Physical Aspects of the Liquefaction of Poplar Chips By Rapid Aqueous Thermolysis

David G. B. Boocock[a]; F. Porretta[a]

[a] Department of Chemical Engineering and Applied Chemistry University of Toronto, Toronto, Ontario, Canada

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David G. B. Boocock and F. Porretta
Department of Chemical Engineering and Applied Chemistry
University of Toronto
Toronto, Ontario, Canada M5S 1A4

ABSTRACT

Hybrid poplar chips (6.35 mm square cross section) are converted to a 45-50 per cent mass yield of acetone soluble products when heated fairly rapidly to 330°C in the presence of water. Virtually no char or unconverted wood is produced at 330°C. Water (15%), carbon dioxide (6.4%), aqueous organics (8.5%), and carbon monoxide (0.4%) are also significant products. Element balances for carbon, hydrogen and oxygen are 86, 98 and 96%, respectively, based on total input, or 86, 80 and 75% based on the wood input.

Extending the heat-up from 3 minutes to 6 and 9 minutes increases the oil yield, although the molecular weight distribution and chemical compositions of the product may be different. Rate of oil production and the oil yield are increased when less water is present, but this oil chars more readily at higher temperature because liquid water acts as a stabiliser.

INTRODUCTION

Any future commercial wood liquefaction process will be based on technology having certain inherent features. First, the wood substrate will be in chip form; secondly it will contain some water; and thirdly, the substrate will be brought to reaction temperature fairly rapidly. Under the latter condition it is doubtful whether heterogenous catalysts have time to intervene in the reactions. Such catalysts are effective under relatively slow heat-

up and may, in the presence of hydrogen, help to stabilise the products. On the other hand, water-soluble catalysts or pH changes are more likely to effect the course of fairly rapid reactions.

As far as we are aware, chip-sized wood has not been studied in water-based processes, although the separation of poplar into its constituents (e.g., hemicellulose, cellulose and lignin) by steam explosion has been carried out at lower temperatures and studied in equipment similar to ours[1]. Chips have been used in the novel vacuum pyrolysis system developed by Roy[2], although some char is formed in this instance. Ablative pyrolysis of chips has been investigated by Diebold in an attempt to overcome heat and mass transfer problems[3].

As an extension of our work on catalytic wood liquefaction, we studied a semi-continuous wood liquefaction unit in which nickel carbonate served as a precursor for the nickel metal catalyst, the latter being formed in situ by reduction with hydrogen[4]. The powdered and slurried feed entered the reactor intermittently, and it was realised that the feed was brought to temperature rather quickly due to the large thermal mass of the reactor and its contents. The nickel carbonate did not reduce (it decomposed to nickel oxide and carbon dioxide) but even if it had, non-catalytic thermal processes would have still dominated. An oil was produced, even in the absence of nickel carbonate and hydrogen, but charring occurred, and the oil yield was low (25%) because of the unavoidable long residence time.

These results prompted a study of the rapid aqueous pyrolysis of powdered poplar wood[5,6]. Temperatures up to 350°C were used and oil yields of 48 per cent chloroform solubles or 53 per cent acetone solubles were obtained. The oxygen contents of the oils were in the range 25-30 per cent when oil yields were highest. Gas yields were in the range 4.5 to 10.0 per cent with values in the upper part of the range being more common. The gas contained 86-90 per cent carbon dioxide and 10-13 per cent carbon monoxide.

Highest oil yields were obtained when the reactor was pressurised
with nitrogen. Only pressures of 0.4, 2.17 and 4.0 MPa were
studied. Oil yields for the two upper pressures were identical
but significantly higher than those obtained at the lower pressure.
Perhaps the only direct relevant study using similar heating rates
and temperatures has been that of Bobleter and Concin[7] who studied
Wilstatter poplar lignin. Results showed that lignin depolymeri-
sation was followed by repolymerisation, the former occurring an
order of magnitude faster than the latter. The kinetics for both
steps conformed to first order. The actual heating rate and time
required to reach temperature were not, however, given in this
study.

