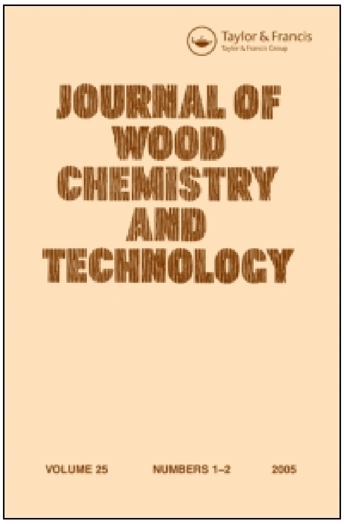

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Studies on the Mechanism of Formation of the Products of Liquefaction of Cellulose and Aspen Poplar Wood

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STUDIES ON THE MECHANISM OF FORMATION OF THE PRODUCTS OF LIQUEFACTION OF CELLULOSE AND ASPEN POPLAR WOOD *

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ABSTRACT

Studies are reported on the chemical nature and mechanism of formation of the components of the oil fraction obtained by the alkali-catalyzed liquefaction of aspen poplar wood and separately of cellulose. Along with the smaller molecular weight compounds reported earlier (5) evidence has been obtained for the presence of polymeric fractions involving ether linkages and which show a bimodal pattern of molecular weights. Using appropriate model substances, some evidence has been obtained for the production and involvement of one- and two-carbon fragments as well as ketene-type intermediates in the liquefaction process. Examination of the role of pH during the conversion process suggests that the initially alkaline medium is required to degrade the cellulose to smaller fragments, including possible saccharinic acids, with a corresponding decrease in pH. Then at an appropriate pH (now acidic) and temperature the resulting degradation products are converted to components of the final oil.

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INTRODUCTION

In recent years considerable attention has been given to the potential use of biomass as a raw material for the preparation of alternate fuels to augment the fossil hydrocarbons. In these laboratories research has been directed towards the alkali catalyzed liquefaction of local aspen poplar (Populus tremuloides, michx.). In successive studies using initially a batch reactor[1], then a semi-continuous reactor[2] and finally a continuous reactor[3], an oil was produced in yields of ~35-40 percent of the initial wood and which had a higher heating value of ~35 MJ/kg. A major portion of the wood was, at the same time, converted to water-soluble products. An examination of the wood degradation products as found in both the aqueous layer[4] and the oil fraction[5] has revealed the presence of a large number of different compounds of multiple functionality. Similar results have been reported by other workers using different liquefaction procedures[6,7]. These data indicate the complexity of the chemical reactions involved during the liquefaction of the original cellulose, hemicelluloses and lignin components of the wood. This paper is concerned with the results of experiments designed to examine these conversion processes and to offer some experimental evidence in support of the tentative explanations of the mechanisms involved.

RESULTS AND DISCUSSIONS

Since the yields of identified low molecular weight compounds that are part of the oil fraction or are found in the aqueous layer are low, the larger and structurally possibly more significant portions, especially of the oil, are not amenable to detection and analysis by simple gas liquid chromatography under the conditions used. They may be larger fragments of the original polymeric wood components. In an earlier publication[5] the oil obtained by liquefaction of pure cellulose, used so that products would be free of the different compounds that may arise from the hemicelluloses and lignin, was separated by silica gel chromatography. Following removal of a n-pentane-soluble fraction, two subsequent fractions (IV and V) obtained using methylene chloride and ethyl acetate respectively, together represented ~50 percent of the original oil. By gas chromatography a series of low molecular weight phenols, naphthols and alcohols were identified but a significant portion was not amenable to such an analysis and was presumably of too high a molecular weight. It was therefore of interest to examine the nature of this fraction by an attempted degradation using two methods that had proved useful in studies of coal degradation, namely, oxidation using alkaline cupric oxide[8] and ether cleavage using zinc chloride in benzene[9]. Isolated lignins had also been degraded using alkaline cupric oxide[10].

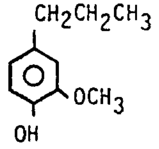
To this end combined fractions IV and V were dissolved in methylene chloride and extracted with 5 percent sodium hydroxide to remove the low molecular weight phenolic and water-soluble components. The residual oil (53%) was brownish-black, analyzing for C, 76.4; H, 7.8; O (by difference), 15.8%. Infrared and ^{13}C-NMR spectra were similar to those of the original oil, thus indicating that it was polymeric in nature and contained free phenolic groups. Molton[11] had suggested that the residue he had obtained after vacuum distillation of an oil derived from cellulose was probably a cross-linked phenolic and/or furan polymer.

