatiles lost the results must be multiplied by about two.

[5] Deduced from spent-gas pressure, uncorrected for possible leaks.

Regarding the composition of acetone soluble material (oil) and spent gas utilization, Run Nos. 17, 20 and 21 are remarkably consistent. On the other hand, with an increase in residence time, we observe a consistent decrease in the oxygen content of the oil made up by increases in hydrogen and carbon contents. This trend is reflected in the calculated calorific values of the oil. Similarly a consistent decrease in the CO content of the spent gas is reflected in increases in the CO_2 content of the spent gas and in the amount of net synthesis gas utilized.

More or less identical trends are indicated, regarding the composition of the oil obtained and of the spent gas in the three runs conducted at a lower temperature, i.e., 330°C. Regarding the discrepancies in the oil yields (acetone solubles) shown in Table 1, we anticipate that the measured values are probably reproducible within ± 25% of those reported. (An improved procedure has since been developed which may reduce loss of volatiles.)

Synthesis Gas Consumption and Influence of Its Composition

Carbon monoxide was regarded as a necessary reactant in the conversion of biomass into oil using an aqueous solution of sodium carbonate as a catalyst.[5] Synthesis gas containing up to 50% hydrogen by volume, was found to be equally effective.[1] (The influence of carbon dioxide was not studied in earlier work; recently this problem has been newly explored[12].)

In Table 2 are listed the results of six runs, conducted under identical conditions except for the pressure and composition of the gas introduced into the autoclave. As judged from the yields of acetone-soluble, water-soluble, and insoluble material, the absence of carbon monoxide in Run Nos. 15 and 19 did not yield significantly different results; the faint trend points to more oil yield and less char. (It is unfortunate that samples of the acetone solubles produced in Run Nos. 15 and 19 were not sent for analysis.) The use of higher starting pressure in Run Nos. 15 and 19 raises the question of whether the absence of carbon monoxide was compensated for by the higher initial pressures imposed; however, pressure appeared to have a minor effect. Under the conditions of these runs, the partial pressure of the reducing gas, H_2, was less than in runs 16-18; moreover, repetition of runs 16-18 at an initial pressure of 700 psi did not lead to any significant differences in the product yields. The results obtained in this phase of the present study are very significant in several respects. 1) They may be contrary to previous conclusions regarding the necessity of carbon monoxide. 2) It is likely that spent synthesis gas can be recycled after removal of sufficient carbon dioxide to prevent buildup. 3) It may not be necessary to scrub carbon dioxide from the raw gas produced in gasifiers. However, the uncertainty involved in translating the results of batch experiments into flow systems dictates verification in flow experiments.

An equally important factor in process economics is the amount of the net synthesis gas utilized in the course of liquefaction. Percentages of synthesis gas utilized in 10 runs are listed in Tables 1 and 2. The results of runs 17, 20, and 21 indicate a consistent trend, with more synthesis gas utilized as residence time is increased at 360°C. At a lower temperature, 330°C, the results of runs 22, 23, and 24 are inconclusive. The relatively high utilizations calculated in runs 22 and 24 must be attributed to leaks. It is evident that accurate determination of the synthesis gas utilized requires better experimental procedures.

Table 2
Influence of Synthesis Gas Composition

Run No.	15	19	16	17	18
Final T, °C	360	360	360	360	360
Hold up time, min	0	0	0	0	0
Initial pressure, psig	680	600	500	500	500
%CO	0	0	60	60	60
%H_2	64	70	40	40	40
%CO_2	36	30	0	0	0
Acetone solubles, %	34	33	33	31	28
Acetone insolubles,%	14	15	16	18	17
Water solubles, %	9	10	11	10	NG
Spent gas pressure, psig	650	740	674	680	745
%CO	1.1	1.7	39.4	23.3	39.4
%H_2	55.0	61.0	32.2	51.1	33.2
%CO_2	44.0	37.3	27.4	26.6	27.4
Synthesis gas utilized, %	17	-10	4	1	-7

A major concern in high pressure experiments is the probability of leaks from the autoclaves when the pressures reach the level of 4000 psig. The leaks lead to overestimation of the amount of synthesis gas used. Considering this factor, it is worthwhile to point out that the calculated amounts of synthesis gas reacted in 18 consecutive runs were less than 0.2 g moles/100 g wood liquefied, a quantity much less than 0.7 g moles/100 g wood used in the cost estimate studies.[6,7] This encouraging observation must be tempered by the observations that the runs made batchwise were conducted under conditions not simulating the optimum in a flow process (conditions favorable for insolubles retention or formation), and that gas sampling and analysis did not provide a complete mass balance.

Influence of Stirring

Stirring or agitation effects become most discernable when diffusion, especially in a liquid phase, constitutes a major obstacle to the reaction(s) taking place. Since diffusion rates are functions of concentration gradients and temperature gradients, which affect reaction kinetics, the diffusional effects are not always properly interpreted. In biomass liquefaction, the role of the diffusion appears to be somewhat restricted. Catalysis appears homogeneous, the solid being permeated rapidly by the reaction medium. The solid particles in the slurry and the liquid medium have about the same specific gravity, and the concentration of the solids is sufficiently high to hinder the motion of individual particles in the slurry. On the other hand, diffusion could be a factor in the dissolution of the synthesis gas in the slurry or the liquid phase. In this regard a rotational motion of the slurry by the conventional impellers of the autoclaves may not be as effective as sparging the synthesis gas. Thus it appeared desirable to investigate the effects of changes in the mode of stirring on the yield and quality of the oil produced in the autoclaves.

In Table 3 are shown the results of four runs. Run No. 17 was performed with the regular impeller of the 1-liter autoclave at a relative speed setting 3.0. In run No. 26, the stirrer was not turned on. In run No. 27 a downward forcing impeller was utilized. In Run Nos. 25 and 28, the impeller of the 1-liter autoclave was replaced by the larger impeller of a 1-gallon autoclave, and the speed setting was increased from 3 to 5. Judging from the yields of acetone solubles, the use of the larger impeller (Run Nos. 25 and 28) appears to have been beneficial. However, the results of Run No. 26 (without stirring) suggest that the effects of stirring, as available in our autoclaves, are not pronounced in batch autoclave experiments. It is not possible to decide whether mixing is truly unimportant or was always at much too low a level in the autoclaves.

Effects of Aqueous Phase Recycling

Total recycle of the aqueous phase is not permissible because a stream containing inorganic materials (sulfate and sodium ions and the mineral matter present in the wood) equivalent to that added to the system and water equivalent to that contained in the green wood fed must be removed from the system continuously in order to achieve a steady state condition. For example, if the green wood contains 50% water and if the water/wood ratio (dry basis) in the hydrolyzer is 2/1, only one-half of the aqueous phase can be recycled, i.e., the ratio of the stream recycled to that removed is 1.0.

Table 3
Influence of Agitation[1]

Run No. Impeller	17 Regular	25 Large	26 None	27 Down flow	28 Large
Acetone Solubles, %	31	37	32	26	38
%C	75.7	NA	NA	75.2	71.5
%H	7.0	NA	NA	7.0	6.6
%O	17.3	NA	NA	17.8	21.9
Heating value, Btu/lb	14,200	NA	NA	14,100	13,063
Residue, %	18	12	18	21	19
Water solubles, %	10	6	10	10	14

[1] In these runs the conditions common were heat-up time (24 to 27 min.) to 360°C, hold up time (zero), initial synthesis gas pressure (500 psig), gas composition (40% H_2 and 60% CO), slurry used (obtained from Albany, Oregon), and amount (300g).
In Run No. 17 the regular impeller of the 1-liter autoclave was used at a relative speed setting of 3.
In Run No. 26, the stirrer was turned off.
In Run Nos. 25 and 28, the impeller of the 1-liter autoclave was replaced by the larger impeller of a 1-gallon autoclave.
In run No. 27, a vane-type downward forcing homemade impeller was used.

In order to aim high it was decided to carry out the investigations under conditions simulating a 2:1 ratio. Further, it was assumed that water/wood ratio in the hydrolyzer would be 7/3. Since it is impractical to use wet wood chips in 1-liter autoclaves, it was decided to use 90 g wood flour (oven-dry basis) and 210 g water in hydrolysis and subsequent liquefaction experiments, with eventual recycle of two-thirds of the aqueous phase (leaving 70 g to be evaporated for contaminant disposal and sodium recover. For start-up purposes, to arrive quickly at steady-state compositions, it was necessary to recycle all of the aqueous phase from the first two sequences and recycle two-thirds thereafter.

The effectiveness of the hydrolysis procedure adopted to produce a pumpable slurry was established at Albany, Oregon using 400 gallon nominal size autoclaves. To simulate the chemical conditions imposed at Albany, aqueous phase (initially water) was acidified to a pH 1.8, the wet wood flour was heated to 180°C (130 psig) and held for 45 minutes. There was no deviation from this procedure. Similarly the conditions employed in liquefaction regarding temperature, pressure, hold-up time, composition of the synthesis gas, etc. were kept the same during the recycling experiments.

The additions and changes in the pH in the course of four sequential hydrolysis and liquefaction runs are shown in Table 4. Fresh demineralized water (210 g) required only 0.16 g H_2SO_4 to bring its pH down to 1.8. After the hydrolysis of 90 g wood flour the pH of the slurry was 2.5. The addition of 2.7 g Na_2CO_3 (3% by weight of the wood hydrolyzed) raised the pH of the slurry to 6.9. The pH of the aqueous phase of the liquefaction products was 3.5. It required about 2.5 g H_2SO_4 to lower the pH of the aqueous phase to 1.8. The changes in the pH before and after liquefaction as a result of acidification of the aqueous phase to a pH of 1.8 and addition of 2.7 g Na_2CO_3 to the hydrolyzed slurry are shown in Fig. 6. The following conclusions can be drawn from a study of Fig. 6 and Table 4.

1. The amount of the sulfuric acid necessary to lower the pH of an aqueous phase is largely determined by the amount of sodium carbonate added to the slurry prior to liquefaction, i.e., by stoichiometric equivalence.
2. Since a very small amount of acid, 0.16 g, is required to acidify 90 g water as compared to 2.5 g when 2.7 g Na_2CO_3 is added prior to liquefaction, the excess sulfuric acid serves the purpose converting the anions of weak organic acids to free acids.
3. The pH of the mix of organic acids and their anions, produced under the conditions employed, is about 3.5 (cf. sequences 3 and 4).

In Table 4 are also included the yields of acetone soluble material and residue obtained in Run Nos. 30 through 33. We note a 20% decrease in the yield of acetone-solubles upon first recycle, none upon second recycle, and 18% upon third recycle; indicating a trend for lower oil yields upon recycle. The significance of the trend is diminished by the fact that the reproducibility of oil yields has been poor and that the results are based on a single set of imposed conditions. However, at the present time, the need for another set of conditions that would offset the adverse trend detected cannot be ignored.