     This paper describes an extension of our rapid pyrolysis
studies to poplar wood chips or chunks. Prior to the study, we
anticipated that heat and mass transfer problems would produce
some charring of the wood. Surprisingly this turned out not to
be the case. The small tube-type reactors for the powdered wood
study were ideal for studying single chips of a suitable size.
In a larger unit, currently under construction, the wood is heated
by live steam and, if necessary, water. Heating rates equal to
or greater than those in the small batch reactors will be
attainable. In the tube reactors water present at the beginning
of the reaction provides the steam and also acts as a heat trans-
fer medium.

     A key parameter for this study was the dryness of the wood.
Recognising that green wood could have variable water contents
from chip to chip, it was decided to dry the chips to about one
per cent moisture. The use of green wood has resulted in similar
oil yields, although the chemical composition of the oils could
be different.

EXPERIMENTAL

     Although the apparatus has been described in part elsewhere[5,6]
we include the full description here, since we believe the results
of this study are significant.

The wood used was _Populus_ x Euramericana clone DN 30, (3-5
years old) provided by the Ontario Ministry of Natural Resources.
It was cut into standard chips 7.6 x 0.64 x 0.64 cm and dried
under reduced pressure of 5 kPa for 36 hours. The chips used in
this study were taken from the sapwood of the tree. Powdered
wood for comparative runs was obtained by grinding the wood in a
Tyler ball mill to less than 200 mesh.

The reactor (178 mm long) was made from 12.7 mm OD 316
stainless steel tube (1.66 mm wall thickness) capped at one end
by a Swagelock fitting. At the other end a Chromel-alumel (Type K)
thermocouple was held in place by another Swagelock fitting
assembly carrying a side arm. A Whitey Union Bonnet valve was
attached to the side arm. The outlet side of the valve had a
quick-connect fitting for attachment to the product gas handling
device described elsewhere[6]. The latter, by a pressure/volume
measurement gave the moles of gas produced. Different heating
rates for the tubes were obtained by using fibreglass insulation
and aluminum foil.

The amount of wood in the reactor was fixed at about one
gram. Water/wood ratios (w/w) between 1 and 5 were used. After
charging and sealing, the reactor was flushed with nitrogen.
However, the reactor was not pressurised, since this did not affect
the yield as in the case of powdered wood.

A Techne SBL-2 Series 3000 fluidised sand bath provided the
heating medium. The bath temperature was fixed at 390°C. The
reactor was suspended in the sand bath from an eccentric drive
which provided mixing. Subsequent experiments have shown that the
mixing mode is not necessary. A 2.5 cm thick steel barrier provided
protection. The barrier, heating bath and cooling bath are mounted
on wheels which run along floor rails. The baths are supported on
a counterbalanced lift which can be raised or lowered manually. A
combination of lateral movements on the floor rails and operation
of the lift successively immersed the reactor in the heating and
cooling baths with very little delay.

The gas phase was measured quantitatively and qualitatively using the gas-handling device and gas chromatographic assembly. The reactor was opened and the aqueous phase poured off. Suspended materials were removed by centrifugation. All remaining material was removed from the reactor with acetone which was then filtered to remove acetone insolubles. Rotary evaporation of the acetone at 50°C (30 kPa followed by 5 kPa) yielded the oil. The procedure thus separated gas, aqueous, oil and solid phases. Previously chloroform had been used for dissolution of the oil[6] mainly because of its anticipated unreactivity towards the substrate. It also does not interfere in the Karl-Fischer determination of water. However, chloroform does not efficiently separate converted and unconverted wood. Materials that were obviously not char, although converted, would have been classified as such because they would not dissolve in chloroform. We believed that only unconverted wood and char should be classified as solids. Further classification of the oil into low molecular weight compounds, dimers and trimers of lignin were made using diethyl ether extraction of the acetone soluble oil. Higher molecular weight oligomers of lignin are not soluble in the diethyl ether.

The experiments were classified into seven sections of which five are discussed here:

1)   Qualitative studies

2)   Heating rate studies

3)   Water:wood ratio effects

4)   Effects of particle size

5)   Mass balances and reproducibility of results.

The product distributions and chemical compositions will be the subject of a separate publication.

