LOW SEVERITY ELECTROCHEMICAL LIQUEFACTION OF WOOD

by

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ABSTRACT

Direct liquefaction of wood with aqueous HI solution to a wood oil product under low severity conditions, atmospheric pressure and low temperature around 125°C, was investigated in two stages. The first stage involved batch reactor studies. The wood-HI liquefaction reaction is fast, nearly complete in as little as 20s when the initial aqueous phase concentration is 57 wt% HI or greater. Yield of the char-type residue, a major problem in other liquefaction processes, is completely eliminated provided the final aqueous phase concentration is 50 wt% HI or above. The performance of this process with wood is better than would be predicted from experiments on the liquefaction of wood components determined separately.

Removal of oxygen from polymeric wood components is accomplished with oxidation of I^- to I_2. The second stage tested a novel concept for closing the HI → I_2 → HI loop, an electrochemical liquefaction reactor (ECLR) with liquefaction in the cathode cell where I_2 is simultaneously reduced back to I^-. Electrolysis of water at the anode generates O_2 and the H^+ required at the platinum cathode for HI regeneration. Without wood liquefaction, current efficiency for I_2 reduction is 90 – 100% and I_2 concentration can be maintained at about 0.1 M, which is about 10% of that without I_2 reduction.

Preliminary ECLR tests in batch and batchwise-continuous modes demonstrated simultaneous wood liquefaction and electrochemical reduction of I_2 in the presence of the viscous wood oil. Also the iodine content of the crude wood oil is thereby reduced by about 60%, where this limit is imposed by the strong physical association between I_2 and various functional groups in the product. Generation of H_2, the competitive reaction, can be avoided.

ECLR characteristics were determined from a continuous run in a sealed reactor at a steady aqueous phase concentration of 55 wt% HI with a cathode current density of 0.81 A/cm^2 at a cell voltage of 6 V. Carbon base yields were 84.2% crude wood oil product, 4.9% methyl iodide from the lignin methoxy groups and no production of the char-type residue common to other biomass liquefaction processes. Of the I_2 produced, 93% would be reduced to HI, the other 7% being I_2 associated physically with the product. Of the H^+ generated at the anode, about half is used for HI regeneration and half for electrochemical liquefaction reactions as reflected by the exceptionally high levels of hydrogen retention and oxygen removal of the wood oil relative to the wood, above 85% in both cases.

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NOMENCLATURE

1 Designation of Reaction Conditions

F_{wood} : wood flow rate, g/min

$[HI]$: HI concentration, M or wt%

$[I_2]$: iodine concentration, M

$[I_2]_i$: initial I_2 concentration, M

$[I_2]_f$: final I_2 concentration, M

j : product fraction

R : stoichiometric ratio on carbon base, gmol HI/gmol C in substrate

R_O : stoichiometric ratio on oxygen base, gmol HI/gatom O in substrate

R_{H^+} : stoichiometric ratio of H^+, gmol H^+/gmol C in wood

R_{I^-} : stoichiometric ratio of I^-, gmol I^-/gmol C in wood

R_{model} : model stoichiometric ratio, gmol HI/gmol C in substrate

s : substrate

t : reaction time, min

T : reaction temperature, °C

V_i, V_f : initial and final volumes in the cathode cell, l

W_{I_2} : amount of I_2, g

W_j : weight of product fraction, g

W_s : weight of substrate, g

2 Designation of product fractions, j

AP : organic product soluble in aqueous HI solution phase

OP : organic phase product, not soluble in aqueous HI (OP = OA + ON)

OA : acetone-soluble part of OP organic phase product

ON : acetone-insoluble part of OP organic phase product

3 Designation of Reaction Terms

$r_{I_2\,red.}$: I_2 reduction rate, g/min

$r_{I_2\,pro.}$: I_2 production rate, g/min

r_{O_2} : O_2 flow rate, g/min

$Z_{C/j}$: weight fraction carbon in product fraction j

$Z_{H/j}$: weight fraction hydrogen in product fraction j

$Z_{I/j}$: weight fraction iodine in product fraction j

$Z_{O/j}$: weight fraction oxygen in product fraction j

$Z_{C/s}$: weight fraction carbon in the substrate

$Z_{H/s}$: weight fraction hydrogen in the substrate

$Z_{O/s}$: weight fraction oxygen in the substrate

X_{HI} : conversion of HI, fraction or %

$X_{HI,\,model}$: model conversion of HI, fraction or %

$Y_{C/j}$: carbon base yield for product fraction j, fraction or %

4 Designation of Reaction Stoichiometry

a : gmol HI reacted per gmol C of substrate

a_O : gmol HI reacted per gmol O of substrate

a_{model} : model gmol HI reacted per gmol C of substrate

A_C : atomic weight of carbon, 12.01

A_H : atomic weight of hydrogen, 1

A_I : atomic weight of iodine, 126.9

A_O : atomic weight of oxygen, 16

b : gmol H_2O produced per gmol C of substrate

b_{model} : gmol H_2O produced per gmol C of substrate

c : gmol I_2 produced per gmol C of substrate

c_O : gmol I_2 produced per gmol O of substrate

c_{model} : gmol I_2 produced per gmol C of substrate
k_s : H/C atomic ratio of the substrate
l_s : O/C atomic ratio of the substrate
k : H/C atomic ratio of the product fraction
l : O/C atomic ratio of the product fraction
m : I/C atomic ratio of the product fraction
$M_{CH_{1.4}O_{0.72}}$: formula weight of wood, 24.92 g/gmol C in wood
M_{HI} : molecular weight of HI, 127.9
M_{H_2O} : molecular weight of H_2O, 18
$M_{H_2SO_4}$: molecular weight of H_2SO_4, 98
M_{I_2} : molecular weight of I_2, 253.8
M_{O_2} : molecular weight of O_2, 32
$(H/C)_j$: H/C atomic ratio of product fraction j
$(I/C)_j$: I/C atomic ratio of product fraction j
$(O/C)_j$: O/C atomic ratio of product fraction j
$(H/C)_s$: H/C atomic ratio of substrate
$(O/C)_s$: O/C atomic ratio of substrate