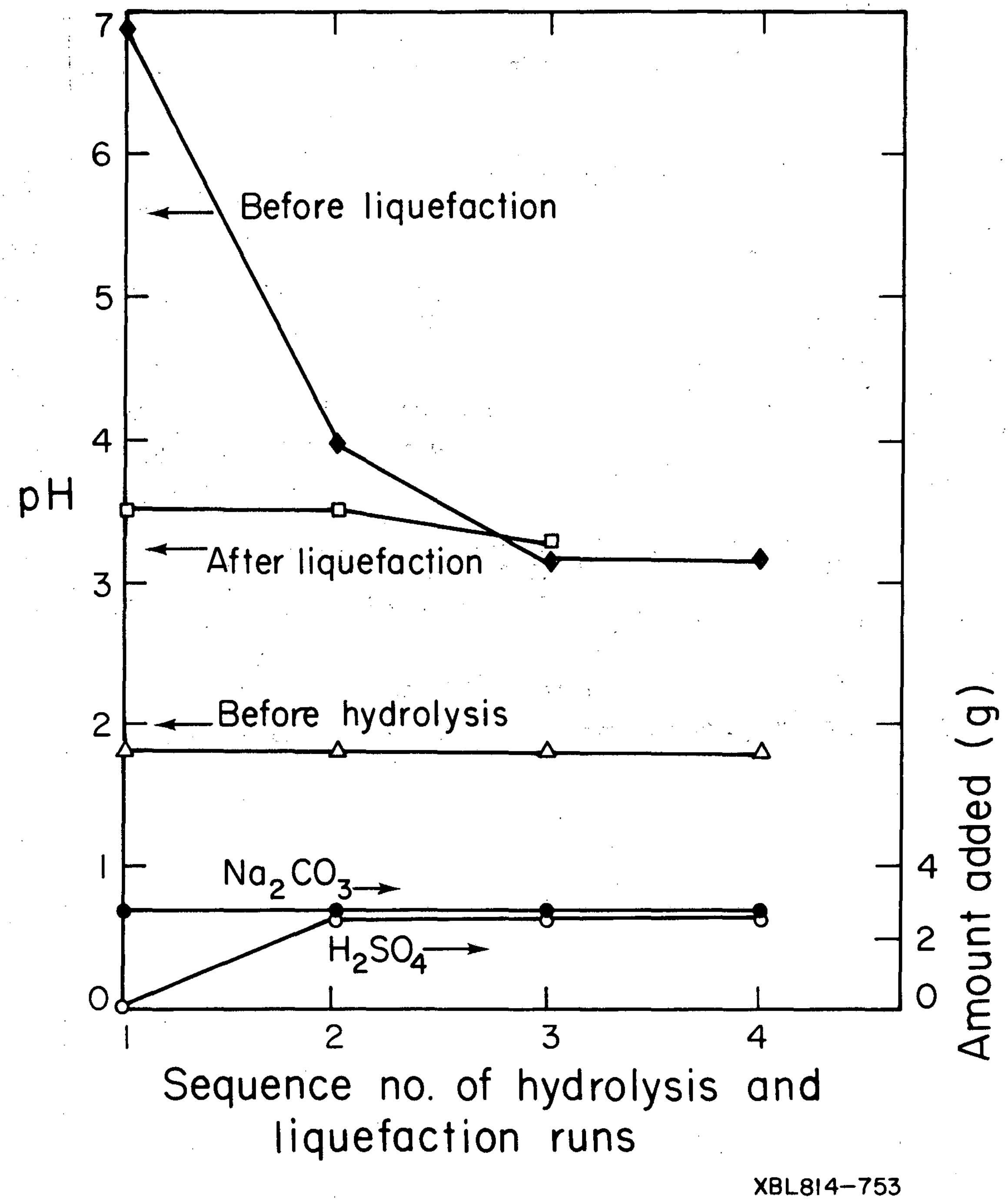

Fig. 6. Sequential hydrolysis and liquefaction of wood flour with aqueous phase recycle (Run Nos. 30-33).

Table 4
Results of Aqueous Phase Recycling[1]

Run No.	30	31	32	33
H_2SO_4 added to pH = 1.8	0.16	2.52	2.50	2.46
pH after hydrolysis	2.5	2.10	2.14	2.10
After Na_2CO_3 addition[2]	6.9	3.76	3.15	3.20
After liquefaction	3.5	3.5	3.30	3.56
Acetone solubles, %	44.0	34.3	34.3	28.0
Heating value, Btu/lb	13,200	12,800	12,900	12,900
Residue, %	14.5	21.7	28.5	28.7
Water-solubles, %	11.9	15	15.3	14.5

[1] In this series the slurry was heated to 340°C in about 27 min and cooled quickly. The results tabulated were normalized to conditions in which 90g wood could be utilized in each run.

[2] Na_2CO_3 added was limited to 3g per 100g wood hydrolyzed.

The next series of experiments was conducted by adding sufficient sodium carbonate to the hydrolyzed slurry to raise its pH to 7.0 before liquefaction, and sufficient sulfuric acid, as before, to the aqueous phase to lower its pH to 1.8 before hydrolysis. The results of six hydrolysis and liquefaction runs conducted during this phase of the study are shown in Table 5, and the additives and changes in the pH in the course of sequential runs are illustrated in Fig. 7.

A clear picture of sodium carbonate and sulfuric acid requirements emerges from sulfate and sodium ion balances, shown in Table 6, for the six consecutive hydrolysis and liquefaction runs included in Table 5 and Fig. 7. Table 6 shows that material subjected to hydrolysis 1 consisted of 92.4 g wood flour, 215.6 g water and 0.8 mg moles of sulfuric acid. Before liquefaction 2, 26.05 mg moles of sodium carbonate was added (as a 20% solution in water) which produced 230.6 g of aqueous phase upon liquefaction. The material subjected to hydrolysis 2 consisted of this aqueous phase acidified with 27.2 mg moles of sulfuric acid and 90 g wood flour. Before hydrolysis 3, about 36 g of aqueous phase from liquefaction 2 was set aside for analysis and 36 g was added to the aqueous phase before hydrolysis 3. The sodium and sulfate ion inventories listed in Table 6 are contained in the charges undergoing hydrolysis. The last column in Table 6 shows the ratios of sodium to sulfate ions in the charges. The values range from 1.81 to 2.19 with average value 2.04 and equal to 2.0 within the estimated accuracy of the data obtained.

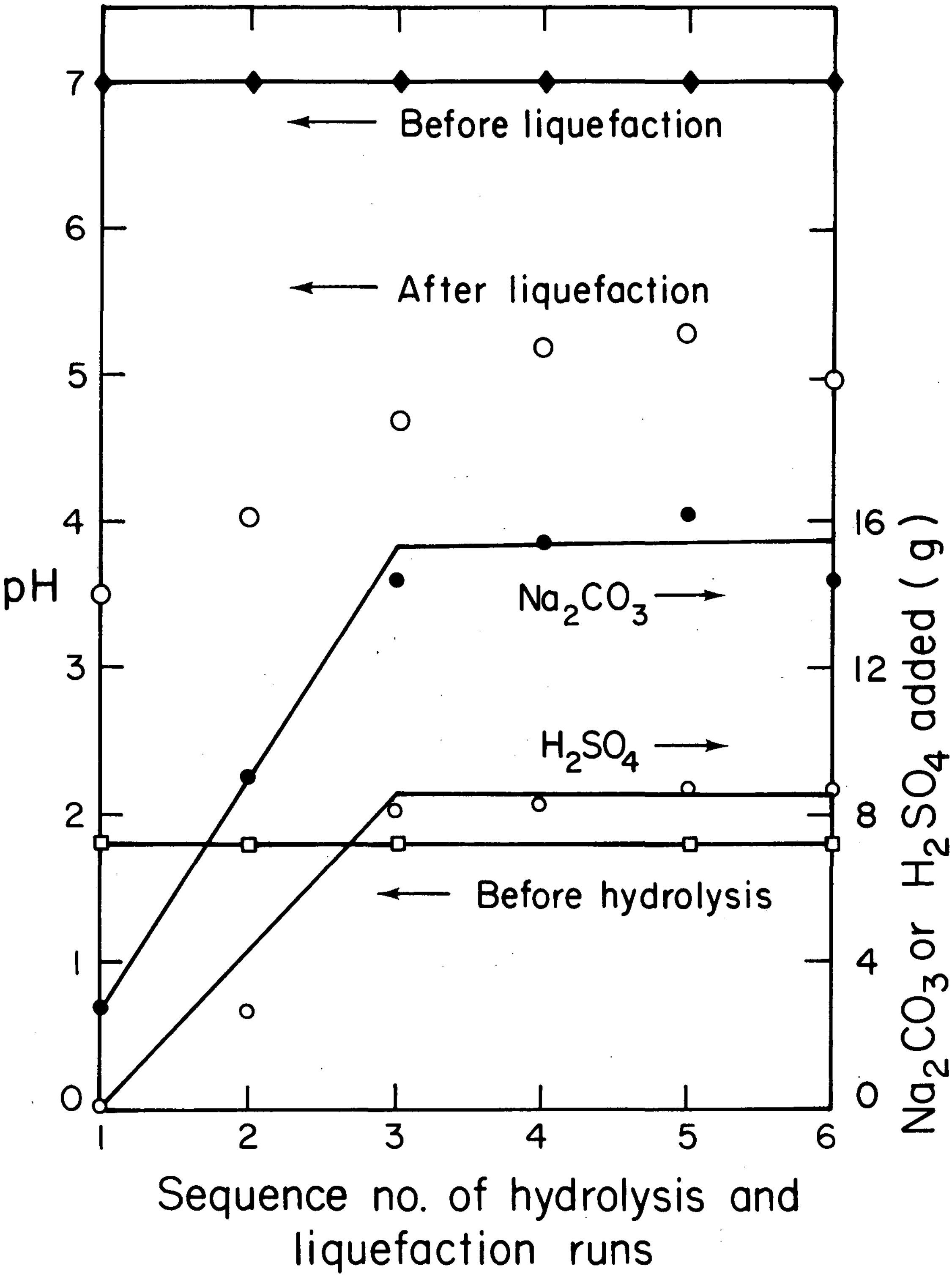

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Fig. 7. Sequential hydrolysis and liquefaction of wood flour (Run Nos. 34-39). Complete recycle in sequences 1-3 and 67% in 4-6.

Table 5
Results of Aqueous Phase Recycling[1]

Run No.	34	35	36	37	38	39
pH of aqueous phase[2]	7.00	4.00	4.70	5.20	5.30	4.97
H_2SO_4 added,[3] g	0.16	2.66	7.07	8.34	8.77	8.76
pH after hydrolysis	2.50	2.10	1.99	1.99	2.10	NR
Na_2CO_3 added, g	2.86	8.99	14.48	15.53	16.24	14.42
Acetone solubles, %	45	62[4]	31	46	42	35
%C	71.1	71.6	73.3	70.9	73.3	74.6
%H	6.6	6.8	7.1	6.9	6.9	6.4
%O	22.3	21.6	19.6	22.2	19.8	19.0
The heating value, Btu/lb	13,000	13,200	13.800	13,100	13,600	13,500
Solid residue, %	12	2.4	21	15	13	30

[1] In these runs the conditions imposed were similar to those in Table 4

[2] After liquefaction

[3] To lower the pH to 1.8

[4] See discussion in text

From an analysis of data listed in Tables 5 and 6, several conclusions can be drawn. First, it is clear that organic acids are produced during both hydrolysis and liquefaction. In terms of 100 g wood processed, the organic acids produced during hydrolysis and liquefaction require roughly 3 and 4 g sodium carbonate, respectively, to neutralize. Using these figures it is possible to predict the sodium carbonate requirements, g/100 g wood processed, using the relations

$$3 + 7\,(n-1) \tag{1a}$$

in which n is the number of sequences of hydrolysis and liquefaction with total aqueous phase recycle and

$$3 + 7\,r \tag{1b}$$

under steady-state conditions in which r represents the ratio of recycle stream to that withdrawn.

In Fig. 7, the solid line shown corresponds to that calculated using equations (1) for 90 g wood (actually processed); and the circles, the experimental values. The agreement is good.

The good agreement observed suggests that under the experimental conditions employed, organic acids present in the aqueous phase are not destroyed either during hydrolysis or during liquefaction to an appreciable degree - at least, not below a steady-state level.