Five identical runs were made and the results from them compared. Experiments were also designed to close a mass balance. A key aspect to this was the determination of the amount of water produced. This was accomplished by dissolving the liquids from the reaction in tetrahydrofuran (THF) of known water content and determining the resultant water content using a Karl-Fischer

Degradation of Wood to Oil   **2.9 MIN.**

original   250   270   278   290   300   310   319   330   350
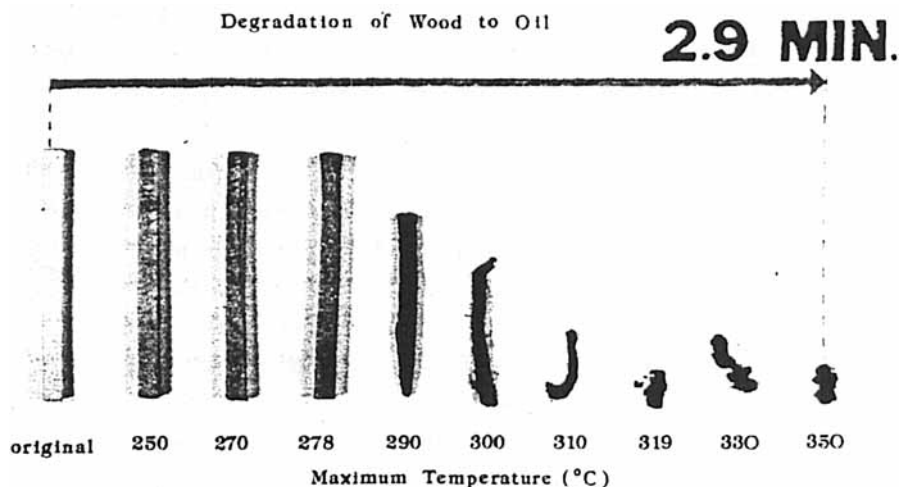
Maximum Temperature (°C)

PLATE 1.   Degradation of a standard poplar chip to oil.

Titrimeter. Acetone could not be used because it interferes with
the reagent. An identical run was performed to collect the
remaining data for the mass balance.

RESULTS

Qualitative Study

This study looked qualitatively at the physical breakdown of
poplar chips under rapid heat-up in water. The observations were
made under the following conditions:

        heating rate   - 2.9 min to 350°C
        water:wood mass ratio - 3
        chip size   - 7.6 cm x 0.64 cm x 0.64 cm.

The various stages in the conversion of wood are shown in plate 1.
The samples were obtained by quenching the reaction at different
temperatures during the heat-up. The samples were allowed to dry
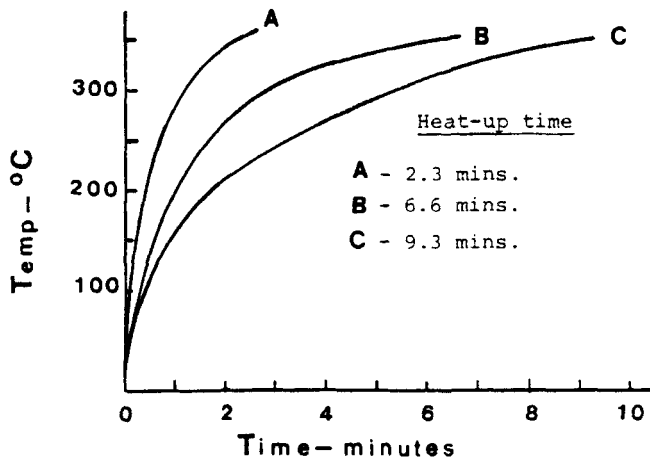
FIGURE 1.   Heating curves for unlagged (A) and lagged (B and C) tubes.

at ambient conditions before the display was made. As the heating progressed, water was vapourised and absorbed by the wood. This absorption continued until at 300°C no separate water phase could be removed from the tube. The wood no longer existed as the chip, the water and wood forming a soft and almost fluid medium. Obviously the steam had passed into the wood. Condensative heat transfer occurred, and the absorped water caused the wood to swell.

Between 300-320°C the wood breakdown continued. The displayed samples obtained from this temperature region occupied a much larger volume when wet and thus are not truly representative of the breakdown sequence.