5 Designation of Electrochemical Characteristics

E : current efficiency, fraction or %
E_a : anode current efficiency, fraction or %
E_c : cathode current efficiency, fraction or %
E_r : I_2 reduction efficiency, fraction or %
F : Faraday constant, C mol^{-1}
ΔG : free energy, kJ/mol
i : current density, A/cm^2
I : current, A
n : number of electrons, equivalent
R : resistance, ohm

V : voltage, volt

V_a : anodic thermodynamic minimum potential, volt

V_c : cathodic thermodynamic minimum potential, volt

V_{min} : overall thermodynamic minimum potential, volt

V^{ohm} : ohmic drop, volt

V^T : total voltage, volt

η_a : anodic overpotential, volt

η_c : cathodic overpotential, volt

ε^o : standard equilibrium potential, volt

CHAPTER 1

INTRODUCTION

1.1 Low severity wood liquefaction in aqueous HI solution

Pyrolysis, gasification, and direct and indirect liquefaction are the major types of chemical processes for biomass conversion to liquid or gaseous products. With indirect liquefaction the final process follows the production first of a synthesis gas from the biomass. Liquefaction processes convert biomass into products of generally lower oxygen content and therefore of higher energy than those from pyrolysis or gasification. As Canada has enormous supplies of natural gas but very limited reserves of oil, direct liquefaction is of greater general relevance here than pyrolysis or gasification. Specialized types of pyrolysis offer particular higher value products. Direct biomass liquefaction processes, investigated since the beginning of this century, require high temperature (250 – 450°C) and high pressure (25 – 500 atm), generally with hydrogen and/or carbon monoxide as the reducing agent in a catalytic reaction. The high cost associated with processing under such extreme conditions render the economics quite unfavourable. The several factors noted above provide an incentive to search for a low-temperature, low-pressure chemical process to convert lignocellulosic material into some type of a liquid organic product, referred to generally as biomass oil.

Douglas and Sabade, 1984, directed attention to the direct liquefaction of cellulose by treatment with aqueous HI solution at low temperature and atmospheric pressure. They reported total conversion of cellulose to a liquid product having a relatively low oxygen and high hydrogen content compared to the substrate. A follow-up study by Douglas et al., 1985, established that with this technique encouraging results could also be obtained for the liquefaction of wood of various of species. With batch reactor investigations they established some of the characteristics of this reaction system, indicating the effects of reaction time and temperature, stoichiometric proportions of HI to wood and of wood species and particle size. In a further study with this batch reactor system Douglas et al., 1990, investigated wood liquefaction in the presence of reactor product solvents and hydrotropic salts.

A bench scale investigation by Douglas et al., 1986, demonstrated that this technique of low severity wood liquefaction could be operated as a continuous reactor system in which the HI in the liquefaction reactor effluent could be recovered and recycled to the liquefaction reactor. Two important findings were made. At steady state, with recycle of the aqueous HI phase back to the reactor, the part of the product which is initially dissolved in the aqueous HI phase was found to be converted to organic phase product, the desired product. Secondly, with recycle of the aqueous HI solution to the reactor the iodine:carbon ratio in the crude reactor product was found to be variable and to be a function of the concentration of I_2 in the reactor. This finding indicated that the major problem in biomass liquefaction with aqueous HI solution, i.e. production a crude product contaminated with iodine, could potentially be eliminated.

Thus it had been demonstrated that a wood oil product of relatively high H:C ratio and low O:C ratio could be produced at atmospheric pressure and low temperature. However basic technical problems remaining to be solved were that the crude product had a relatively high I:C ratio, considered to be as organic iodide, which must be eliminated, and that the I_2 produced from the oxidation reaction $2I^- \rightarrow I_2$ must be converted back to the reactant HI in order to have a potentially viable biomass liquefaction process. The most promising alternative for closing the $HI \rightarrow I_2 \rightarrow HI$ loop is the documentation by Carlin, 1977, that I_2 dissolved in aqueous HI solution can be reduced electrochemically to HI. However nothing at all is known concerning the possibility of electrochemical reduction of I_2 to HI in the presence of liquefaction of biomass to a viscous wood oil. Thus investigation of the possibility of a unique coupling of two processes: wood liquefaction in aqueous HI solution and electrochemical reduction of I_2 back to HI, constitutes the basic problem to be studied here.

1.2 Objectives of present study

The overall objective of the present study was to investigate a novel concept – the **electrochemical wood liquefaction reactor** (ECLR) whereby the wood liquefaction reactor is simultaneously the reactor for electrochemical reduction of the liquefaction reaction product, I_2, back to the liquefaction reactant, HI. This concept would close the HI → I_2 → HI loop while also potentially reducing the iodine content of the crude product. The objectives may be detailed as:

(1) To add to the basic knowledge of this low severity technique for wood liquefaction in experiments first without the complication of the electrochemical process, determining specifically the effects of short reaction time, of the concentration of aqueous HI, and the behaviour of various single component liqnocellulosic substrates.