Table 6
Sulfate and Sodium Ion Balances in Six Consecutive Prehydrolysis and Liquefaction Experiments
(Runs Nos. 34,39)

Operation	Wood g	Aqueous Phase g	Water g	$SO_4^=$ mg moles	Na^+ mg atoms	pH	$\frac{Na^+}{SO^=}$
Hydrolysis 1	92.4		215.6	1.6		1.8	
Liquefaction 1					52.1	7.0	
Hydrolysis 2	90.0	230.6		27.2		1.8	
Inventory				28.8	52.1		1.81
Liquefaction 2					169.6	7.0	
Hydrolysis 3	90	194	36	69.5		1.8	
Inventory				93.2	187.2		2.01
Liquefaction 3					273.2	7.0	
Hydrolysis 4	90	125	98.8	71.3		1.8	
Inventory				123.4	257.4		2.09
Liquefaction 4					293.0	7.0	
Hydrolysis 5	90	120	100	73.2		1.8	
Inventory				140.6	300.4		2.14
Liquefaction 5					306.0	7.0	
Hydrolysis 6	90	144	86	89.2		1.8	
Inventory				181.2	397.0		2.19
Liquefaction 6					196.0	7.0	

From an analysis of Table 6 we have already observed that the amount of sulfuric acid necessary to lower the pH of the aqueous phase of a liquefaction experiment roughly corresponds (stoichiometrically) to the amount of of sodium carbonate added to the slurry before liquefaction. In addition, we also observed that the amount of sulfuric acid necessary to reduce the pH of 210 g demineralized water is small (0.16 g) compared to the amounts found to be necessary after liquefaction (2.7 to 8.9 g, cf. Table 5). From these observations, it is obvious that the sulfuric acid needed to lower the pH of the aqueous phase to a value of about 2 is largely consumed in converting the sodium salts of the weak organic acids into sodium sulfate and free organic acids. Based on this observation and equations (1) we may now write expressions to predict the amounts of sulfuric acid used in runs 34-39, viz.,

$$0.18 + (98/106)\ (n-1)(3 + 7\ (n-2)) \quad \text{for } n = 1 \text{ and } 2 \qquad (2a)$$

and

$$0.18 + (98/106)\ r\ (3 + 7\ r)/(1 + r). \qquad (2b)$$

under steady state conditions. The experimental results of the sulfuric acid needed in the sequences 1 through 6, i.e., runs 34-30, are shown in Fig. 7 as circles; and those calculated using equations (2), multiplied by 0.9, as solid lines. Again we observe a good agreement between the calculated and experimental results.

The pH of the aqueous phase obtained upon liquefaction of a slurry having a pH of 7.0 is more difficult to predict than the amount of sodium carbonate to neutralize it because it requires a knowledge of the distribution of the organic acids produced and their dissociation constants. For this reason no attempt has been made to draw a line through the experimental points, circles, in Fig. 7.

The oil and solid residue yields obtained in this series of runs are given in Table 5. The oil yield ranged from 31 to 62% with an average value of 43.5 ± 10.8%. The yield obtained in Run No. 35, 62 , appeared to be excessive when compared to the average of the other five companion runs, 39.8 ± 6.5%. An attempt to reextract a sample of the acetone-soluble material obtained in Run No. 35 yielded a 32% residue reducing the net acetone soluble yield from 62% to 42% thus bringing it to a level more consonant with the results obtained in the other runs. By the same token one may be inclined to reject the result obtained in Run No. 36 because it is lower by 48% then the average of the other five. The point of contention is the reproducibility of oil yields; obviously it is not better than ± 25% of the values reported. Incidentally, the nonaqueous phase of the product obtained in all of these runs was solid at room temperature, adhering to the cooling coil and the impeller of the autoclave; each had to be shipped away with a spatula, to be recovered and rinsed with acetone. In contrast, the product oil obtained at Albany, Oregon (Run TR-7) was fluid at 45°C and showed creep at 10 to 20°C. This may, at least in part, result from loss of volatiles during pressure let-down of the autoclave.

Experiments with Calcium Hydroxide

Replacement of sodium carbonate with calcium carbonate would be advantageous because calcium is more easily removed than is sodium, provided, of course, that calcium carbonate is effective in promoting liquefaction. Two consecutive hydrolysis and liquefaction experiments were conducted using calcium hydroxide to neutralize the hydrolyzed slurry. The oil yield in the first liquefaction was 29%, suggesting that calcium carbonate or hydroxide is suitable. The oil yield in second run was unfortunately voided. The insoluble material obtained amounted to 30% and 20% of the wood charged in the two runs conducted. The sulfate and calcium balances in the aqueous phase are shown in Table 7; precipitated calcium sulfate was recovered as a byproduct.

The first option to recycling considered in this study was simply to add the same amount of sodium carbonate as before. Recycling necessitated the addition of sufficient sulfuric acid to the recycled aqueous phase to lower its pH to 1.8. If six parts of sodium carbonate (per 100 part of dry wood) is added to the slurry before liquefaction, roughly 3 parts of sulfuric acid will be needed to acidify the recycle stream. From the point of view of process economics all that is necessary is to weigh the cost benefits of reducing the amount of the water to be treated from 200 to 100 parts versus the cost of 3 parts of sulfuric acid. In this situation the benefits to be gained outweigh the cost of the increased acid consumption. Unfortunately, data obtained in this study indicated that the pH of the slurry to be liquefied will be below 4.5 and that the lower pH values lead to lower oil yields. Whether or not this adverse effect can be offset by changes in the reaction temperature and/or residence time needs to be determined.

The second option considered was to raise the pH of the slurry to a neutral level prior to liquefaction. For a recycle ratio of 1.0, roughly 10 parts of sodium carbonate are needed to raise the pH of hydrolyzed slurry to about 7.0 and 4.7 parts of sulfuric acid are needed to reduce the pH of the recycle stream to 1.8. The material balances given in Fig. 12 correspond to

Table 7
Sulfate and Calcium Ion Balances in Two Consecutive Prehydrolysis and Liquefaction Experiments
(Run Nos. 41-42)

Operation	Wood g	Aqueous phase, g	Water g	$SO_4^=$ Millimoles	Ca^{++} Millimoles	pH
Hydrolysis 1	90		210	1.63		1.80
Liquefaction 1					27.3	9.30
Hydrolysis 2	90	136[a]	74	18.22		1.80
Liquefaction 2					61.49	7.90
Acidification [b] *				58.37		1.80

[a] 74 g of the aqueous phase was set aside for titration experiments. Upon acidification $CaSO_4$ precipitated, and 2.5 g $CaSO_4$ was recovered.

[b] Upon acidification $CaSO_4$ precipitated.

*Upon acidification of the aqueous phase from liquefaction 2 (cf. Figure 8) $CaSO_4$ started to precipitate when pH3 was reached. The measured amount of precipitate in a 20g sample was about 1.06g (or about 78 millimoles in a 202g sample). The solubility of calcium sulfate at the endpoint is such that about 7 millimoles of sulfate plus acid sulfate remain unprecipitated.

equations 1 and 2 of this study. In this case the benefits to be gained by reducing the amount of waste water to be treated by one-half must be weighed against the cost of increased amount of sodium carbonate (from 6 to 10 parts) and that of sulfuric acid necessary for hydrolysis (4.7 parts). The amount of sulfuric acid necessary to lower the pH of the aqueous phase was dictated largely by the amount of calcium in the liquid, cf. Table 7.

The aqueous phase resulting from the liquefaction tests was always clear; it became dark upon exposure to air. The resulting black or dark blue regions assumed a yellowish color when acidified with H_2SO_4 when its pH reached a value of about 3. When calcium hydroxide was used to neutralize the hydrolyzed slurry, calcium sulfate started to precipitate during H_2SO_4 addition when the pH of the liquor had dropped to about 3. The changes in the pH of the aqueous phase of the second liquefaction run with the addition of sulfuric acid is shown in Fig. 8. The measured amount of the precipitate agreed with the total calcium and sulfate ions added within the limits of the precision of the experiments conducted (cf. Table 7).

The titration of the filtered aqueous phase with calcium hydroxide is shown in Fig. 9. The titration curves seen in Figs. 8 and 9 are superimposed in Fig. 10. The close agreement of the two curves indicates that the calcium salts of the organic acids are soluble under acidic conditions as would be expected from known solubility data. A sample of pre-filtered aqueous phase, brought to a pH of 7 by the addition of calcium hydroxide, was filtered to see if any significant amount of insoluble calcium salts of organic acids was produced. A small weight of precipitate was observed, less than 15%of the weight of the total calcium hydroxide added. At least some of this can be accounted for as calcium sulfate. That there was some precipitation was

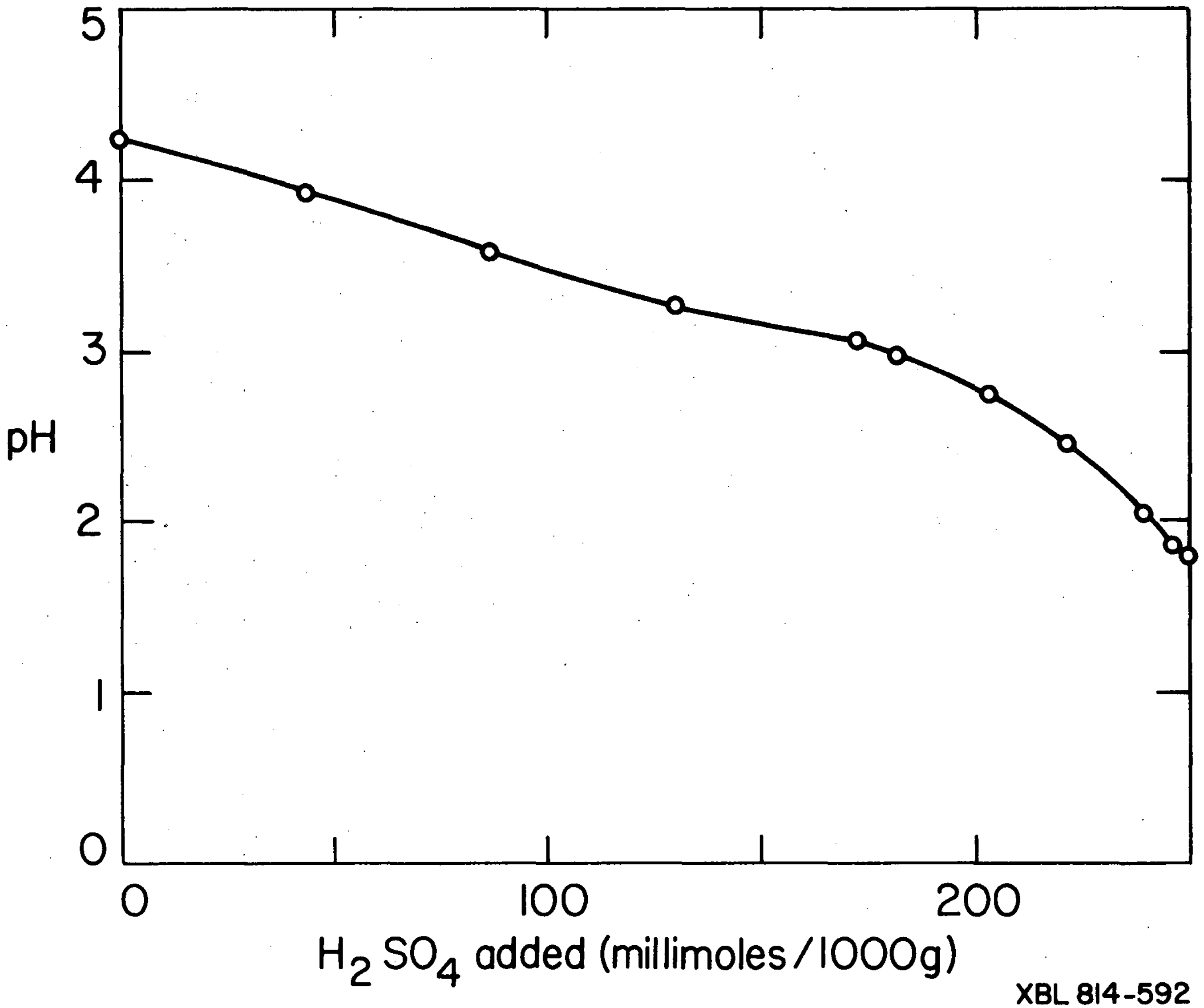

Fig. 8. Acid titration characteristics of aqueous phase from Run No. 42.