By 320°C the aqueous phase began to reappear and at 330°C this was complete as was the physical disintegration of the wood. Distinct oil and water phases were present in the reactor at this point. Cellulose begins degradation at temperatures as low as 225°C, and the discolouration of the wood at 250°C is presumably a result of degraded carbohydrates. Measureable amounts of acetone-
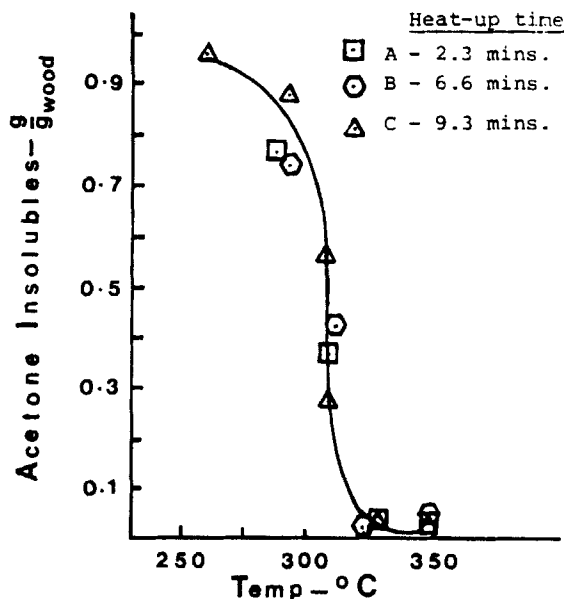
FIGURE 2.   Acetone-insoluble material as a function of final
            temperature.

soluble material can be extracted at this point. Lignin degrades
most rapidly at temperatures above 300°C, and thus it appears
that the disruption in the lignin structure causes the ultimate
wood breakdown.

Heating Rate Study

     By insulating the outside of the tubes, it was possible to
reduce the heating rates while maintaining the desired asymptotic
approach to 350°C.   The following conditions were used:

         heating rate   A   2.3 min to 350°C
                            B   6.6 min to 350°C
                            C   9.3 min to 350°C
         water/wood mass ratio   5
         chip size   7.6 cm x 0.64 cm x 0.64 cm.
The results are plotted in Figures 1-6.   Figure 1 shows the
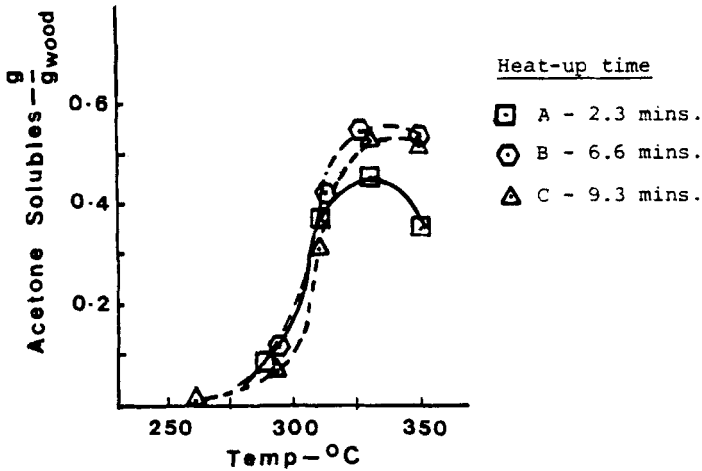
FIGURE 3.   Acetone-soluble material (oil) as a function of
            temperature.

temperature, as measured by the internal thermocouple, as a
function of time. In Figures 2-6 temperature has been chosen as
the independent variable. Time could have been chosen, but
Figure 2 in which acetone-insolubles are plotted shows why it was
not. In the range studied, the heating rate had no significant
effect, and the acetone insolubles were controlled by the tempera-
ture at any time. The system appears to conform to one in which
bonds of greater thermal stability are broken as the temperature
rises. There is little evidence of fast recondensation reactions
leading to acetone-insoluble material as reported by Bobleter[7] in
his study of poplar lignin. However, acetone-soluble materials
are undoubtedly undergoing further chemical reactions. The
absence of significant amounts of char was surprising, particularly
at the slower heating rates. In batch autoclaves employing heat-up
times of an hour or more, considerable amounts of char are formed[8].
Presumably recondensative reactions become more prominent under
slower heating rates, and the more stable polymers yield char.