(2) To design an electrochemical liquefaction reactor, an ECLR, for the direct liquefaction of wood in concentrated aqueous HI solution in the cathode cell so that the I_2 produced by the liquefaction reactions can simultaneously be reduced electrochemically back to the HI reactant, with an appropriate anode cell for generation of the H^+ ions required for the regeneration of HI in the cathode cell.

(3) To determine the electrochemical performance characteristics of such an ECLR with an appropriate anode cell design.

(4) To determine practical conditions for electrochemical reduction of I_2 to HI in aqueous HI solution in the cathode cell of the ECLR system without the complication of wood liquefaction.

(5) To determine the extent to which electrochemical reduction of I_2 to HI, with the exclusion of competing electrochemical reactions, may still be obtained simultaneously with wood liquefaction through examination of the ECLR process first in the simpler modes of batch and then batchwise-continuous electrochemical wood liquefaction.

(6) To operate the ECLR technique under steady-state reaction conditions with continuous wood liquefaction and simultaneous electrochemical reduction of I_2 back to HI directly in the liquefaction reactor, thereby closing the HI $\rightarrow$ I_2 $\rightarrow$ HI loop.

(7) To initialize an analysis of the continuous electrochemical wood liquefaction process, including the reaction stoichiometry, I_2 reduction efficiency, current efficiency, energy required and other characteristics affecting the potential industrial feasibility of the electrochemical reactor system.

CHAPTER 2

PRIOR KNOWLEDGE AND RESEARCH STRATEGY

2.1 Evolution of conventional biomass liquefaction

2.1.1 Perspective on biomass conversion processes

In response to the oil crisis of the mid-1970's many countries focused attention on alternative, non-petroleum sources of energy and chemical feedstocks. With fossil fuel supplies becoming scarcer and more costly, first in the 1970's and in the future, the use of renewable biomass becomes steadily more attractive. Wood and crop residues comprise the vast majority of biomass feedstocks available for conversion to liquid and gaseous fuels, 96% according to Schiefelbein, 1983. Compared to solid fossil fuels such as coal, biomass feedstocks have unique properties that offer potential advantages for development as energy sources, principally a much higher H:C ratio and very low sulphur and ash contents. However biomass has the disadvantages of being a less concentrated source, having a relatively high moisture content and, because of a higher O:C ratio, a lower thermal content than fossil fuels (Sajdak et al., 1981).

Since the discovery of fire biomass has been used directly for energy by combustion, but recent interest is in its conversion to a product of higher energy density and hence more conveniently transported, stored and used. The two principal classes of conversion processes, thermochemical and microbiological fermentation, were reviewed by White and Plaskett, 1981, and Chum, 1993. Thermochemical conversion processes generally employ elevated temperatures and in some cases high pressures to convert biomass through combustion, pyrolysis, gasification and liquefaction (Gambles and

Zsuffa, 1988).

Pyrolysis, the process of thermal decomposition, is the age-old way of making charcoal and has typically given about equal parts of three products: gas, pyrolysis oil and char. In recent years the concept of rapid pyrolysis has emerged as a promising alternative for specialized purposes (Graham, Bergougnou and Overend, 1984; Graham et al., 1988; Scott et al., 1991; Palm et al., 1993). Graham et al., 1988, reported that at rapid heating rates, 1000°C/second, the char yield from poplar decreased from 18% at 500°C to 3% at 800°C. Thermochemical gasification converts biomass by partial oxidation at elevated temperatures in various reactor types such as moving bed and fluid bed gasifiers to a product used as fuel or synthesis gas.

The thermochemical conversion of biomass to liquid product can be achieved by indirect or direct liquefaction. With indirect liquefaction the reactive synthesis gas from pyrolysis or gasification of biomass is converted catalytically to liquid fuel and chemical products. In conventional direct liquefaction the biomass is reacted catalytically at high temperature and pressure in a reducing atmosphere of hydrogen and/or carbon monoxide.

As the present thesis is concerned with a novel process of direct chemical liquefaction of biomass, the processes of biomass fermentation, pyrolysis and gasification are not considered further here.

2.1.2. Conventional biomass liquefaction

Conventional direct thermochemical liquefaction is carried out in either aqueous or solvent media in the presence of catalysts (carbonate, formate, nickel, etc.) with various reducing agents (H_2, CO, acid, etc.) at temperatures of 250 – 400°C and high pressure. Typically the conversion of lignocellulosic material produces four product fractions, gas, biomass oil, water-soluble or solvent-soluble product and solid residue – a char. As biomass has a higher oxygen to carbon ratio than solid fossil fuels such as coal, direct reduction can therefore be accomplished either by removal of oxygen with carbon monoxide or by the addition of hydrogen. A hydrogen medium, from either H_2, H_2/CO, H^+ of an acid media, or H-donor solvent, has a threefold action (Chornet and Overend, 1985 and 1987; Chum and Baizer, 1985), i.e. to hydrogenate or deoxygenate terminal O-containing functional groups, to limit the extent of high molecular weight product from condensation reactions induced by free radicals and to hydrocrack the lignin and the tarry intermediate product material formed in the early stages of thermal treatment.

In *acid media* the reaction may affect both carbohydrates and lignin. Carbohydrates are involved in two types of important reactions: glucoside hydrolysis and dehydration, Fengel and Wegener, 1984; Goldstein, 1984. Monosaccharides form rapidly from depolymerization of carbohydrates, and would subsequently be dehydrated to furfural and hydroxymethyl-furfural (HMF), to levulinic acid, and to other derivative acids. Lignin undergoes extensive cleavage in acid media, especially cleavage of arylglycerol-β-aryl ethers, Lundquist and Lundgren, 1972. The yield of low-molecular weight products (dimers and monomers) has been reported as 17% with spruce lignin and 30% with birch lignin in acid hydrolysis liquors (0.2 M hydrogen chloride in dioxane-water 9:1), Lundquist, 1976.