Oxidation of the residual oil with the alkaline cupric oxide resulted in several ether-soluble degradation products including pentanoic acid, phenol, cresol, ethylphenol, benzoic acid, methylbenzoic acid and hydroxybenzoic acid. Similarly, treatment of the residual oil in benzene with zinc chloride at 360° for one hour gave rise to a product in ~79% yield. This was separated into an alkali-soluble fraction representing ~16% of the original oil residue and which was shown to contain phenols and naphthols and an alkali-insoluble fraction representing ~44% of the oil and which was shown by gc-ms analysis to contain the following polycyclic derivatives: indan, methyl- and dimethylindan, tetralin, methyl-, dimethyl- and ethyltetralin, methyl-, dimethyl- and trimethylnaphthalene, and diphenylmethane.

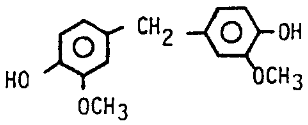
These results suggest that the residual oil had a highly cross-linked structure involving ether linkages, the oxygens of which are most likely bonded to a phenyl or naphthyl group. Oxidative cleavage of a benzyl ether would yield the benzoic acid fragments. Such structures must arise from cellulose by an initial degradation to reactive units and subsequent recombination to the more complex structures.

Having now recognized the presence in the original oil derived from cellulose of a polymeric fraction an attempt was made to examine its molecular weight distribution pattern. Gel permeation studies were conducted using either Sephadex LH-20 and LH-60 or using HPSEC with columns of Zorbax porous silica microsphere 60 S and 1000 S. Several pure reference compounds (I → V) as well as a series of polystyrene standards of molecular weights 50,000, 17,500, 9,000, 4,000, 2,000 and 800 were used for calibration.

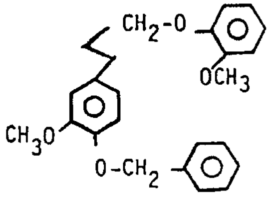
I. MW 94



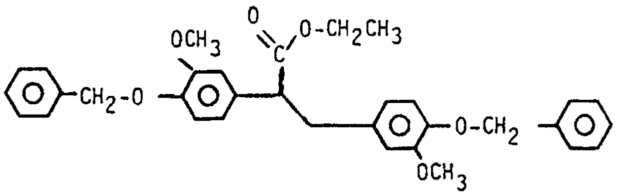
II. MW 166



III. MW 260



IV. MW 378



V. MW 526

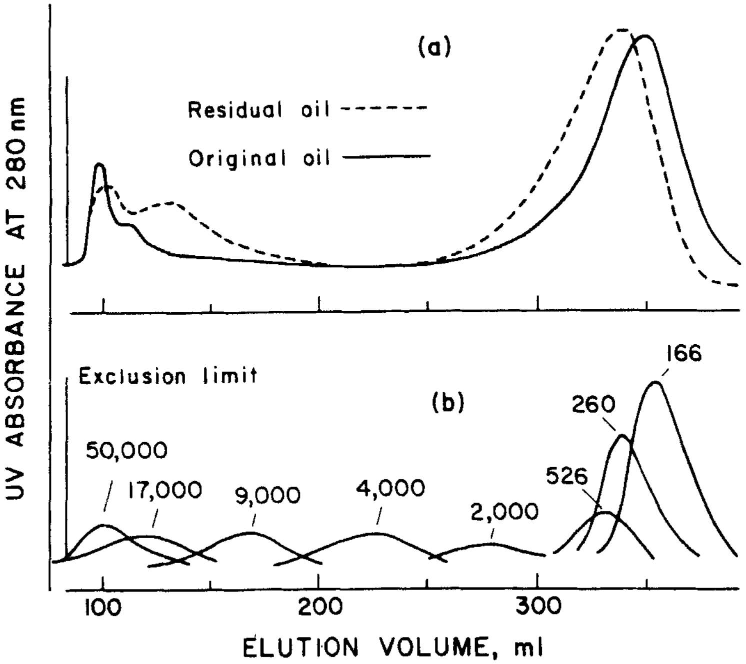


Figure 1. Gel-permeation chromatograms of (a) cellulose oils and (b) model compounds on Sephadex LH-60.

In both cases bimodal distribution patterns were obtained with the major fraction in the molecular weight range of ~200 - 400 and some components over 50,000 as seen in Figure 1. A similar profile was obtained[12] in a study of Kraft, synthetic and Brauns native lignin.