     Figure 3 shows that the fastest heating rate produces a
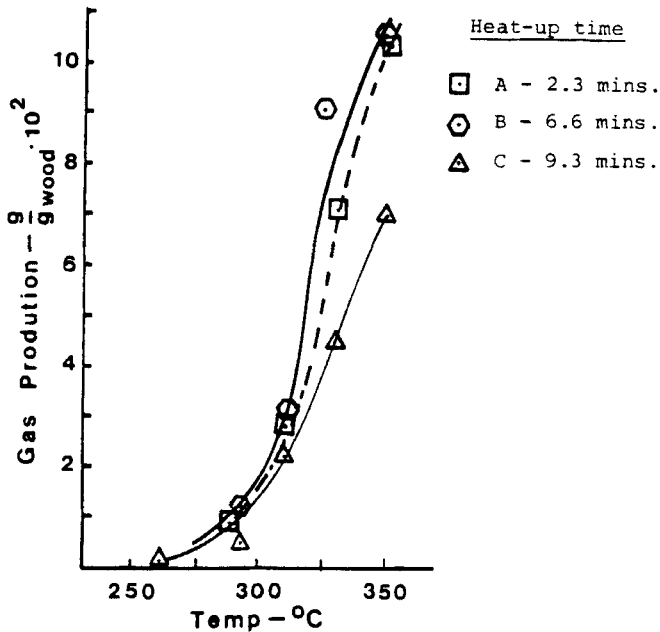lower maximum in the oil yield than the other slower heating rates.

FIGURE 4. Total gas production as a function of temperature.

The molecular weight distribution and chemical composition of these oils may be different. Also the maximum yield is reached earlier such that at 350°C the yield is substantially lower than those for the other heating rates. Measurement of gas production (Figure 4) shows that less gas is produced at the slowest heating rate, whereas at the other two heating rates it is not significantly different. Approximately 90 per cent of the total gas is carbon dioxide, but there is an increase in the carbon monoxide production for temperatures over 325°C at the slowest heating rate, even though the overall gas production is lower (Figure 5).