In *alkaline media* with the wood liquefaction process operated at about 300 – 500°C and 3000 – 5000 psig with aqueous sodium carbonate as the catalyst and CO/H_2 as the cover gas, a variety of organic acids can be produced by alkaline degradation, Elliott, 1981 and 1985; Pepper et al., 1985. Further dehydration synthesizes phenolics, furans and other chemicals if the aqueous medium becomes acidic by the organic acids produced, Miller et al., 1981; Molton et al., 1981.

In *organic media* the chemistry of liquefaction depends upon the nature of the solvent-substrate interactions, Chornet and Overend, 1985. The choices of solvents are motivated by considerations of solubility and their availability as products derived from lignocellulosics, like creosote oil and ethylene glycol which have been used. Hydrogen-donor solvents like tetralin and isopropanol are very effective in reducing the required severity of reaction conditions and maximizing biomass conversion and oil yield.

In *hydrogen media* and with *catalysts* like Raney-nickel, palladium, platinum, Fe_3O_4, lignocellulosic materials can be catalytically liquefied at 200°C – 350°C and 5 – 10 MPa pressure (Boocock et al., 1979 and 1980; Datta et al., 1993).

2.1.3 Status of conventional biomass liquefaction

Conventional biomass liquefaction has been explored only in the laboratory as the unattractive economics have prevented industrial scale development. Research by Appell, 1975 and 1977, at the Pittsburgh Energy Research Centre (PERC) led to a pilot plant for wood liquefaction (1 – 3 tonne/day of 40% moisture content wood) at Albany, Oregon. Wood as a slurry in the recycled product oil was liquefied in the presence of a 60:40 mixture of carbon monoxide:hydrogen and a catalyst consisting 5% aqueous sodium carbonate, in a stirred tank reactor at 290 – 370°C and over 3000 psig, for 20 min to 2h residence time (Molton et al., 1981). The Albany work revealed serious operational and economic problems including a pumpability limit of 8 wt% of wood flour in aqueous suspension and a low oil product yield, and demonstrated the need for further investigation of pretreatment of the wood flour prior to liquefaction and other basic aspects.

To investigate the problem of low oil yield at the Albany pilot plant and to further develop the aqueous alkaline-based process, a chemical and mechanical pretreatment option was investigated at the Lawrence Laboratory in Berkeley, California, by Schaleger et al., 1982. They used a bench-scale continuous liquefaction unit for the production of wood oil from aqueous slurries of wood at 330 – 360°C in the presence of reducing gas. Wood chips were subjected to chemical pretreatment (dilute acid hydrolysis then neutralization with sodium carbonate) at 180°C followed by mechanical refining. The aqueous slurry was pumped at a concentration over 30% wood chips. Such wood liquefaction results in formation of a variety of carboxylic and water soluble acids to 25% yield, causing an increase in acidity of the aqueous phase from a pH of about 6 – 9 to 4 – 5. The maximum yield of wood oil was 40 – 42%. The yield of char varied from 1 – 10%. Carbon dioxide was formed in about 25% yield.

At the University of Saskatchewan, Pepper et al., 1985, and Eager et al., 1985, used screw feeders to introduce wood flour continuously as a 28 wt% aqueous slurry to a liquefaction reactor. They converted a variety of lignocellulosic materials to wood oil in yield up to about 50% by use of carbon monoxide at 300 – 400°C and 40 – 50 MPa with aqueous sodium carbonate as a catalyst. The product oils, an aqueous phase product and an acetone soluble organic phase product which might be rendered fluid on mild warming, had a heating value of 35 – 40 MJ/kg, contained 70 wt% carbon, 7 – 8 wt% hydrogen and 20 wt% oxygen, and constituted a carbon recovery to wood oil and water-soluble oxygenated products of about 66%. The char yield was 4 – 10%. About 35% yield of carbon dioxide was reported, probably by decomposition of the wood or as a result of oxidation of carbon monoxide by oxygen from wood.

The serious disadvantage of biomass liquefaction in alkaline media under H_2/CO atmospheres is that the carbon recovery to wood oil from the substrate is only 65 – 75% while about 25 – 35% of the carbon of substrate is converted to carbon dioxide, not a desired product.

A two-stage liquefaction reactor system with preheating separate from hydrogenolysis/hydrogenation was investigated with an organo-solvent at the University of Sherbrooke by Chornet et al., 1985. A 12 – 15% suspension of wood (about 10% moisture content) in anthracene oil was used. In the preheating reactor (230 – 250°C, 4 – 8 MPa, 0 – 60 minutes) about 45% solubilization of the lignocellulosic suspension was achieved. Overall conversion of 90% was obtained at short residence times (5 – 12 minutes) in the hydrogenation stage reactor (300 – 340°C and 3 – 7 MPa). Further development by Chornet et al., 1988, and Vanasse et al., 1988, of the organo-solvolytic pretreatment technology showed that the high consistency wood slurries (20 – 32 wt%) needed for a continuous liquefaction unit could be prepared and pumped with a screw feeder in both creosote and ethylene glycol solvent. They obtained about 50% solvent-soluble product. The solvent-soluble oil product has about 90% carbon content and 6% hydrogen content, i.e. a very low elemental H/C ratio of about 0.8. This low hydrogen content was reported due to little or no hydrogenation under non-catalytic conditions and suggested a solvolytic route towards solubilization.