It was now apparent that under the alkaline reaction conditions, cellulose is rapidly degraded to reactive species, some of which are stabilized and appear as water-soluble components, others as low-molecular weight oil components and others recombine or polymerize to oligomeric substances. To gain further insight into the possible nature of these complex reactions, a study was made of the reactions of pure model compounds that were treated under similar conditions to those used for the cellulose.

Earlier in these laboratories[4] several runs had been made using model substances (glucose, xylose, fructose and cellulose) in a study of the water-soluble products resulting from the liquefaction process. As reported then, an oil fraction was also produced as a result of these reactions and, since these oils were available, it was of interest to compare them to that obtained from cellulose. The gas-chromatographic profiles, using a SP-1200 packed column, obtained from the 5% sodium bicarbonate-soluble fraction of these oils and of that from cellulose were very similar indicating that these monosaccharides gave rise to the same types of phenolic compounds as did cellulose.

This observation then raised the question as to whether the five- and/or six-carbon units represented the level of degradation of cellulose prior to conversion to the recognized products or whether further fragmentation occurred. To test the potential role of one-, two-, or three-carbon units a series of runs was made, under the same conditions of liquefaction. The following compounds were used: formaldehyde, acetaldehyde, glycolaldehyde, glycerol and ethylene glycol. The yields of an oil fraction that resulted were 29, 45, 23, 5 and 0 percent respectively. All the oils were shown to contain phenolic components. It may be significant to note that only the aliphatic aldehydic compounds, or those capable of producing such a functional group by dehydration, were involved in oil formation. A similar observation had been made when it was shown that fructose had behaved quite differently to glucose in giving mainly a char-like product under standard liquefaction conditions[4]. There is an indication as well that significant degradation of the polymeric cellulose to small units may occur prior to their conversion to aromatic and other liquefaction products.

On the other hand the initial production of low molecular weight ketones may lead to the production of the water-soluble compounds such as the aliphatic alcohols and acids. Molton[13] has suggested that acetone may be one of the major intermediates in cellulose liquefaction. However, in this laboratory, the treatment of acetone under standard conditions did not give rise to an oil fraction although other lower-boiling products may have been formed (acetic acid was so identified) but removed during the drying process. Such a conversion can be visualized through the mechanism of ketene formation followed by hydration.

$$CH_3\text{-}CO\text{-}CH_3 \xrightarrow{-CH_4} CH_2{=}C{=}O \xrightarrow{+H_2O} CH_3\text{-}COOH$$

Under similar conditions it was shown that other methyl ketones, namely 2-butanone and 3-methyl-2-butanone, gave rise to the predicted ethanoic and propanoic acids in the first case and

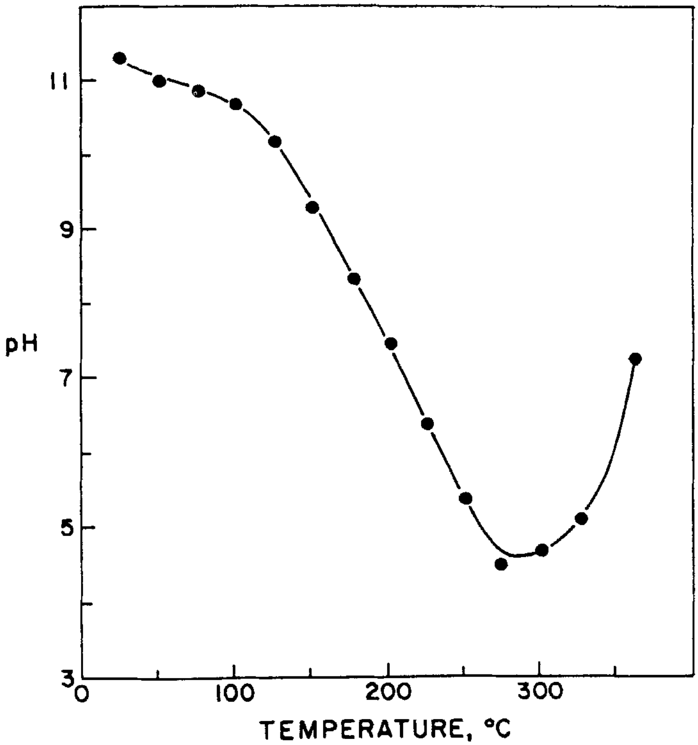


Figure 2. Effect of temperature on the pH of the aqueous phase during cellulose liquefaction.

ethanoic and 2-methylpropanoic acids in the second case. Similar reactions using ethanol instead of water gave rise to the corresponding ethyl esters. The presence then of aliphatic acids in the aqueous phase of a liquefaction reaction may arise via ketene intermediates. The increased acidity thus generated may be important in the overall oil production process as will be discussed later.