Water/Wood Ratio Study

Using the same particle size as the previous study, water/ wood mass ratios of 1, 3 and 5 were used. This resulted in variations in the time required to reach 350°C as shown in Figure 6. The mass of wood was kept constant in these runs and
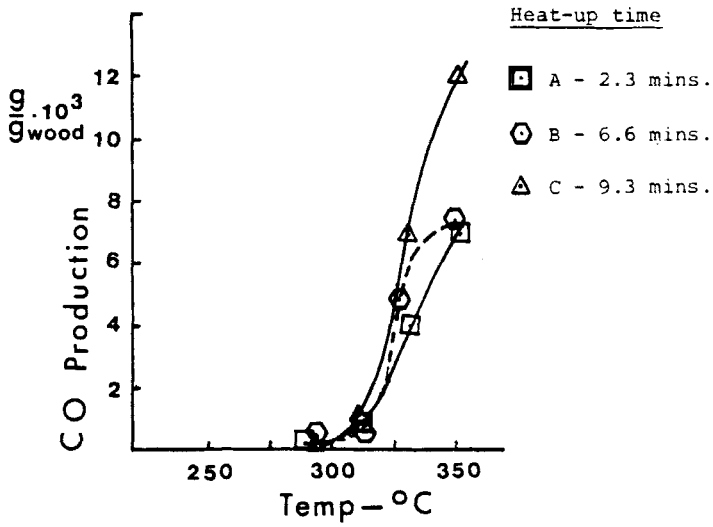
FIGURE 5. Carbon monoxide production as a function of temperature.
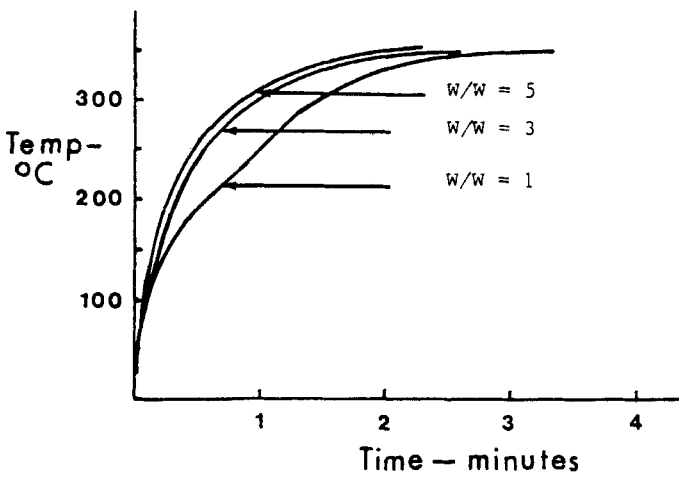
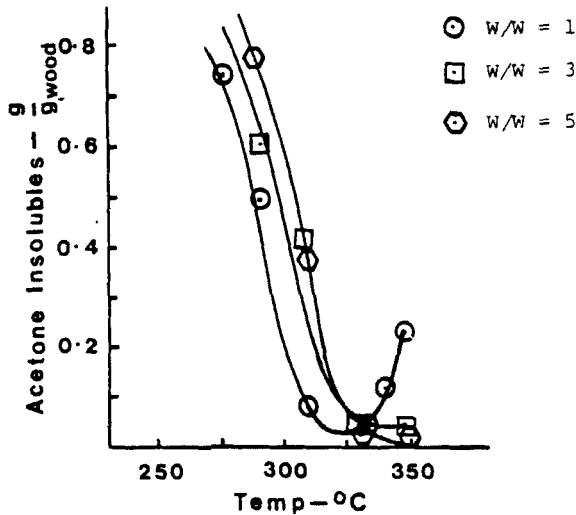FIGURE 6. Heating curves for water/wood ratios of 1, 3 and 5.

FIGURE 7. Acetone-insoluble material as a function of temperature
           for water/wood ratios of 1, 3 and 5.

thus more water was added to obtain the higher ratios. At first

glance the heating curves appear anomalous, since the system with

the highest thermal mass heats up the fastest. However, at the

lower water/wood ratio, there is insufficient water to satisfy

the absorption capacity of the wood and liquid water is depleted,

resulting in decreased heat transfer to the thermocouple. As the

swelled wood becomes mobile and particularly as liquid water

reappears, the heat transfer to the thermocouple increases

again as can be seen clearly in Figure 6. Somewhat unexpectedly

the conversion of wood at the lowest water/wood ratio is faster

(Figures 7 and 8), and the changes in slope of the heating curve

occur at temperatures lower than would be predicted by considera-

tion of Plate 1 which shows wood samples for the water/wood ratio

of 3. We thus conclude that it is steam that primarily causes

the conversion and that liquid water retards the process.

Presumably liquid water can be forced into the wood, but it does
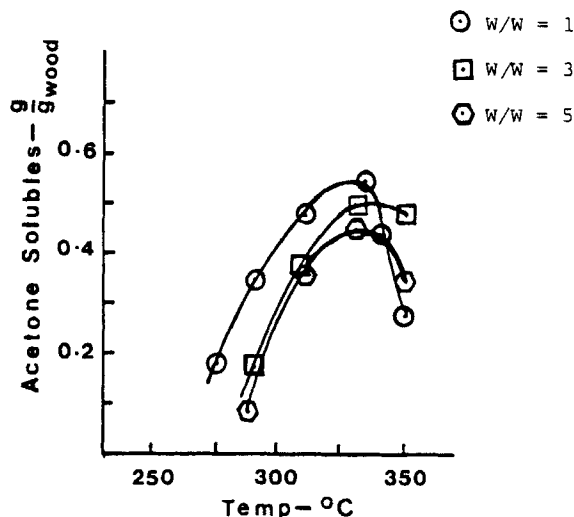
FIGURE 8.   Acetone-soluble material (oil) as a function of
            temperature for water/wood ratios of 1, 3 and 5.

not provide the condensative heat of the steam. Thus it is likely
that initially the heat transfer to the wood is higher at the
lower water-loading. This augers well for our larger scale
system in which live steam will be injected into the substrate.
It can also be seen from Figure 7 that liquid water prevents
charring of the oil once it is formed, and that in the absence of
sufficient liquid water, the rate of char formation is consider-
able. The results also show that the char comes from the oil and
is not a direct product from the wood.