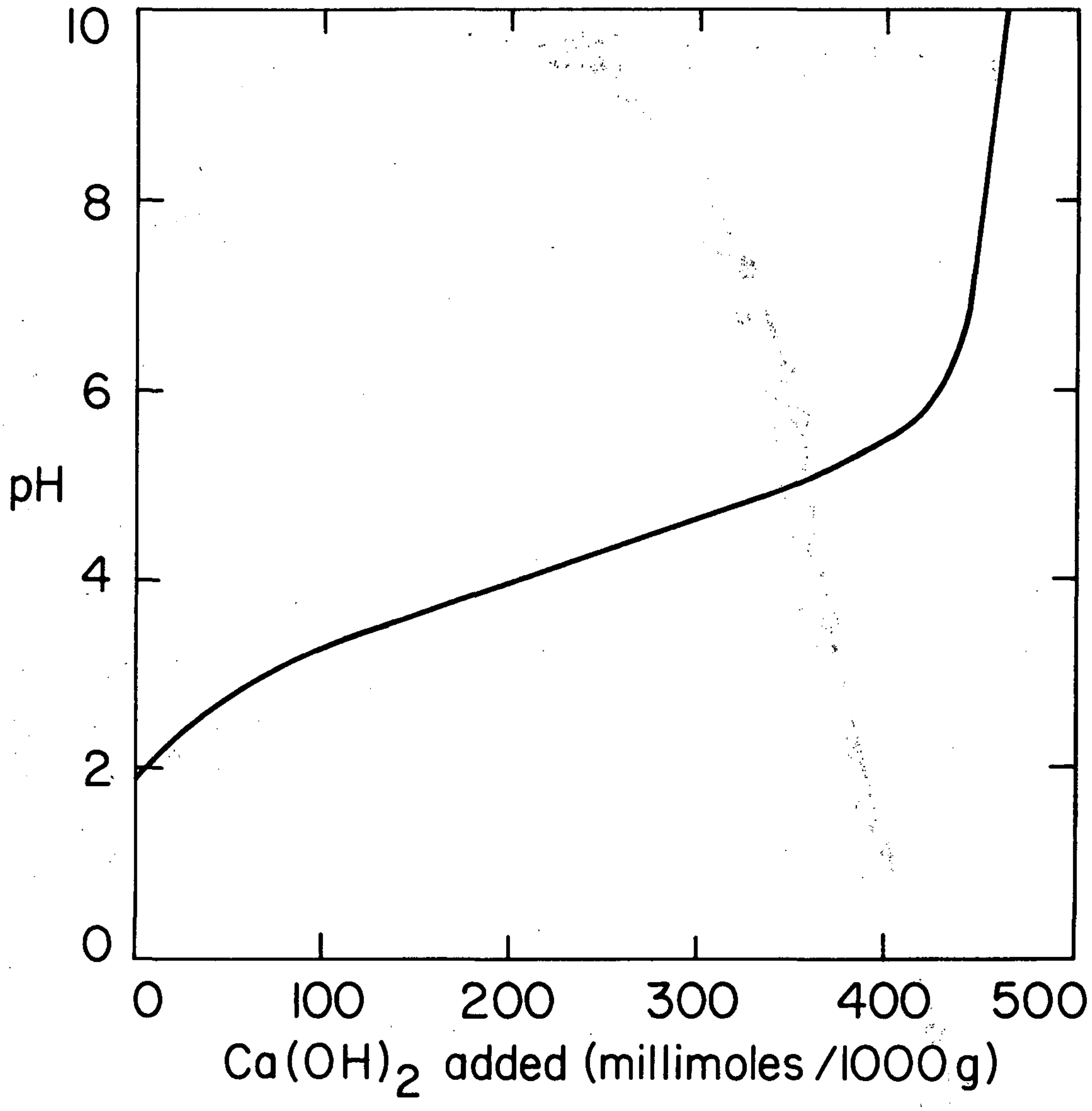

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Fig. 9. Alkali titration of acidified aqueous phase from Run No. 42 after filtration of precipitated calcium sulfate.

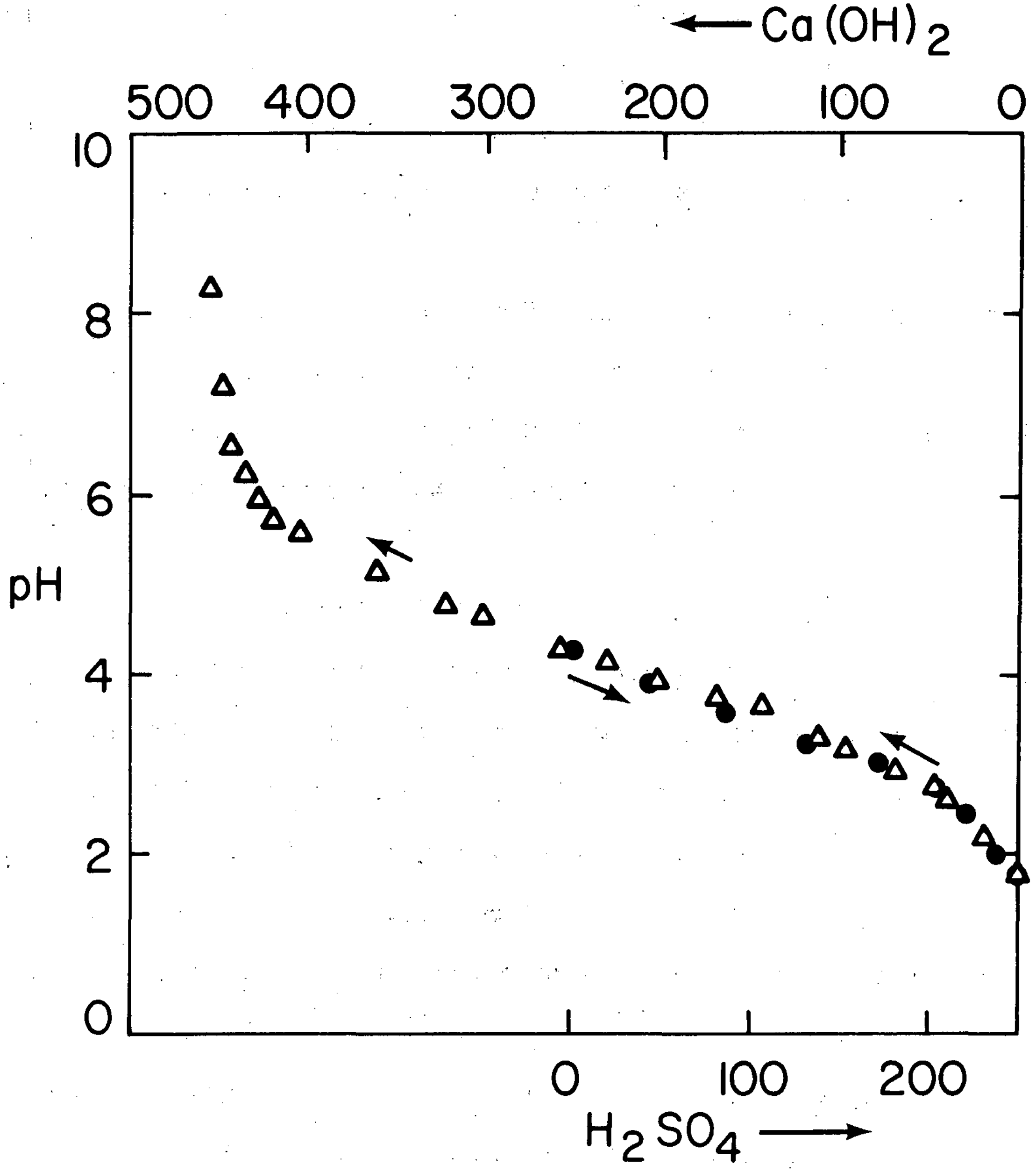

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Fig. 10. Superimposition of acid and alkali titration curves shown in Figs. 8 and 9.

confirmed by back titration of the neutralized liquid with sulfuric acid which is shown in Fig. 11. The hysteresis observed in Fig. 11 confirms that some precipitation had occurred; i.e., about seven percent of the calcium ions remained unaccounted for. This amount is close to the amount of change of solubility with pH, but probably some calcium carboxylate is included in the precipitate.

In terms of the relative amounts of organic acids produced during hydrolysis and liquefaction, Table 7 suggests that about 3 g of calcium carbonate would suffice to neutralize the organic acids produced during a liquefaction run. The results of Tables 6 and 7 are consistent to within 10 percent.

ECONOMIC ASPECTS OF RECYCLING AQUEOUS PHASE

In the LBL liquefaction process it was originally postulated that 335 parts (by weight) water would be needed to convert 100 parts (dry basis) wood into a pumpable slurry using only 1.25 parts sulfuric acid. About 6 parts of sodium carbonate would be added to the slurry, as a catalyst, before the subsequent liquefaction step. It was further postulated that the aqueous phase exiting the reactor would contain sodium salts and soluble organic material and had to be treated to meet the EPA standards for effluent streams. Economic feasibility analyses of the process revealed that engineering judgment needs to be exercised regarding the procedures for, and cost of, water treatment.[6-10] In one estimate, water treatment was one of the costliest unit operations.[10]

A logical solution to reducing the cost of aqueous-phase treatment was to recycle part of the aqueous phase to the hydrolyzer. However, because