A more detailed examination of the products of liquefaction was initiated by a modification of the reactor such that samples of both the gaseous phase and the liquid phase could be collected separately, through ports in the head of the reactor, at specific temperatures and pressures throughout the period of heating. The condensable components of the gaseous phase were collected using a liquid nitrogen trap. An initial examination by gas-liquid chromatography of the ether-soluble extracts of the gaseous and liquid phases collected at ~230, ~250, ~300 and ~360°C revealed a marked similarity in their profiles and with only minor differences in the relative abundance of those compounds represented by the multiple peaks. Similar results were obtained using glucose and cellulose and indicate that the production of the low-molecular weight compounds as described earlier[4], occurs at a relatively low temperature.

Role of pH in the Liquefaction Process

It had been observed consistently that in any typical cellulose or wood liquefaction experiment the pH of the aqueous phase, initially at ~11.5 due to the addition of the sodium bicarbonate, was finally at ~7. It was of interest to follow this change in pH as the reaction temperature was increased. To this end aliquots of the liquid phase were collected, using the modified apparatus referred to above, at several temperature intervals during a typical run starting at ~50°C and ~4 MPa pressure up to 360°C and ~29 MPa pressure. These data along with some visual observations are given in Table 1 and plotted in Figure 2.

TABLE 1: Effect of Temperature on the pH of the Aqueous Phase from Cellulose Liquefaction*

Temperature of the Liquefaction Process (°C)	pH of Aqueous Phase	Colour of Solution	Characteristics of the Aqueous Phase
25†	11.3	colourless	transparent
50	11.0	light yellow	"
75	10.9	"	"
100	10.7	light brown	"
125	10.3	brown	"
150	9.3	deep brown	"
175	8.0	"	"
200	7.5	golden yellow	cloudly with some undissolved materials
225	6.4	"	"
250	5.4	"	cloudy with some oil
275	4.5	yellow	clear with some oil
300	4.7	"	clear with some undissolved char
325	5.1	black	"
360	7.3	brownish black	"
360 for 1 hr and cooling down	6.6	black	clear

* Time required to reach 360°C was ~ three hours

† Initially cellulose was mixed with Na_2CO_3 solution at room temperature and the pH measured.

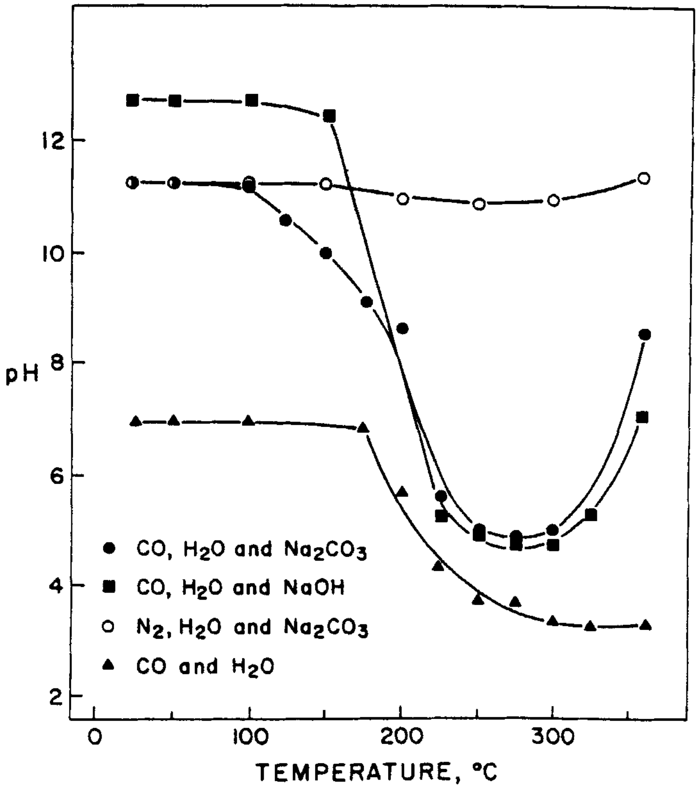


Figure 3. Effect of temperature and initial gas phase on the pH of the aqueous phase.

It was becoming clear that an initially alkaline medium was responsible for the cellulose degradation but that there was a concurrent production of acidic fragments to lower the pH. Oil formation began to appear only after the medium had become acidic. In support of this conclusion it was shown that in a two-step procedure whereby glucose was first refluxed for one hour in a sodium carbonate medium of pH ~11.5 and then the resulting solution of pH ~7 was treated under standard liquefaction conditions some oil and some char were obtained similar in nature to those products from the direct liquefaction of glucose. However the explanation of the initially increasing and ultimately decreasing acidity was not yet clear, nor was the role of pH in the final production of the oil substance.