     Total gas production (Figure 9) (90% CO_2, 10% CO) is initially
faster when insufficient liquid water is present. The charring
process at this ratio is accompanied by an increase in gas produc-
tion rate beyond 325°C.

Particle Size Study

     The effect of reducing the chip size was investigated by
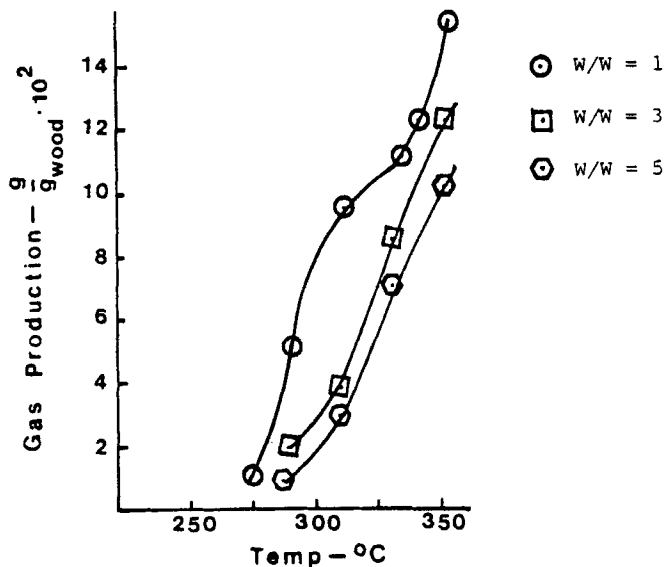using chips with half of the cross section dimension of the

FIGURE 9.   Total gas production as a function of temperature for
           water/wood ratios of 1, 3 and 5.

standard chip. The sides of these chips were thus 3.2 mm. For
a further comparison, we also ran powdered wood (less than 200
mesh) under the same conditions. A water/wood ratio of 5 was
used throughout and the time taken to reach 350°C was approximately
2.3 minutes.