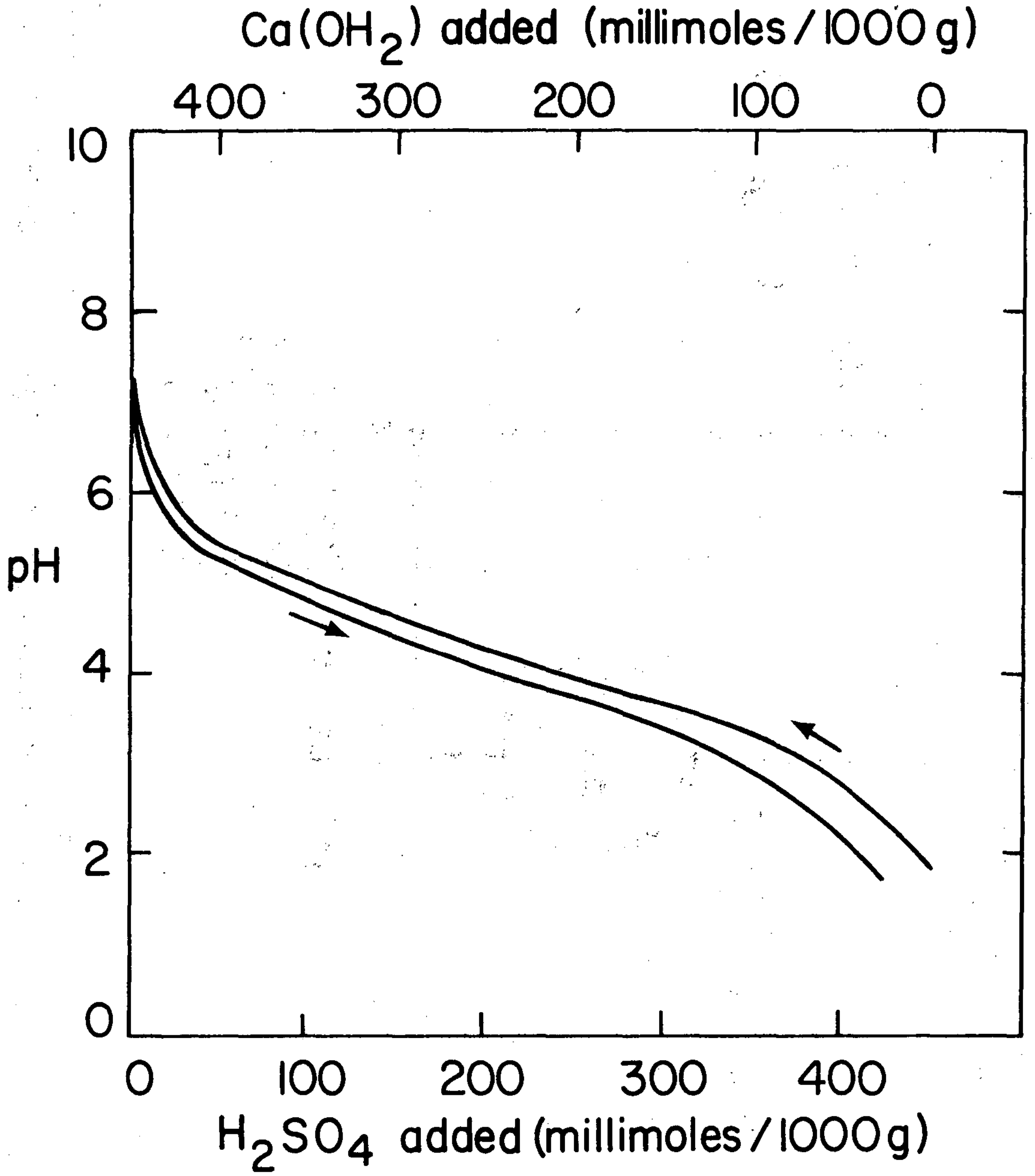

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Fig. 11. Reacidification of neutralized aqueous phase from Run No. 42. Hysteresis indicates precipitation of calcium salts.

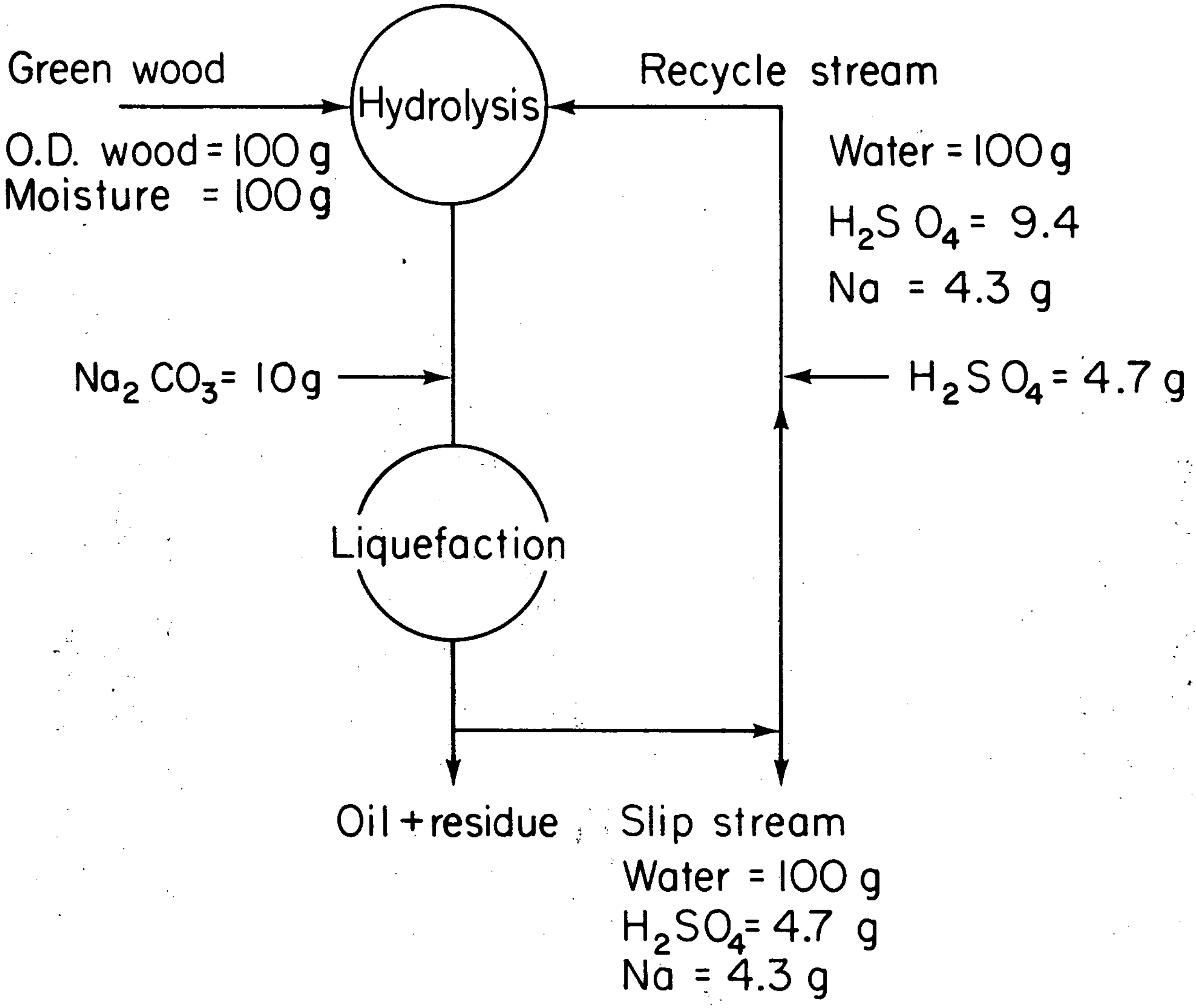

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Fig. 12. Sodium carbonate and sulfuric acid requirements of a recycle ratio of 1.0.

hydrolysis was done at a low pH, < 2.0, and liquefaction at a neutral pH, 7.0, and because the necessary pH oscillation in a continuous operation would result in utilization of large amounts of sulfuric acid and sodium carbonate, the experiments that would fully establish the benefits at this approach were postponed. Instead, rheological investigation of the hydrolyzed wood slurries was undertaken.[11]

Rheological studies at LBL quickly yielded very promising results that led to test runs at Albany, Oregon, involving the hydrolysis of wood chips in 1000-liter batches, with refining and pumping tests at rates of about 200 liters/hr. In these tests it was established that the water/wood ratio could be reduced from 3.35 to 2.0 or lower, potentially reducing the amount of the water to be treated by about 40%.

Further reduction in the amount of waste water to be treated can be effected simply by recycling a portion of the aqueous phase. However, as mentioned earlier, there is a limit to the amount that can be recycled, dictated by the water content of the green wood processed. It appears that the cost benefits are marginal.

If calcium carbonate can be substituted for sodium carbonate, the economics of the process would be improved because limestone is much cheaper and calcium sulfate recovered may be saleable. This case is illustrated in Fig. 13. Whether or not calcium carbonate is as effective as sodium carbonate has not been fully established. It is also possible that a calcium cycle can be imposed upon a sodium cycle, as is done in the pulp and paper industry alkaline pulping process. The complications of this process make us believe that economic benefits would be, at best, marginal.

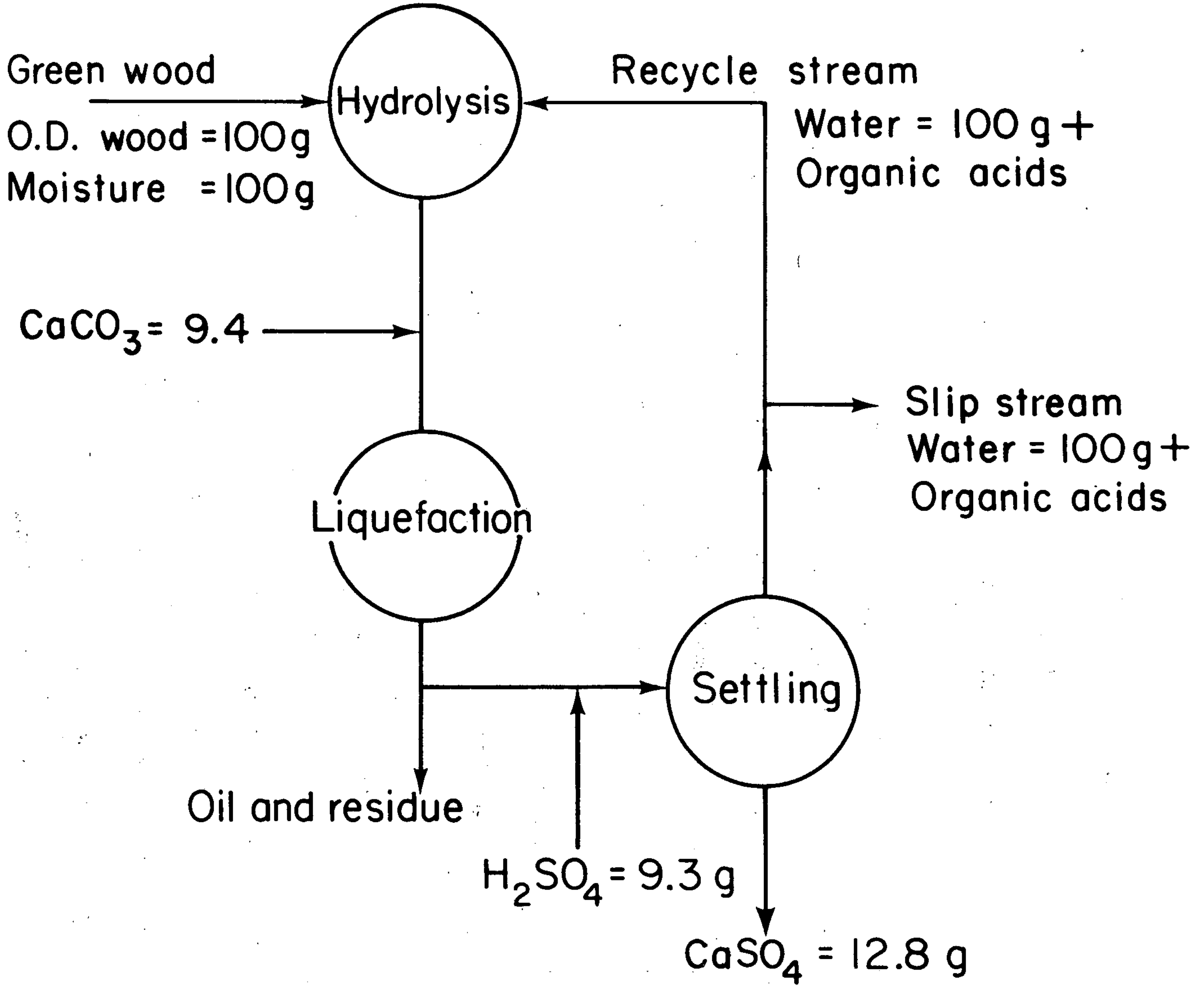

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Fig. 13. Calcium carbonate and sulfuric acid requirements of a recycle ratio of 1.0.

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Appendix

Summary of Data Collected

RUN No. 15L (Influence of synthesis gas composition)[1]
Slurry = 302.6 (Albany)[2]
Synthesis gas: 36% CO_2, 64% H_2, P = 680 psig (21°C).
T and P as a function of time:

θ, min:	0	1	10	18	23	29	31	NR[3]
T, °C:	73	89	245	321	344	360	300	21
P, psig:	680	1100	1500	2700	3800	4300	2000	644

Products:

Acetone solubles = 30.4g (34%).[4] Analysis not available.

Insolubles = 12.9g (14%). Analysis not available.