Four experiments were thus designed and run to assess the role of the carbon monoxide, water and alkali in an attempt to understand this pH change. In each case aliquots of the aqueous phase were collected using the modified reactor and the pH measured at different temperatures ranging from 50°C and 4 MPa pressure through 360°C and 29 MPa pressure. The results are given in Figure 3. It would appear that only if carbon monoxide is present initially is there any significant lowering of the pH and only if the original solution is alkaline does the pH subsequently increase at the elevated temperatures. For further clarification another series of runs was made involving carbon monoxide in alkaline or non-alkaline media. The approximate analyses of the residual gases is given in Table 2.

From the final gaseous composition it is clear that the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) has occurred at the higher temperature. The resulting high partial pressure of carbon dioxide may be responsible for the reduction in pH of the aqueous phase[14]. Therefore if it were only an acidic pH that was required for cellulose conversion to oil then a two-step reaction involving

TABLE 2. Approximate Analysis of Residual Gases from the Run with CO/H_2O/Alkali

Run	Mole Percentage		
	CO	CO_2	H_2
Cellulose/$Na_2CO_3/CO/H_2O$ (Standard run)	2	65	33
$Na_2CO_3/CO/H_2O$ (360 °C for 1 hr)	--	55	45
$Na_2CO_3/CO/H_2O$ (250 °C for 1 hr)	99	--	1
$NaOH/CO/H_2O$ (360 °C for 1 hr)	--	40	60
CO/H_2O (360 °C for 1 hr)	25	20	55

initially the generation of an acidic aqeuous medium to which, in a second step, cellulose were added and heated to 360°C for one hour should result in oil formation. Two such experiments involving the preparation of an aqueous phase by heating sodium carbonate, water and carbon monoxide at 250°C for one hour or at 360°C for one hour produced initial aqueous phases of pH ~4 and ~7 respectively. The subsequent reaction of these solutions with cellulose at 360° for one hour resulted in mostly a charry product. It was becoming more evident that an initially alkaline medium was necessary to effect cellulose degradation but that the conversion of these degradation products was catalyzed by an acidic medium.

Attention was then directed to the nature of these initial cellulose degradation products. An examination of the non-volatile water-soluble residues collected at several temperatures in a manner discussed earlier was made by passing the aqueous phase through a cation exchange column (Rexyn 101 resin(H)) to remove the sodium ions prior to evaporation of the water at 70°C. The residues were reddish-brown syrups. The effect of the reactor temperature on the yields of these syrups is portrayed in Figure 4. These data support further the belief that the cellulose is initially degraded under alkaline conditions to a water-soluble fraction, but, at the same time, the pH is being lowered until around 200°C the conditions become suitable for conversion of these soluble components into the oil product.

These non-volatile syrups had carbon and hydrogen contents of ~42-45 and ~6.5% respectively indicating that they were still of a carbohydrate nature. They were soluble in water to give a solution of pH 3-4, and sparingly soluble in methanol. The infrared spectrum showed broad absorption bands due to both hydroxyl and carbonyl functional groups. The ^{13}C-NMR spectrum (Figure 5) indicated the presence of carbonyl carbons of carboxylic acids; different types of alkoxy carbons including -C-O-, -CH-O- and $-CH_2-O-$, and alkyl carbons. These data strongly suggest that the initial alkaline degradation produces saccharinic