     Figure 10 shows that, as expected, the powdered wood initially
converts faster than the chips; the smaller chips also liquefy
faster than the standard chip. Heat transfer to the powder is
obviously faster than the chips, but there is not a dramatic
difference between the liquefaction curves for the powder and
smaller chips. Similar effects are noted in the acetone oil
yields and gas production for the powder and smaller chips
(Figure 11). The oil production for the standard chip is delayed
in comparison, and the maximum oil yield is lower than that for
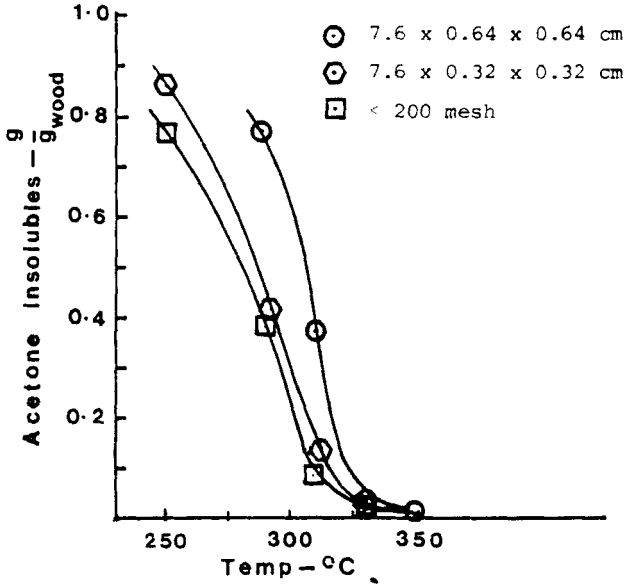
FIGURE 10. Acetone-insoluble material as a function of
temperature for two chip sizes and powdered wood.
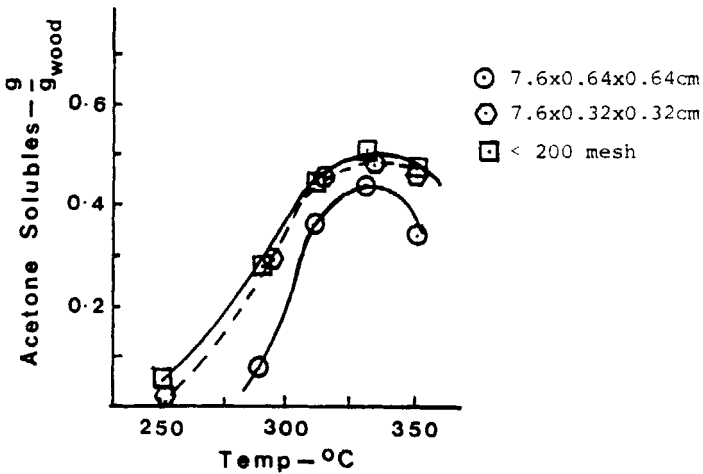
FIGURE 11. Acetone-soluble material as a function of temperature
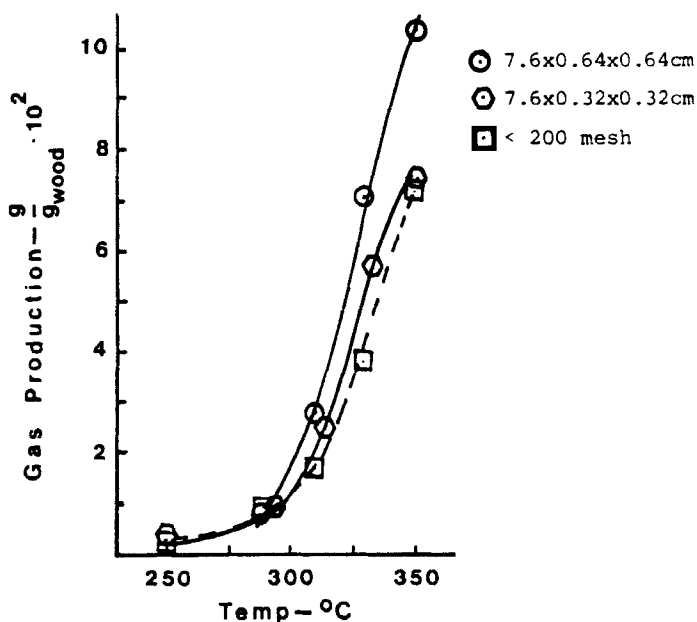for two chip sizes and powdered wood.

FIGURE 12.   Total gas production as a function of temperature for
             two chip sizes and powdered wood.

the other two substrates.   More gas is also produced for the
standard chip (Figure 12).

Reproducibility of Data

     Five tubes containing standard chips of similar weight range,
(0.8175 g - 1.0993 g) at water/wood ratios of 5 were heated to 330°C
in 1.7 minutes.   Computed average yields with 95% confidence limits
were:

oil yield	47.6	± 3.5%
carbon dioxide	4.28	± 0.43%
carbon monoxide	0.456	± 0.02%
solids	2.38	± 0.69%

The large error in the solids is due to the low yield at this
temperature.

Mass and Element Balances

The total mass balance showed that 96.6% of the original mass was accounted for, but this included the water added in five-fold excess. If the mass balance was performed considering only products (including product water) and the mass of the wood, then 80% of the wood was accounted for. On the same basis, the element balance accounted for 86.4% of carbon, 80.0% of hydrogen and 75% oxygen. Some of the carbon is inevitably lost in the rotary evaporation of the oil. There would also be liquid losses when the tubes are vented.

CONCLUSION AND FUTHER WORK

It is thus concluded that chipped poplar wood will completely yield acetone solubles, water solubles, and gases if heated under the correct conditions in water. The chemical composition of these oils will be reported shortly. The reactions of other poplar clones as well as the heartwood, sapwood and bark compo- nents is progressing. The major finding is that different clones and components yield different product slates. The details of this study will also be published in the near future.

ACKNOWLEDGEMENTS

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