A 900 kg/h system (Brennan et al., 1986) was built at the Solar Energy Research Institute (SERI) in Colorado to hydrolyse low solids wood slurries (10 wt%) using a dilute acid (1 – 2%) process at 200 – 260°C, 4 – 6 MPa and 4 – 20s residence time in a plug flow reactor which was operated for a number of hours. Only the conversion of cellulose and hemicellulose of wood was considered for the mass base yields of glucose 50%, xylose 60% and furfural 40% at reactor conditions of 253 – 255°C and 1.6% sulphuric acid.

A one-stage process of a continuous plug flow reactor for rapid dilute acid hydrolysis of hardwood to produce furfural and fermentable sugars was also investigated in the University of Sherbrooke, Abatzoglou, et al., 1990. They pumped wood suspensions up to 13 wt% solids in dilute H_2SO_4 solution at flow rates up to 90 kg/h. Their reaction conditions were 190 – 240°C, 10 – 32 Mpa and 20 – 120s residence time. The mass base yields reported were 30% hexoses and 65% furfural, derived mainly from cellulose and hemicellulose. The insoluble residue, 40% yield on a mass basis, was the remaining lignin.

2.2 Biomass liquefaction in aqueous HI solution

2.2.1 General background studies

Studies of the action of aqueous HI solution on carbohydrate and polyhydroxy compounds were begun as far back as 1866 by some of the greatest 19th century chemists. Early studies reported that polyhydroxy compounds thereby undergo iodination and reduction, with only one of the hydroxyl groups replaced with hydrogen or removed with the formation of double bonds (Markownikoff, 1866; Erlenmeyer, 1866). Aqueous HI solution was found by Berthelot, 1870, to be an efficient reagent for coal liquefaction. Geerards et al., 1957 and 1958, reported that carbohydrates, coal and wood could be converted to liquid hydrocarbons by hydrogen and iodine through catalytic decomposition at high temperature (300 – 325°C) and high pressure (200 atm) in aqueous HI solution. Vassallo and Wilson, 1985, also carried out coal liquefaction with aqueous HI.

By heating a glucose solution with aqueous HI in a sealed tube to 100°C Vintilescu and Faltis, 1923, produced a liquid product containing formaldehyde, fumic acid and traces of saponifiable esters. Interestingly, they found that the organic products were not iodinated. Ssorbitol can be converted into an oxygen-free product, 2-iodohexane, using aqueous HI, Morrison and Boyd, 1977. Alkyl iodides were converted to olefins by treatment with gaseous HI at 250 – 320°C (Ogg, 1934; Benson and O'Neil, 1961; Sullivan, 1961).

Hydrogen iodide is reported to be a mild cleaving agent for lignins, attacking the β-aryl ether bonds in the lignin subunits which have α-hydroxy or α-etheric groups (Shevchenko et al., 1991; Akim et al., 1993). In mild conditions the cleavage is more selective. Treatment of milled wood lignin by dry HI in dry dioxane leads to iodinated and partly depolymerized lignin. The methoxyl groups could be split off from the lignin unit using the aqueous HI to produce methyl iodide (Freudenberg et al., 1929). Reduction of methoxyl groups to methyl iodide with aqueous HI solution was developed as the standard micro-determination method for methoxyl groups (Mitchell and Williams, 1938; Browing, 1967; ASTM standards, 1984).

The combined reducing action of aqueous HI solution and phosphorous has been investigated in several studies. Willstatter and Kalb, 1923, studied the action of aqueous HI and red phosphorous on lignins and carbohydrates at 250°C. Perlin, 1949, reported finding that cellulose in cotton linters can be converted to a neutral oil (yield about 44%) by a reducing mixture of red phosphorus and 57% aqueous HI solution at 127°C. Groner et al., 1972, reported that glucose could be converted to hexane by reduction with red phosphorous and aqueous HI.

Paudler and Walton, 1981, studied the general utility of reactions of microcrystalline cellulose with hydrogen and iodine, and with hydrogen and hydrogen iodide. They reported that iodine, whether in molecular form or as HI, acted simply as a catalyst. An iodine catalysis effect in H_2 media at 425°C was patented by Waterman, 1932, and was reported by Fraenkel et al., 1991, for coal liquefaction in aqueous HI solution at 300°C.

Thus many researchers have found that aqueous HI acting on sorbitol, glucose, cellulose, lignin and coal can be effective for producing low molecular compounds of low oxygen content, and in the limit, hydrocarbons. As aqueous HI is a strong reducing agent the oxygen in biomass materials is removed to a significant extent by HI breaking the O-C bonds. Hydrogen iodide acts not only a strong reducing agent, but also as an iodinating agent. Organic iodides produced from biomass conversion by aqueous HI can react further with HI, eliminating I_2 and forming a product of lower O/C ratio, a desired property of biomass oil from a liquefaction process. HI in aqueous solution is thermodynamically more stable than is HI gas, Kirk and Othmer, 1981, and with an atmospheric pressure azeotrope at 127°C, aqueous HI solution may provide a potentially attractive reagent for chemical conversion of biomass under low severity conditions to liquid products.

2.2.2 Cellulose liquefaction

Subsequent to the finding by Perlin, 1949, of the effectiveness of the combination of red phosphorus and aqueous HI solution on cellulose, the liquefaction of cellulose in aqueous HI solution alone was investigated by Douglas and Sabade, 1984. Cellulose (elemental formula $(C_6 H_{10} O_5)_n$ or $CH_{1.67} O_{0.83}$) was rapidly depolymerized and deoxygenated under mild conditions of temperature (<127°C) and atmosphere pressure through the use of 57 wt% aqueous HI solution. Cellulose was essentially completely liquefied in about 3 minutes of batch reaction. Even with only 30s reaction, cellulose conversion to a biomass oil was as high as 87%. For the HI/cellulose stoichiometric ratio R in the range of 1.6 – 3.8 gmol HI/gmol C, conversion of cellulose to biomass oil increased significantly with the stoichiometric ratio R for reaction time as short as 1 min, but became independent of this stoichiometric ratio for reaction time as long as 120 min.