Water solubles = 7.8g (9%)

Residual gas: 55% H_2, 44% CO_2, 11% CO. P = 644 psig at 21°C

RUN No. 16L (Influence of synthesis gas composition)

Slurry = 300 g (Albany)

Synthesis gas: 40% H_2, 60% CO; P = 500 psig at 21°C

T and P as a function of time:

θ, min:	1	3	12	19	24	28	NR
T, °C:	75	163	284	322	349	360	21
P, psig:	900	1000	1500	2600	3500	4200	674

Products:

Acetone solubles = 25.0g (28%). Analysis not available.

Insolubles = 15.5g (17%)

Water solubles: NA

Residual gas: 32.2% H_2, 27.4% CO_2, 39.4% CO; P = 674 psig

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[1] L designates liquefaction and H, hydrolysis. The purpose of the run is as indicated between parentheses.

[2] The slurry was prepared at the Albany, Oregon Biomass Liquefaction Facility of DOE. Its total solid content = 29.8% and neutralized with Na_2CO_3 to a pH = 7.0

[3] NR designates not recorded and NA, not available.

[4] Percentages shown in parentheses are based on the total solid content of the slurry or the dry wood flour used if hydrolysis was done at the laboratory.

RUN NO. 17L (Duplicate of 16L)

Slurry = 300g (Albany)

Synthesis gas: 40% H_2, 60% CO, P = 500 psig at 21°C

T and P as a function of time:

θ, min:	0	2	7	12	22	27	30	NR
T, °C:	70	120	202	269	319	347	360	21
P, psig:	500	930	1100	1300	2300	3000	3400	680

Products:

Acetone solubles = 28g (31%); 75.7% C, 7.0% H, 17.3% O; 1.7% ash.

Insolubles = 16g (18%) ; 77.2% C, 5.1% H, 17.7% O; 4.3% ash.

Water solubles = 9.4g (10%)

Residual gas: 51.1% H_2, 26.6% CO_2, 23.3% CO; P = 680 psig at 21°C

RUN NO. 18L (Triplicate of 16L)

Slurry = 300g (Albany)

Synthesis gas: 40% H_2, 60% CO; P = 500 psig at 21°C

T and P as a function of time:

θ, min:	5	11	18	26	31	33	NR
T, °C:	95	158	251	288	328	360	20
P, psig:	900	1000	1400	2100	2700	3600	745

Products:

Acetone solubles = 25g (28%). Analysis not available.

Insolubles = 15.5g (17%). Analysis not available.

Water solubles = NA.

Residual gas: 33.2% H_2, 27.4% CO_2, 39.4% CO; P = 745 psig at 21°C

RUN NO. 19L (Duplicate of 15L)

Slurry = 300g (Albany)

Synthesis gas: 30% CO_2, 70% H_2; P = 600 psig at 21°C

T and P as a function of time:

θ, min:	3	10	15	22	27	33	NR
T, °C:	91	189	224	315	335	360	20
P, psig:	1000	1200	1500	2200	2900	3700	740

Products:

Acetone solubles = 29.05g (32.5%). Analysis not available.
Insolubles = 13.76g (15.4%). Analysis not available.
Water solubles = 9g (10%)
Residual gas: 61.0% H_2, 37.3% CO_2, 1.7% CO; P = 740 psig at 20°C

RUN NO. 20L (Effect of time and temperature)
Slurry = 300g (Albany)
Synthesis gas: 60% CO, 40% H_2; P = 500 psig at 20°C
T and P as a function of time:

θ, min:	2	6	15	20	31	41	50	60	71	75	140
T, °C:	60	106	182	241	300	356	362	359	358	300	54
P, psig:	500	900	1050	1200	2170	3240	3730	3740	3930	2320	950

Products:

Acetone solubles = 24.50g (27.4%); 79.0% C, 7.3% H_2, 13.7% O; 0.5% ash
Insolubles = 16.09g (18.0%); 79.5% C, 4.7% H, 15.8% O; 3.8% ash
Water solubles = 7.03g in 213g.
Residual gas: 42.2% H_2; 40.8% CO_2; 17.0% CO; P = 770 psig at 20°C

RUN NO. 21L (Influence of time and temperature)
Slurry = 300g (Albany)
Synthesis gas: 40% H_2; 60% CO; P = 500 psig at 20°C
T and P as a function of time:

θ, min:	0	5	10	15	20	26	30	32	45	62	75	86	92
T, °C:	47	101	170	238	270	319	346	360	359	360	359	360	360
P, psig:	500	960	1100	1400	1810	2560	3100	3500	3720	4200	4300	4350	4350

Products:

Acetone solubles = 26.37g (29.5%); 80.8% C, 7.7% H, 11.5% O; 0.4% ash
Insolubles = 9.30g (10.4%); 84.0% C, 4.7% H, 11.3% O; 11.9% ash
Residual gas: 45.8% H_2, 45.8% CO_2, 8.5% CO; P = 760 psig at 20°C

RUN NO. 22L (Influence of time and temperature)
Slurry = 300 g (Albany)
Inlet gas: 40% H_2, 60% CO; P = 500 psig at 21°C
T and P as a function of time

θ, min:	5	10	20	25	45	60	70	85	NR
T, °C:	151	227	284	330	328	327	332	333	21
P, psig:	900	1250	1950	2500	2900	3100	3250	3300	710

Products:

Acetone solubles = 28.8g (32%); 76.3% C; 7.2% H, 16.5% O; 0.1% ash
Insolubles = 15.4g (17%); 76.4% C, 5.3% H, 18.3% O; 7.7% ash
Residual gas: 43.6% H_2, 43.3% CO_2 12.6% CO; P = 710 psig at 21°C

RUN NO. 23L (Influence of time and temperature)
Slurry = 300g (Albany)
Synthesis gas: 40% H_2, 60% CO; P = 500 psig at 21°C
T and P as a function of time:

θ, min:	0	5	10	15	20	25	30	35	40	50	60	70	80
T, °C:	32	97	182	228	254	296	330	331	329	331	329	223	179
P, psig:	500	700	1050	1200	1600	2200	2600	2600	2650	2900	3000	1300	1050

Products:
Acetone solubles = 33.6g (37.6%); 76.0% C, 7.0% H, 17.0% O; 0.4% ash
Insolubles = 16.3g (18.2%); 77.9% C, 5.4% H, 16.7% O; 3.4% ash
Residual gas: P = 620 psig at 34^{o}C (Composition = unknown)

RUN NO. 24L (Influence of time and temperature)
Slurry = 300g (Albany)
Inlet gas: 40% H_2; 60% CO; P = 500 psig at 21^{o}C
T and P as a function of time:

θ, min:	0	8	13	18	23	25	33	48	NR
T, ^{o}C:	63	203	260	284	321	330	247	171	60
P, psig:	500	1000	1300	1700	2600	2800	1400	900	600

Products:
Acetone solubles = 32.73g (36.6%); 72.6% C, 6.4% H, 21.0% O; 0.1% ash
Insolubles = 13.57g (15.2%); 74.7% C, 5.7% H, 19.6% O; 3.5% ash
Residual gas: 29.5% H_2, 25.0% CO_2, 43.3% CO; 0.7% N_2; P = 600 psig at 60^{o}C

RUN NO. 25L (Influence of stirring-The larger impeller of a 1 gallon autoclave was used)
Slurry = 300g (Albany)
Inlet gas: 40% H_2, 60% CO; P = 500 psig.
T and P as a function of time:

θ, min:	0	10	15	20	25	29	33	NR
T, ^{o}C:	44	163	232	318	332	350	360	40
P, psig:	500	1050	1400	2400	3050	3500	4000	720

Products:
Acetone solubles = 33.2g (37.1%). Analysis not available.
Insolubles = 10.96g (12.2%). Analysis not available.
Water solubles = 4.49g (5.5%)
Residual gas: 47.2% H_2, 43.7% CO_2, 16.12% CO; P = 720 psig at 40^{o}C

RUN NO. 26L (Influence of stirring-the impeller was turned off)
Slurry = 300g (Albany)
Inlet gas: 40% H_2, 60% CO; P = 500 psig at 20^{o}C
T and P as a function of time:

θ, min:	0	10	15	20	25	29	33	NR
T, ^{o}C:	44	163	232	318	332	350	360	40
P, psig:	500	1050	1400	2400	3050	3500	4000	720

Products:
Acetone solubles = 28.23g (31.5%) Analysis not available.
Insolubles = 16.2g (18.1%) Analysis not available.
Water solubles = 8.85g (10%)
Residual gas: 36.7% H, 29.3% CO_2, 35.2% CO; P = 650 psig at 32^{o}C

RUN NO. 27L (Influence of stirring-A vane type downward foreign impeller was used)
Slurry = 300g (Albany)
Inlet gas: 40% H, 60% CO_2; P = 500 psig at 20°C
T and P as a function of time:

θ, min:	0	5	10	17	21	24	35	NR
T, °C:	70	150	236	308	323	348	360	40
P, psig:	500	950	1100	2250	2700	3300	3850	600

Products:
Acetone solubles = 23.5g (26.3%); 75.2% C, 7.0% H, 17.8% O; 0.4% ash
Insolubles = 18.6g (20.8%); 78.2% C, 5.6% H, 16.2% O; 5.6% ash
Water solubles = 8.63g in 212.5g phase (9.6%)
Residual gas: 44.2% H, 40.9% CO_2, 14.5% CO; P = 600 psig at 40°C

RUN NO. 28L (Stirrer effects-Duplicate of 25L)
Slurry = 300g (Albany)
Inlet gas: 40% H_2; 69% CO; P = 500 psig at 20°C
T and P as a function of time:

θ, min:	0	4	9	14	19	24
T, °C:	35	114	164	209	289	330
P, psig:	500	900	1000	1000	1550	2800

Products:
Acetone solubles = 28.5g (37.5%); 71.5% C, 6.6% H, 21.9% O; 0.8% ash
Insolubles = 17.05g (19%); 72.3% C, 5.9% H, 21.8% O; 2.3% ash
Aqueousphase = 224.3g; water solubles 12.8g (14.3%)
Residual gas: 35.2% H_2, 26.0% CO_2, 38.7% CO; 680 psig at 37°C

RUN NO. 29L (Pretreatment effect)
Slurry = 300g (Albany) subjected to 170°C for 2 hours.
Synthesis gas: 40% H_2, 60% CO; 500 psig (20°C)
T and P as a function of time:

Time, min:	0	5	10	15	20	25	30	35	40	NR
Temp °C:	26	98	146	254	304	320	337	355	360	40
P, psig:	500	950	1020	1200	1650	2500	2850	3500	3750	610

Output:
Acetone solubles = 38.1g (42.5%). Analysis not available.
Insolubles = 10.4g (11.6%) Analysis not available.
Water solubles = 36.46g in 200 g
Final gas: 47.7% H_2, 46.7% CO_2, 5.3% CO; P = 610 at 40°C.

RUN NO. 30H (Hydrolysis 1-Aqueous phase recycle)
Wood flour = 210g, water = 490g, H_2SO_4 = 0.38g; pH = 1.8.
Temperature as a function of time: NR. It took 1 hour and 22 min. to reach 180°C.
Product: Prehydrolyzed slurry having a pH of 2.5.

RUN NO. 30L (Liquefaction 1-Aqueous phase recycle)

Slurry = 300g (obtained in RUN NO. 30H); pH = 2.5; pH as a function of NA_2CO_3 added: 2.5 (0.0g); 4.1 (0.9g); 5.7 (1.8g); 6.9 (2.8g).

Synthesis gas: 40% H_2, 60% CO; P = 800 psig.

T and P as a function of time:

θ, min:	0	5	10	15	20	25	30	35	40	NR
T, °C:	47	124	274	290	325	340	231	181	148	40
P, psig:	800	1400	2100	2600	3450	3900	2000	1500	1350	950

Products:

Acetone solubles = 40.1g (44.0%); 73.3% C, 6.3% H, 20.4% O; 0.5% ash

Residue = 13.0g (14.5%); 59.3% C, 4.3% H, 35.4% O; 18.2% ash

Aqueous phase: 215g (pH = 3.5%).