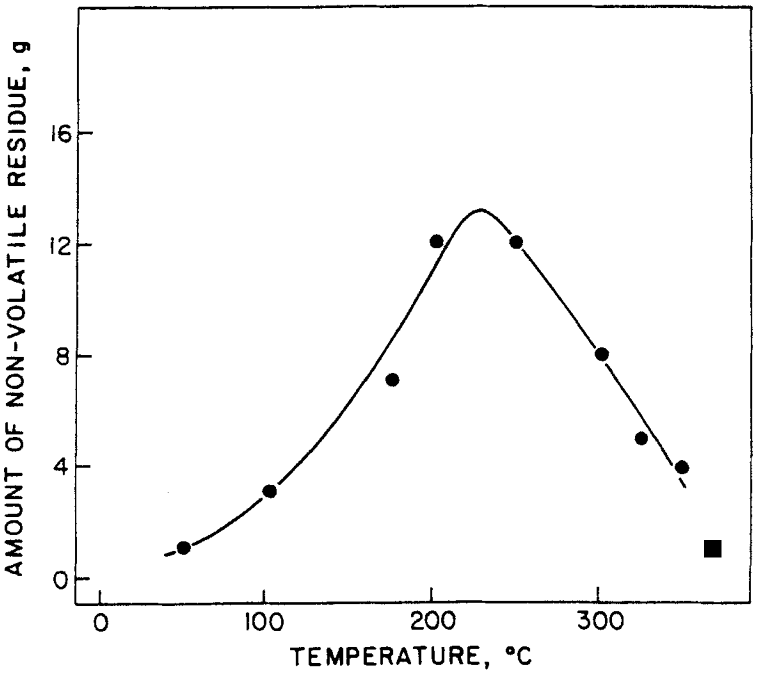


Figure 4. Effect of temperature on the non-volatile residue of the aqueous phase from cellulose liquefaction. ■ Amount of non-volatile residue in the final aqueous phase after one hour at 360° and cooled.

acids which are the intermediates in the subsequent conversion to oil. In support of this belief the aqueous phase (pH 4) of a cellulose run made under standard reaction conditions for five hours at 210 ± 10°C (for maximum yield of non-volatile residue (Fig. 4)) was then reheated at 360°C for one hour in the presence of carbon monoxide. The products of this reaction were an oil fraction (yield, 4.5%; C, 79.9%; H, 8.7%) and an aqueous fraction of pH 7. In this experiment at 210 ± 10°C a residual modified cellulose residue remained; yield, 47.7%; C, 50.0; H, 6.4%. In an attempt to ensure greater degradation of the cellulose in the first step a higher concentration of alkali (10%) was used. This step was conducted in carbon monoxide and in nitrogen. The

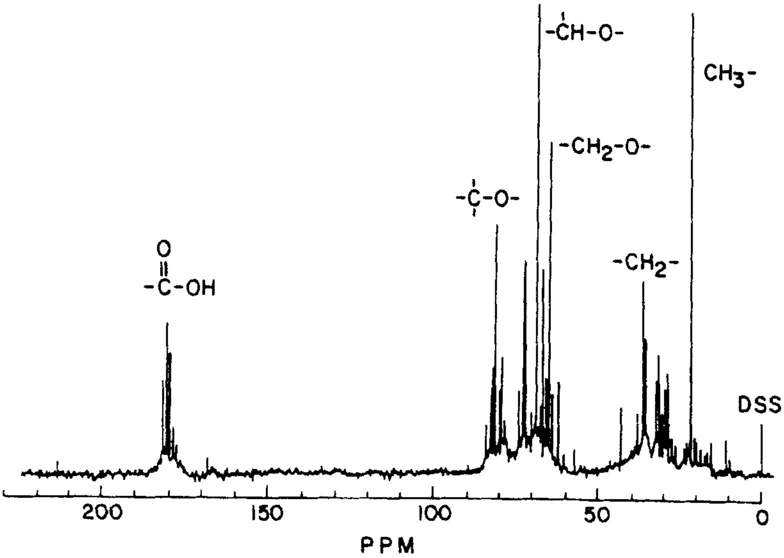


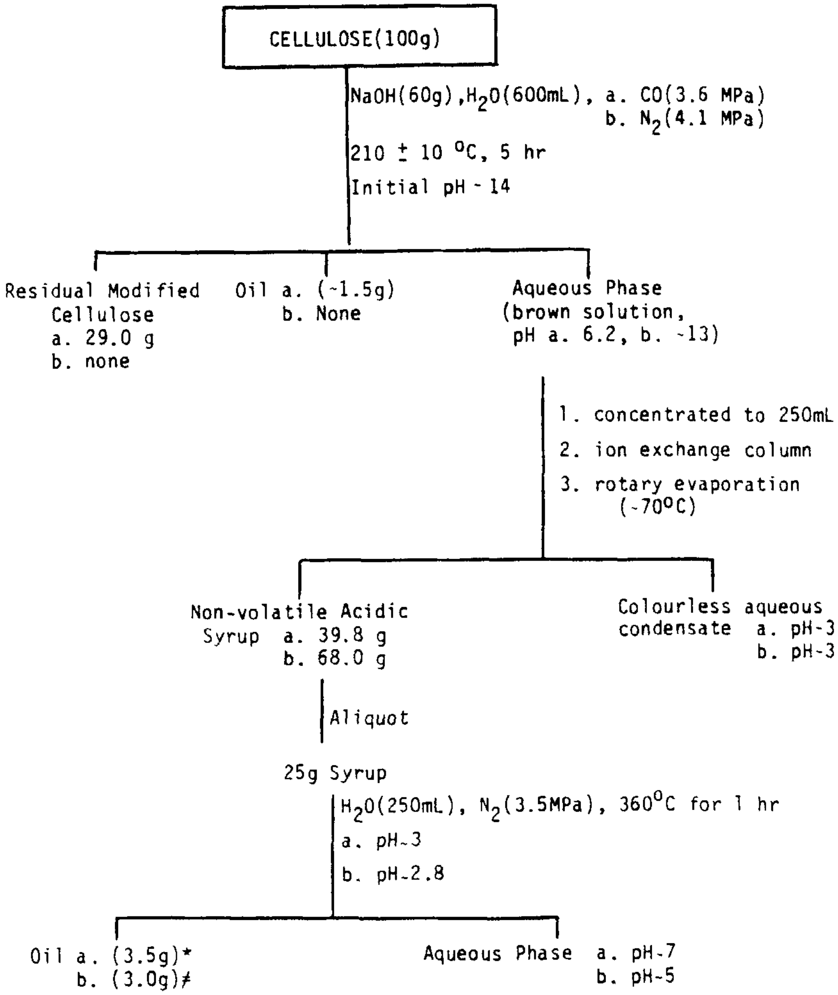
Figure 5. ^{13}C-NMR spectrum of the non-volatile acidic residue of the aqueous phase from cellulose degradation at 210±10°C.