They reported that cellulose appeared to be converted initially and very quickly to an aqueous phase product dissolved in the HI solution, then more slowly to an organic phase product insoluble in the aqueous solution. The yield of aqueous phase product reached a sharp maximum, about 65 – 70%, very quickly at a reaction time as short as 30s. The ratio of the yields, organic phase product to aqueous phase product, was about 25:75 after 5 min reaction, about 60:40 at 2h reaction time.

When subjected to examination by TLC, NMR, GC, MS, density and molecular weight determination, the product was found to consist of a complex mixture of primarily non-polar compounds in the $C_{10} - C_{20}$ range, including aliphatic, cyclic or alicyclic compounds, with some olefinic double bonds. The average molecular weight of the product was estimated, with considerable uncertainly, to be about 310.

The overall reaction stoichiometry for HI being oxidized to I_2 in proportion to the removal of oxygen by reduction, at R = 3.8 gmol HI/gmol C, was reported as:

$$CH_{1.67}O_{0.83} + 0.89\ HI \rightarrow CH_{1.64}O_{0.39}I_{0.09} + 0.46\ H_2O + 0.40\ I_2 \qquad (\text{1 min reaction})$$

$$CH_{1.67}O_{0.83} + 1.11\ HI \rightarrow CH_{1.52}O_{0.20}I_{0.11} + 0.63\ H_2O + 0.50\ I_2 \qquad (\text{30 min reaction})$$

$$CH_{1.67}O_{0.83} + 1.38\ HI \rightarrow CH_{1.52}O_{0.067}I_{0.03} + 0.77\ H_2O + 0.68\ I_2 \qquad (\text{24h reaction})$$

The product at 30 min reaction may be expressed as constituting 91% retention of hydrogen and 76% removal of oxygen relative to the cellulose. Although by some indications the reaction with HI was essentially complete in 3 min, as reaction time was increased from 1 min to 30 min then to 24h the amount of HI reacting increased, producing a more highly deoxygenated product. The hydrogen retention of the biomass oil product relative to the cellulose remained over 90% at all reaction times. The iodine content of the product, a central problem with this process, was found to decrease to an I/C atomic ratio of just 0.03 at 24h reaction time, much lower than the I/C of about 0.1 produced for 1 – 30 min reaction.

The definition by Douglas and Sabade, 1984, of reaction conditions in terms of the stoichiometric proportion of HI to the substrate and their determination of stoichiometric equations for the reaction provided a more quantitative treatment of biomass liquefaction in aqueous HI than that given by earlier studies.

2.2.3 Batch wood liquefaction

Results were reported by Douglas et al., 1985, and Ng, 1985, for bench-scale experiments at 1 atm and 127°C with black spruce wood (elemental composition $CH_{0.46}O_{0.64}$) and other wood species, with commercial grade 57 wt% aqueous HI solution containing 1.5 wt% H_3PO_2 as stabilizer, for reaction times in the range 1 min to 2h. In these batch reactor experiments as for the earlier work with cellulose, some of the product remains dissolved in the HI solution as an aqueous phase product while the major part separates as an organic phase product. When the latter was solvent fractionated by acetone only a small yield of acetone-insoluble residue remained, generally less than 10% relative to the wood. All yields were given on a carbon basis, the most informative basis of expression. Similarly to the definition adopted with cellulose as the substrate, the stoichiometric ratio for HI was defined as gmol HI/gmol C in wood, R. For an ideal reaction in which all oxygen is removed through reduction to H_2O by the HI, yielding a pure hydrocarbon, H_2O and I_2, two hydrogen iodide molecules are required per oxygen atom in the wood. Thus for this model reaction with black spruce of composition $CH_{1.46}O_{0.64}$, it follows that R_{model} = 1.28 gmol HI/gmol C.

The overall reaction stoichiometry for a base case, R = 5.7 gmol HI/gmol C in wood, t = 2h, T = 118°C, with black spruce in HI solution of initial concentration about 56 – 57 wt% HI was reported by Ng, 1985, as:

$$\mathrm{CH_{1.46}O_{0.64} + 0.70\ HI \rightarrow 0.73\ CH_{1.26}O_{0.14}I_{0.05} + 0.27\ CH_{1.58}O_{0.48}I_{0.20}}$$
$$\mathrm{+ 0.41\ H_2O + 0.31\ I_2}$$

where the carbon-base yields of organic phase and aqueous phase product fractions are, respectively, 73% and 27%, as indicated by the corresponding stoichiometric coefficients above. With R = 5.7 gmol HI/gmol C in wood, the above case corresponds to (0.70/5.7=) 12% conversion of HI. If the organic phase and aqueous phase products were combined, the overall stoichiometric equation would be:

$$\mathrm{CH_{1.46}O_{0.64} + 0.70\ HI \rightarrow CH_{1.34}O_{0.23}I_{0.09} + 0.41\ H_2O + 0.31\ I_2}$$

with the total product corresponding to retention of 92% of the hydrogen and removal of 64% of the oxygen of the wood.