Water solubles = 10.8g (11.9%)

Residual gas: 37.1% H_2, 19.5% CO_2, 43.4% CO; P = 950 psig at 40°C

RUN NO. 31H (Hydrolysis 2-Aqueous phase recycle)

Wood Flour = 81.0g; 90% of the aqueous phase from 30L, H_2SO_4 added = NR, (the estimated amount is 2.24g)

T as a function of time:

θ, min:	0	5	10	15	20	25	26	60	95
T, °C:	15	29	80	105	137	172	180	180	115

Product: Hydrolyzed slurry (276g) having a pH = 2.1.

RUN NO. 31L (Liquefaction 2 - Aqueous phase recycle)

Slurry = 90% of the slurry (276g) obtained in 31H; pH = 2.1.

pH as a function of Na_2O_3 added: 2.1 (0.00g), 2.9 (0.81g), 3.7 (1.62g), NR (2.43g)

Synthesis gas: 40% H_2, 60% CO; P = 800 psig at room temperature

T and P as a function of time:

θ, min:	0	5	10	15	20	25	27	30	35	40	45	105
T, °C:	32	101	220	279	318	332	340	299	224	190	178	50
P, psig:	810	1300	1600	2300	3000	3580	3800	2850	1750	1400	1270	900

Products:

Acetone solubles = 24.9g; (34.35); 71.4% C, 6.2% H, 22.4% O; 1.2% ash

Residue = 15.8g (21.7%). Analysis not available.

Aqueous phase = 174g; pH = 3.5

Residual gas: 39.1% H_2, 17.0% CO_2, 43.9% CO; P = 900 psig at 50°C

RUN NO. 32H (Hydrolysis 3-Aqueous phase recycle)

Wood flour = 58.2g; 82% of the aqueous phase from 31L; pH = 3.5.

H_2SO_4 added = 1.74g (to pH = 1.8); the amount calculated = 1.72 g

T as a function of time:

θ, min:	0	15	20	23	25	30	35	40	45	55	60
T, °C:	15	132	160	180	181	180	179	180	182	179	180

Product: 204g slurry with pH = 2.14.

RUN NO. 32L (Liquefaction 3-Aqueous phase recycle)

Slurry = 204g (from 32H); pH = 2.14; Na_2CO_3 added = 1.8g; pH = 3.15.

Synthesis gas: H_2 46%, CO 54%; P = 800 psig at 30°C
T and P as a function of time:

θ, min:	0	7	12	17	22	27	28
T, °C:	53	151	264	309	319	333	340
P, psig:	800	1400	2000	2700	2900	3250	3400

Products:
Acetone solubles = 19.81g (34.3%); 71.5% C, 6.3% H, 22.2% O; 1.4% ash.
Insolubles = 16.56g (28.5%) 69.6% C, 4.9% H, 25.5% O; 4.9% ash.
Aqueous phase = 144g; pH = 3.3
Residual gas: 44.2% H_2, 12.3% CO_2, 43.5% CO.

RUN NO. 33H (Hydrolysis 4-Aqueous phase recycle)

Wood flour = 90g; 84% (121g) of aqueous phase from 32L;
Fresh Water = 89g; H_2SO_4 = 1.0g (to pH = 1.8).
T and P as a function of time: not recorded except that heat up to 180°C was 35 min and hold time was 30 min.
Product: 300g slurry with pH = 2.1.

RUN NO. 33L (Liquefaction 4-Aqueous phase recycle)

Slurry = 300g (from 33H); Na_2CO_3 = 2.7g to pH = 3.4.
Synthesis gas: 40% H_2; 60% CO; P = 820 at room temperature.
T and P as a function of time:

θ, min:	0	5	10	15	17	20	25	30	42
T, °C:	88	205	276	331	340	342	246	198	90
P, psig:	820	1470	1800	3050	3300	3400	1600	1250	850

Products:
Acetone solubles = 24.5g (28%) after evaporation; 19.8g (22.6%) after overnight drying; 71.5% C, 6.3% H, 22.1% O; 3.2% ash.
Insolubles = 25.1g (28.7%); 73.3% C, 5.5% H, 21.2% O; 1.3% ash.
Off gas: 40.9% H_2, 22.5% CO_2, 36.6% CO, P = 850 psig at 90°C

RUN NO. 34H (Hydrolysis 1 - New series)

Wood = 92.4g; H_2O = 214.8g; H_2SO_4 = 0.07g (to pH = 1.8); total = 307.3g
Conditions: Silicone oil heated to 200°C, furnace heated to 550°C;

θ, min:	0	8	13	23	33	43	53	66	83	93	103
T, °C:	17	63	78	97	107	113	123	136	156	165	180

Product = Prehydrolized wood flour; pH = 2.5

RUN NO. 34L (Liquefaction 1 - New series)

Slurry from No. 34H = 306.8; Na_2CO_3 = 2.76g; H_2O = 11.05g
pH = 7.0; Total weight = 320.6g.
Synthesis gas: 40% H_2, 60% CO; P = 820 psig at 28°C
Conditions: Silicone oil heated to 330°C, furnace to 600°C;

θ, min:	0	5	9	14	20	24	29	31	33	35	37	97	NR
T, °C:	43	95	152	278	316	329	341	322	282	249	226	53	40
P, psig:	1100	1400	1600	2250	2650	2400	3150	----	----	----	----	----	500

Products:

Acetone solubles = 41.19g (44.9%); 71.1% C, 6.6% H, 22.3% O; 1.1% ash.
Residue = 11.09g (12.1%); 62.5% C, 5.3% H, 32.2% O, 1.4% ash.
Aqueous phase = 230.6g; pH = 4.0.
Residual gas: 35.2% H_2, 30.5% CO_2, 34.3% CO; P = 500 psig at 40°C

RUN NO. 35H (Hydrolysis 2)

Aqueous phase from No. 34L = 230.6g with pH = 4.0; H_2SO_4 added = 3.45g to pH 1.7; Na_2CO_3 added = 0.85g to pH 1.8; H_2O in the carbonate solution = 3.38; Sample set aside = 17.63g.

Aqueous solution used for hydrolysis = 221g (pH = 1.8%); H_2SO_4 (estimated) = 3.26g, total Na as Na_2CO_3 = 3.34g.

Wood = 90.0g; Wood moisture = 2.78g; Total input = 313.8g.

Conditions: Silicone oil at 200°C, furnace at 500°C.

θ, min:	0	7	22	25	32	39	47	55	60
T, °C:	18	79	167	180	182	181	181	172	---

Product: Prehydrolyzed slurry having a pH = 2.1.

RUN NO. 35L (Liquefaction 2)

Slurry from No. 35H = 314g; pH = 2.1.; Na_2CO_3 added = 8.99g to pH = 7.0; H_2O in the 20% solution = 35.97g; Total weight = 355.04 (probably less by about 2g); H_2 = 320 psi; CO = 480 psi at 24°C (total P = 800 psig)

Recovery factor in transferring the slurry = 0.97

Conditions: Oil at 332°C, furnace at 621.

θ, min:	0	5	12	15	20	25	30	34	35	40	NR
T, °C:	24	47	153	210	295	312	330	340	327	230	40
P, psig:	800	1150	1500	1600	2150	2200	2650	3000	2800	1200	580

Products:

Acetone solubles = 54.54g (62.5%); 71.5% C, 6.8% H, 21.6% O; 3% ash.
Residue: 2.09g (2.4%); 28.2% C, 2.6% H, 59.2% O; 45.4% ash; 7.1% Na.
Aqueous phase = 256g with pH = 4.70.
Residual gas pressure: 38.0% H_2, 38.3% CO_2, 23.7% CO; P = 580 psig at 40°C.

RUN NO. 36H (Hydrolysis 3)

Wood flour = 90g.

Aqueous phase from No. 35L = 256g, pH = 4.70; less 33.3g set aside for analyses = 223 (content factor = 0.871); H_2SO_4 added = 7.17 x 0.95 = 6.81g to pH = 1.8; Total aqueous phase acidified = 229.8g; H_2SO_4 in it = 0.97 x 0.871 x 3.26 + 6.81 = 9.56g.; Na_2CO_3 added = (3.34 + 8.99) x 0.97 x 0.871 = 10.42g; Total charge = 323g.

Conditions: Oil at 200°C, furnace at 500°C

θ, min:	0	5	10	15	20	25	30	35	40	45	55	60
T, °C:	29	73	103	125	149	174	185	180	185	184	182	179

Product: Prehydrolyzed slurry (about 323g) with pH = 1.99.

RUN NO. 36L (Liquefaction 3)

Slurry from 36H = 323g; pH = 1.99; Na_2CO_3 added = 14.48g (to pH = 7.0);
H_2O in the solution = 57.9g; Total slurry = 395g.
Synthesis gas: 40% H_2, 60% CO; P = 800 psig at 24°C.
Recovery in slurry transfer = 0.97%
H_2SO_4 = 9.27g; Na_2CO_3 = 24.13.

Conditions: Oil at 390°C, Furnace at 550°C

θ, min:	0	5	10	15	20	25	30	NG
T, °C:	64	156	273	294	311	333	341	40
P, psig:	800	1200	1900	2300	2300	2500	2650	580

Products:
Acetone solubles = 28.1g (31.2%); 73.3% C, 7.1% H, 19.6% O; 9.3% ash.
Residue: 18.35g (21.0%); 74.6% C; 5.4% H; 20.0% O; 3.1% ash.
Aqueous phase = 293g; pH = 5.18.
Synthesis gas: 39.8% H_2, 45.1% CO_2, 15.2% CO; P = 580 psig at 40°C.

RUN NO. 37H (Hydrolysis 4)

Wood flour = 90g

Aqueous phase from 36L = 293.4g; pH = 5.18; less 129.5g set aside for tests = 163.9g; Content factor = 0.56; Water added = 62.8g; H_2SO_4 added = 7.36 x 0.95 = 6.99g to pH = 1.8; total = 231.3g; H_2SO_4 in it = 6.99 + 9.56 x 0.56 x 0.97 = 12.17g; Na_2CO_3 in it = 13.49g; Total = 324g.

Conditions: Oil at 483°C; furnace at 542°C; heat up period to 180°C; 25 min;
held for 25 min at 180°C.

Product: 324g slurry, pH = 1.99.

RUN NO. 37L (Liquefaction 4)

95% of prehydrolized slurry = 308g; Na_2CO_3 added = 15.53g; pH = 7.1;
H_2O added = 62.13g (as 20% solution 77.66g); recovery factor = 97.3%;
Total weight = 369g; H_2SO_4 in it = 11.25g; Na_2CO_3 in it = 27.57g.

Synthesis gas: 40% H_2; 60% CO; P = 800 psig at 24°C.

Conditions: oil at 370°C, furnace at 700°C;

θ, min:	0	5	10	15	20	25	30	32	35	36	37	38	40
T, °C:	21	90	256	292	297	320	336	340	334	326	315	293	256
P, psig:	780	1150	1700	2350	2400	2700	3100	3200	3050	----	----	----	---

Products:
Acetone solubles = 38.05g (45.72%); 70.9% C, 6.9% H_2, 22.2% O; 0.6% ash, 0.35% Na.
Residue = 12.38g (14.9%); 73.4% C, 5.8% H, 20.8% O; 14.7% ash; 5.8% Na.
Aqueous phase = 285.4g; pH = 5.3
Residual gas: 43.4% H_2, 41.3% CO_2, 15.3% CO; P = 700 psig at 40°C.

RUN NO. 38H (Hydrolysis 5)

Wood flour = 90g

Aqueous phase from No. 37L = 285.4g; pH = 5.3; less 125.43g set aside for tests = 160g; content factor = 0.561; water added = 62.8g; H_2SO_4 added = 7.55 x 0.95 = 7.17; pH = 1.80; Total weight = 227.55g; H_2SO_4 in it = 11.25 x 0.561 + 7.17 = 13.47; Na_2CO_3 in it = 15.44 (probably much less, e.g., 14.6g); Total = 320g.