resulting non-volatile water-soluble components were isolated using the cation exchange treatment and subsequently retreated to examine their potential conversion to an oil. These experiments are outlined in Figure 6.

From the above experiments, it is now clear that the alkaline degradation of cellulose produces saccharinic acids(7) that on hydropyrolytic condensation yield an oil product. The oil produced via these two step processes contained no char and had similar carbon and hydrogen contents of ~80 and ~9% respectively. The infrared and nmr spectral features of the oil were found to be similar to those of the oil produced by the one step process.

All these observations suggest that this alkaline degradative route would be one possible mechanism by which the conversion of cellulosic materials to oil could take place.

In this study of the two-step processes, an observation was made which may be of some significance in alkaline pulping.



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* 5.6g based on 100 g cellulose
≠ 10.2g based on 100 g cellulose

FIGURE 6. Oil production via two-step processes

Treatment of cellulose in strong aqueous alkaline medium under nitrogen atmosphere resulted in a complete degradation of cellulose into water-soluble components while after a similar treatment using CO instead of N_2, an insoluble residual cellulosic mass remained which represented 29% of the original cellulose. This observation may be explained on the basis of the participation of CO in lowering the pH of the aqeuous medium as discussed earlier and causes less degradation of cellulose. Added support for this was obtained from a similar experiment on the alkaline degradation of cellulose using CO_2 instead of CO, which, as expected, showed even less degradation. In order to compare the results, similar alkaline degradation experiments using wood meal under a nitrogen atmosphere were also performed. All these results are given in Table 3.

It is clear that alkaline degradation of wood under a nitrogen atmosphere resulted in complete degradation to alkali-soluble products. In contrast to the cellulose degradation experiment, a water-insoluble powdery solid was isolated from the wood degradation experiment. The carbon, hydrogen analysis of this solid suggested that this may have originated from the lignin component of the wood.

TABLE 3: Alkaline Degradation of Cellulose and Aspen Poplar Wood

Raw Material	Initial Condition			pH		Residue	Remarks
	Water (mL)	NaOH (g)	Gas	Initial	Final	Left (g)	
Cellulose	600	60	N_2	14	13.2	----	
Cellulose	600	60	CO	14	6.2	29.0	1.5 g oil
Cellulose	600	60	CO_2	14	7.0	65.0	
Wood	600	60	N_2	14	13.0	----	*8g powder isolated

* On neutralization of the aqueous alkaline products a powdery precipitate was isolated, dried and analysed for carbon and hydrogen (C, 66.7 ; H, 7.1%).

Discussion of Results

From the above described results, a few general observations about the nature of the cellulose conversion process may now be made. It is the alkalinity of the aqueous medium that was found to be essential to initiate the liquefaction process. The liquefaction of cellulose in an alkaline medium occurs at least in part, via aqueous soluble intermediate products produced as a result of the degradation of cellulose. Alkaline degradation of carbohydrate materials is believed to be a peeling process[15] from the end of the cellulose chain to generate saccharinic acids.