Although most of their tests were performed with black spruce, by a series of experiments they found that with hybrid poplar the stoichiometric equation at reaction time t = 2h and R = 3.6 gmol HI/gmol C is:

$$\mathrm{CH_{1.63}O_{0.73} + 0.73\ HI \rightarrow 0.81\ CH_{1.40}O_{0.22}I_{0.07} + 0.19\ CH_{1.76}O_{0.55}I_{0.20}}$$
$$\mathrm{+ 0.45\ H_2O + 0.32\ I_2}$$

for the yields of organic phase and aqueous phase as 81% and 19% as indicated by the respective stoichiometric coefficients above. The equation for the combined products is:

$$\mathrm{CH_{1.63}O_{0.73} + 0.73\ HI \rightarrow CH_{1.47}O_{0.28}I_{0.09} + 0.45\ H_2O + 0.32\ I_2}$$

indicating overall a 90% retention of hydrogen and 62% removal of oxygen. Comparison with the stoichiometric equations for cellulose of Douglas and Sabade, 1984, indicates that the reactivity of HI decreases from cellulose to hybrid poplar to black spruce, but the hydrogen retention is about the same in all cases while the oxygen removal for the wood oil product is lower than that from cellulose. A basic problem of this process, the contamination of the crude wood oil product with iodine, is seen by the I/C atomic ratios ranging between 0.05 and 0.09 in the above results.

The effect of process variables found in this study of wood liquefaction in 56 – 57 wt% aqueous HI solution is now reviewed.

(1) Effect of reaction time

With HI to wood stoichiometric ratio R = 5.7 gmol HI/gmol C in wood, the yield of aqueous phase product at 1 min reaction time was very high, about 60%, while it appeared that subsequent transformation of aqueous phase product to organic phase product led to the yield of aqueous phase product steadily decreasing with longer reaction time. The yield of organic phase product increased to its maximum value, about 70%, at 2h reaction time. For very long (24h) reaction time some product was converted to the undesired insoluble residue, which increased to about 17% yield, while otherwise the yield of this undesired product remained about constant at about 10% for reaction time from 1 min to 2h. The organic phase product elemental composition varied relatively little with reaction time. A good hydrogen retention of product was obtained, averaging about 85% relative to the hydrogen content of wood.

(2) Effect of HI/wood stoichiometric ratio

With initial concentration of aqueous HI solution always about 56 – 57 wt% HI and 2h reaction time the effect of HI/wood stoichiometric ratio was studied for black spruce in the range of 1.1 – 5.7 gmol HI/gmol C in wood. The yield of the undesired acetone-insoluble residue decreased rapidly with increasing R up to 2.5 gmol HI/gmol C, becoming constant at about 8% for values of R of 3.5 gmol HI/gmol C or above. A maximum in yield of the organic phase product, 93%, occurred at a stoichiometric ratio of about R = 3.5 gmol HI/gmol C.

The extent of deoxygenation of the organic product relative to the wood, about 78% at R = 3.4 gmol HI/gmol C was, as expected, less at lower values of R, dropping to only 53% at R = 1.1 gmol HI/gmol C. The contamination of the organic phase product with iodine was recorded by its I/C atomic ratio, which showed some sensitivity to stoichiometric ratio, the I/C ratio decreasing from about 0.11 at R = 1.1, to about 0.05 at R = 5.7 gmol HI/gmol C, as follows:

R, gmol/gmol	H/C	O/C	I/C
1.1	1.37	0.30	0.11
5.7	1.26	0.14	0.05

Thus to avoid excessive yield of the acetone-insoluble residue and low deoxygenation of product for batch liquefaction with initial HI concentration about 56 – 57 wt%, one should use a value of HI to wood ratio not less than R = 2.5 gmol HI/gmol C in wood, i.e. about double the value of R_{model} = 1.28 gmol/gmol for ideal reaction giving total removal of oxygen to yield a pure hydrocarbon.

(3) Effect of reaction temperature

The yield of the acetone insoluble-residue remained at about 8% for 2h reaction time and R = 5.7 gmol HI/gmol C, effectively independent of reaction temperature from 118°C down to 90°C, and remained impressively low, only 23%, at as low a reaction temperature as 60°C. The maximum yield of organic phase product, 70%, was obtained around 90 – 130°C, the remainder being product dissolved in the aqueous phase of HI solution. Product elemental compositions appeared relatively unaffected by reaction temperature down to 90°C.

(4) Effect of I^-/wood ratio at fixed H^+/wood ratio

A set of experiments was carried out in which the ratio of I^-/wood, R_{I^-}, was varied at constant ratio of H^+/wood, R_{H^+} by using mixtures of KI-HCl and HI-HCl. Thus R_{I^-} was varied over the range of 0.3 – 5.7 gmol I^-/gmol C in wood while the ratio H^+/wood, R_{H^+}, was maintained constant at 5.7 gmol H^+/gmol C in wood.

For the upper range of R_{I^-}, i.e. 4.6 – 5.7 gmol I^-/gmol C in wood, neither yields nor product compositions were affected by R_{I^-}. However for the case of $I^- - H^+$ uncoupled in this way at the lower range of $R_{I^-} < 4.6$, the distribution of yields was affected, with a higher yield of aqueous phase product and a correspondingly lower yield of organic phase product fraction than in the standard case of $I^- - H^+$ coupled. At low R_{I^-} with $I^- - H^+$ uncoupled, a product composition obtained was of lower H/C, lower extent of oxygen removal and very low I/C ratio.

The authors speculated that the effect of lower I^- concentration while maintaining high H^+ concentration was caused by acid hydrolysis of the wood cellulose and hemicellulose but with less of the dehydration reactions that give a product of lower O/C ratio. Thus the extent of the series of dehydration and other reactions which, in aqueous HI solution, follow acid hydrolysis was believed to be decreased or incomplete due to the low concentration of I^- at low R_{I^-}.