Conditions: silicone oil at 180°C; furnace at 500°C.

Time:	0	10	27	57
Temp:	40	116	180	180

Products: 320g slurry; pH = 2.1.

RUN NO. 38L (Liquefaction 5)

98.7% of the slurry from No. 38H = 316g; Na_2CO_3 required to raise the pH to 1.8 = 16.24g; total weight = 332g; H_2SO_4 in it = 13.3g; Na_2CO_3 in it = 16.24 + 14.6 x 0.987 = 30.65;

Synthesis gas: 40% H_2; 60% CO; P = 800 psig at 24°C

Conditions: Oil temp at 356; furnace at 600°C at start.

Time:	0	5	10	15	20	25	30	40	55
Temp	18	97	153	279	298	321	330	204	39
Press:	1000	1600	1750	2350	2850	3500	3800	1600	890

Products:

Acetone solubles = 37.1g (41.73%); 73.3% C, 6.9% H, 19.8% O; 0.9% ash. 0.5% Na.

Insolubles = 11.67g (13.1%)

Aqueous phase = 227.4g; pH = 4.97

Residual gas: 40.0% H_2, 32.5% CO_2, 27.5% CO; P = 890 psig at 39°C.

RUN NO. 39H (Hydrolysis 6)

Wood flour = 90g; Aqueous phase from No. 38L (227.4g); pH = 5.0; H_2SO_4 added = 13.83 x 0.95 = 13.14 to pH = 1.8; Amount utilized = 160g; f = 0.665; H_2O added = 62.8g; total weight = 312.8g; H_2SO_4 in it = 17.6g (estimated); Na_2CO_3 in it = 20.4g (estimated).

Conditions: Heat-up time = 31 min; Hold time = 30 min. (Note: an estimated amount of 15g solids were stuck to the bottom of the liner.)

RUN NO. 39L (Liquefaction 6)

Slurry = 279g; wood in it = 70g; pH = 5.0; Na_2CO_3 added = 10.42g to pH = 7.0.

Synthesis gas: P = 1000 psig (45% H_2, 55% CO).

T and P as a function of time:

θ, min:	0	5	10	15	20	25	80
T, °C:	29	82	116	153	230	340	34
P, psig:	1000	1600	1700	1900	2300	2800	85

Products:

Acetone solubles = 25g (25/70 x 100 = 35.2%); 74.6% C, 6.4% H, 19.0% O; 0.6% ash; 0.24% Na.

Insolubles = 21.45g (21.45/70 x 100 = 30%); 63.2% C, 4.5% H, 32.3% O;

20.0% ash; 2.8% Na.
Water extracted residue: 70.1% C, 5.4% H, 24.5% O; 3.2% ash; 0.58% Na.
Aqueous phase = 209g; pH = 5.1; salts in it = 10.5%.
Residual gas: 36.3% H_2, 21.7% CO_2, 42.0% CO.

Titration of 150g aqueous phase + 60g water:

pH :	5.05	4.40	3.94	2.89	2.08	1.91	1.80
H_2SO_4, g:	0	1.19	2.56	5.25	5.51	6.82	7.08

RUN NO. 41H (Hydrolysis 1)
Wood = 90.0g; Water = 212.8g; H_2SO_4 = 0.16g to pH = 1.77;
Recovery factor = 0.984.
Conditions:

Time, min.:	0	5	10	15	20	25	35	45	55
T,^{o}C:	19	48	69	100	140	177	182	182	185

Output: Product: 298g slurry with pH = 2.12.

RUN NO. 41L (Liquefaction 1)
298g Slurry (88g wood equivalent); $Ca(OH)_2$ = 2.00 g to pH = 9.30.
Conditions: P = 1000 psig; 40% H_2; 60% CO.

Time, min:	0	5	10	15	20	25	30	35
Temp ^{o}C:	38	87	170	254	286	298	317	340
P, psig:	1100	1550	1800	2150	2600	2900	3450	4050

Products:
Acetone Solubles: 24.25g (24.25 x 100/88 = 27.5%).
Residue = 20g (25%).

Table 1
Influence of Reactant Gas Composition

Run No.	15	19	16	17	18
Initial Pressure, psig	680	600	500	500	500
CO, %	--	--	60	60	60
H_2, %	64	70	40	40	40
CO_2, %	36	30	--	--	--
Final Pressure,[2] psig	650	740	674	680	745
CO_2, %	1.0	1.7	25.4	23.3	39.4
H_2, %	55.0	61.0	37.4	51.1	33.2
CO_2, %	44.0	37.3	35.1	26.6	27.4
Acetone Solubles, %	33.7	32.5	32.8	31.3	28.0
Residue,[3] %	14.3	15.4	15.6	17.8	17.4
Water Solubles,[3] %	8.7	10.1	10.6	10.4	

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[1] In these runs the slurry used (300g) was obtained from Albany, Oregon (pH = 7.0, Total solid content = 29.8%); Heat up time 30 2 min.; final temperature = 360°C; hold time = none.

[2] Inadvertedly some gas was vented off in Run No. 15.

[3] Based on the total solids present in the slurry, i.e., 90g.

Table 2
Influence of Temperature and Hold Time[1]

Run No.	16-18	20	21	22	23	24
Final Temp, ^{o}C	360	360	360	330	330	347
Hold up time, min.	0	41	32	60	30	0
Hold time, min.	0	30	60	60	30	0
Final gas, pressure, psig	700	770	764	709	620	600
CO, %	29.5	17.0	8.5	12.6	NA	43.3
H_2, %	40.7	42.2	45.8	43.6	NA	29.5
CO_2%	29.8	40.8	45.8	43.3	NA	25.0
Acetone Solubles,[3] %	30.7	27.4	29.5	32.2	33.6	36.6
C, %	75.7	79.0	80.8	76.3	76.0	72.6
H, %	7.0	7.3	7.7	7.2	7.0	6.4
O, %	17.3	13.7	11.5	16.5	17.0	21.0
Colorific Value[4]	14,200	15,000	15.700	14.400	14.200	13,100
Residue,[3] %	16.9	18.0	10.4	17.2	18.2	15.2

[1] In these runs 300g slurry obtained from Albany, Oregon was used; Synthesis gas, introduced at 500 psig, contained 60% CO and 40% H_2.

[2] Average of the three runs.

[3] Based on the solid content (9.8%) of the slurry fed.

[4] Calculate from the chemical analysis,. Btu/lb.

Table 3
Influence of Agitation[1]

RUN NO.	17	25	26	27	28
Acetone Solubles, %	31	37	32	26	38
% C	75.7	NA	NA	75.2	71.5
% H	7.0	NA	NA	7.0	6.6
% O	17.3	NA	NA	17.8	21.9
Heating value, Btu/lb	14,200	NA	NA	14,100	13,063
Residue, %	18	12	18	21	19
Water solubles, %	10	6	10	10	14

[1] In these runs the conditions common were heat-up time (24 to 27 min.) to 360°C, hold up time (zero), initial synthesis gas pressure (500 psig), its composition (40% H_2 and 60% CO), slurry used (obtained from Albany, Oregon), and its amount (300g).

o In Run No. 17 the regular impeller of the 1 liter autoclave was used at a relative speed setting.

o In Run No. 26, the stirrer was turned off.

o In Run Nos. 25 and 28, the impeller of the 1 liter autoclave was replaced by the longer impeller of a one gallon autoclave.

o In run No. 27, a vane type downward forcing homemade impeller was used.

Table 4
Results of Aqueous Phase Recycling[1]

RUN NO.	33	31	32	33
Heat-up period, min.	25	27	28	16(+9)
H_2SO_4 added to pH = 1.8	0.16	NR	2.50	2.46
Predicted,[2] g	0.16	2.52	2.52	2.52
pH after hydrolysis	2.5	2.10	2.14	2.10
Na_2CO_3 addition[3]	6.9	NR	3.15	3.20
liquefaction	3.5	3.5	3.30	NR
Acetone solubles,[4] %	44.0	34.3	34.3	28.0
Heating value, Btu/lb	13,200	12,800	12,900	12,900
Residue,[4] %	14.5	21.7	28.5	28.7
Water solubles,[4] %	11.9	NR	NR	NR

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[1] In this series it was intended to heat the slurry to 340°C and cool it quickly. In Run No. 33, the heat-up period was relatively short (16 min.) and was compensated by holding (9 min.). The results tabulated were normalized to conditions in which 90g wood could be utilized in each run which was not the case.

[2] By molar equivalency to Na_2CO_3 added.

[3] Na_2CO_3 added was limited to 3g per 100g wood hydrolyzed.

[4] Percentages are based on the dry wood flour utilized.

Table 5
Results of Aqueous Phase Recycling[1]

Run No.[2]	34	35	36	37	38	39
pH of aqueous phase[3]	7.00	4.00	4.70	5.20	5.30	4.97
H_2SO_4 added,[4] g	0.16	2.66	7.07	8.34	8.77	8.76
pH after hydrolysis	2.50	2.10	1.99	1.99	2.10	NR
Na_2CO_3 added, g	2.86	8.99	14.48	15.53	16.24	14.42
Acetone solubles,[5] %	45	62	31	46	42	35
% C	71.1	71.6	73.3	70.9	73.3	74.6
% H	6.6	6.8	7.1	6.9	6.9	6.4
% O	22.3	21.6	19.6	22.2	19.8	19.0
The heating value, Btu/lb	13,000	13,200	13.800	13,100	13,600	13,500
Solid residue, %	12	2.4	21	15	13	30

[1] In these runs the conditins listed.

Table 6
Sulfate and Sodium Ion Balances in Six Consecutive Perhydrolysis and Liquefaction Experiments
(Runs Nos.   )

Operation	Wood g	Aqueous Phase g	Water g	$SO^=$ mg moles	Na^+ mg atoms	pH	Na^+ $SO^=$
Hydrolysis 1	92.4		215.6	0.8		1.8	
Liquefaction 1					52.1	7.0	
Hydrolysis 2	90.0	230.6		27.2		1.8	
Inventory				28.0	52.1		1.86
Liquefaction 2					169.6	7.0	
Hydrolysis 3	90	194	36	69.5		1.8	
Inventory				93.2	187.2		2.01
Liquefaction 3					273.2	7.0	
Hydrolysis 4	90	125	98.8	71.3		1.8	
Inventory				123.4	257.4		2.09
Liquefaction 4					293.0	7.0	
Hydrolysis 5	90	120	100	73.2		1.8	
Inventory				140.6	300.4		2.14
Liquefaction 5					306.0	7.0	
Hydrolysis 6	90	144	86	89.2		1.8	
Inventory				181.2	397.0		2.19
Liquefaction 6					196.0	7.0	

Table 7
Sulfate and Calcium ion Balances in Two Consecutive Prehydrolysis and Liquefaction Experiments
(Run Nos.)

Operation	Wood g	Aqueous phase g	Water g	$SO^=$ Millimoles	Ca^{++} Millimoles	pH
Hydrolysis 1	90		210	1.63		1.80
Liquefaction 1					27.3	9.30
Hydrolysis 2	90	136	74	18.22		1.80
$CadSO_4$ inventory				19.27	17.45	
Liquefaction 2					61.49	7.90
Acidification *				58.37		1.80
$CaiSO_4$ Inventory				77.64	78.94	
After fillering		202				1.88
Neutralization		202			90.2	7.20

* Upon acidification of the aqueous phase from liquefaction 2 (cf. Figure) $CeSO_4$ started to precipitate when the pH reached a value below 3. The measured amount of the total precipitate in a 20g sample was about 1.06g (or about 78 millimoles in 202g sample).

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