The analysis of the intermediate acidic products obtained from the degradation of cellulose in alkaline medium also indicated the possible presence of these acids. It is now reasonable to believe that the thermo- chemical liquefaction of cellulose in an initially alkaline medium occurs in part via the following route:

$$\text{CELLULOSE} \xrightarrow[360^{\circ}\text{C/1h}]{\text{Alkali/CO}} \begin{matrix}\text{SACCHARINIC ACIDS}\\ \text{IN AQUEOUS SOLUTION}\end{matrix} \rightarrow \text{OIL}$$

The formation of oil from the degraded cellulose intermediates is facilitated if the aqueous medium becomes acidic during the run (Table 1). The presence of carbon monoxide at elevated pressures enhances the decrease of pH of the aqueous phase from the initial alkalinity. This could be the reason that carbon monoxide concentration affected the rate faster as reported by Ostermann.

EXPERIMENTAL

Standard Liquefaction Procedure

Air-dried wood meal (~4.5% moisture, 100 g) from local aspen (Populus tremuloides, michx) or cellulose (Brinkman Instruments (Canada) Ltd., 100 g) was placed in the reaction vessel (1410 mL capacity) of a Model 406-010A Amino high pressure hydrogenator. To this, 10 g of sodium carbonate dissolved in 500 mL of water was added. Carbon monoxide was introduced to an initial pressure of 3.45 MPa after flushing out the reactor twice. The reactor was heated with continuous shaking to the required temperature, 360°C and held at this temperature (±5°C) for one hour. The heating was stopped but shaking continued for a further 1h and then allowed to cool overnight. The excess gases were released and the reactor contents separated by decantation into an oil phase and an aqueous phase. The reaction vessel was then washed with acetone. The acetone was only used to get the total yield of oils and not for analytical purposes. The decanted oil phase was dried in a fume hood for several days until its water content was determined to be less than 1% measured by the Karl-Fisher titration method.

In a similar fashion cellobiose, D-glucose, glycerol, ethylene glycol, glycolaldehyde, glycol, acetaldehyde, formaldehyde, and acetone were subjected to the same liquefaction process.

Treatment of Aqueous Phase by Ion Exchange Technique

All ion exchange reactions were effected using Rexyn 101 resin (H) in columns of either 1.6 x 58 cm (5 mL sample) or 3.4 x 50 cm (250 mL sample). Elution at 3 mL/min was continued until the effluent was neutral. Excess water was removed in a rotary evaporator at 70° and the residue weighed.

Ether Cleavage of Residual Oil

With Zinc Chloride - A mixture of residual oil (0.5 g), benzene (20 mL) and $ZnCl_2$ (3 g) was placed in the reaction vessel used for the liquefaction studies. After pressurizing with hydrogen to 5.1 MPa, it was heated and maintained at 360° for one hour. After cooling the liquid layer was decanted from the $ZnCl_2$ and the excess solvent removed.

With Cuprous Oxide - Residual oil (0.25 g) was oxidized with alkaline cupric hydroxide ($Cu(OH)_2$(1 g) dissolved in 2M NaOH

(20 mL)) at 200 - 220° for 2 hours in the liquefaction reactor. After cooling the solution was acidified (HCl) and extracted with ether to yield the oxidation products (0.15 g) which were analysed by GC-MS.

Chromatographic Separations

For the experiments with Sephadex LH-20, a chromatographic column (1.5 x 74 cm) was prepared by packing with a slurry of Sephadex LH-20 in DMF (stirred for 12 hr before packing). Approximately 2 mg of oil samples/1 mg of phenolic model compound/30 mg of polystyrene standards, dissolved in 0.5 mL DMF were used and eluted with DMF. The flow rate was maintained at ~32 mL/hr. The eluted substances were monitored using a spectrophotometer (Bio-Rad Model 1300) at 280 nm. For the experiments with Sephadex LH-60, the Sephadex materials were stirred with DMF for 24 hours before being packed into a column (2.5 x 82 cm).

The HPSEC analyses were carried out using a Varian liquid chromatograph Model 5000, equipped with a variable wavelength detector (Perkin-Elmer LC-55) set at 254 nm. Columns used were Zorbax porous silica microsphere 60S and 1000S. All samples were monitored at 254 nm using THF mobile phase at a flow rate of 1 mL/min. Each sample (~2 mg) dissolved in 1 mL THF and in each case 10 μL of the solution were applied to the column through a 10 μL sample loop. The calibration of the columns was achieved using six standard polystyrenes (MW 50,000; 17,500; 9,000; 4,000; 2,000; 800) and the four phenolic model compounds. The standard samples were injected as either pure samples or as mixtures of two or three.

Gas Phase Analysis

Gas phase analysis was made using a copper column (1/8" x 15") packed with silica gel (60 - 100 mesh), with helium as the carrier gas at a flow rate of 18 mL/min. Peak areas for individual gases were measured and their abundance determined from a previously prepared calibration curve.

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