(5) Effect of recycling the reaction aqueous phase to the reactor

A batch reactor experiment was made to investigate what the effect on yields and composition of the products would be from operation with recycling of the aqueous phase back to the reactor. This question is of great practical importance because in a continuous reactor system the aqueous phase would be recycled back to the liquefaction reactor. The aqueous phase obtained after reacting wood with HI in a batch reactor was sparged with pure HI to bring the HI concentration back to the standard 57 wt%. This solution was then used instead of fresh aqueous HI for reaction with wood. For 2h reaction time at R = 5.7 gmol HI/gmol C in wood, very good results were obtained. Specifically, with recyling of the aqueous HI solution an even lower yield was obtained of the acetone-insoluble residue, only 1.3%, while maintaining product quality essentially unchanged. The importance of this experiment is in indicating good potential for converting the process from a batch reactor to a continuous reactor with recycle of the aqueous HI phase back to the reactor.

(6) Effect of hypophosphorous acid

The commercial aqueous HI used contained 1.5 wt% H_3PO_2, hypophosphorous acid, a preservative to prevent oxidation of HI to I_2. One experiment done at t = 2h and R = 5.7 gmol HI/gmol C in wood but using HI solution containing no hypophosphorous acid indicated no change in yield of the acetone-insoluble residue but a change in product distribution, with the organic phase product yield increased by one third while the aqueous phase product yield was correspondingly reduced. This shift in distribution of the total product between the two phases reflects a decrease in product solubility in the aqueous phase that could be anticipated in the absence of the phosphorous compound. There was no significant change in the elemental composition of any of the product fractions.

(7) Effect of wood species and particle size

Batch reactor test runs were made at 15 min reaction time and R of about 3.5 gmol HI/gmol C with three hardwoods (aspen poplar, hybrid poplar and white birch) and with the wood as chips rather than wood flour. The wood liquefaction process was found to work better with hardwoods than with black spruce, with the yield of acetone-insoluble residue reduced from about 8% to 1 – 2%. Both the hydrogen retention and the extent of oxygen removal for the total organic product were slightly better (higher) for hardwood than for black spruce. For 2h reaction time, variation in wood particle size had no effect on the results but for the short reaction time, $t = 5$ min, wood chips gave a somewhat higher yield of the aqueous soluble product. Thus over this size range at least, the wood liquefaction reactions appear to be controlled more by the reaction kinetics than by diffusion in the wood particles fed to the reactor.

2.2.4 Continuous wood liquefaction

Demonstration of continuous liquefaction reactor operation, with and without the recovery and recycle of the aqueous HI phase, was provided by Douglas et al., 1986, and Ladanowski, 1986. They used a bench-scale facility for treatment of lignocellulosic material (hybrid poplar and cellulose) under low severity conditions of atmospheric pressure and about 125°C in aqueous HI solution. The liquefaction reactor was a continuous stirred tank reactor (CSTR) operated at a mean residence time of 10 min for runs extending to 8.5h. The system involved a continuous reactor and batchwise-continuous removal of organic product from the reactor effluent by solvent extraction with methylene chloride. Because of the small scale of the operation the reactor was operated at about R = 13 gmol HI/g atom C simply to avoid plugging of the small diameter reactor effluent lines with the viscous product, while the earlier batch reactor experiments had established that the requirements of the chemistry of liquefaction were satisfied with a stoichiometric ratio of about R = 3.5 gmol HI/gmol C in wood when the initial concentration of the aqueous solution was about 56 – 57 wt% HI.

Reaction characteristics were investigated first for the CSTR system but with a continuous feed of aqueous HI, i.e. without recycle of the aqueous stream carrying unreacted HI. Such operation is a direct extension of batch reactor operation. For comparable conditions, organic product yield and elemental composition of the extracted product from a batch reactor and the CSTR fed with fresh aqueous HI were indeed found to be effectively the same.

All continuous systems with recycle to a CSTR of a reactor effluent stream have an unsteady state period after start-up. For this wood liquefaction CSTR, four criteria were used to monitor the approach to steady state, i.e. product yield, and H/C, O/C, and I/C atomic ratio of the extracted product. Of these, only H/C and O/C ratio of the product did not change appreciably from start-up to the end of 8.5h of continuous reactor operation. Yield of extracted product increased rapidly after start-up, becoming steady after about 2h operation with cellulose as the substrate, after about 4h with hybrid poplar. The steady state yield from hybrid poplar was 2.5 times the yield at start-up. This very large change from start-up to steady state established one of the two key findings of this study, i.e. that with recycle of the aqueous HI phase to the reactor the product fraction initially dissolved in the aqueous phase is eventually converted to the organic phase product. This investigation thereby established the new and important characteristic that when the continuous reactor system is closed up by recycle, all of the liquefaction product leaves the system as organic phase product, with no build up of organic products dissolved in the recirculating aqueous phase.

The final criterion, I/C atomic ratio of the extracted product, never approached a steady state value but increased continuously, reaching after 8.5h of operation a value of about five times the initial value. Measurements confirmed that the concentration of I_2 in the reactor also increased continuously, a consequence of more I_2 being produced by the liquefaction reaction then was removed by the methylene chloride extraction. The increase in I/C ratio of the extracted product was then simply a consequence of the increase in I_2 concentration in the reactor. Thus a second important outcome of this investigation was finding that the I/C ratio of the product is coupled to the I_2 concentration in the reactor. This finding opened the possibility of reducing the I/C ratio of the product, which must eventually go to zero, by some kind of improved continuous reactor operation that maintains the I_2 concentration at a low level.

2.2.5 Product solubility

(a) Solvent reactor

The organic product, a sticky viscous liquid at reactor temperature, adheres to all surfaces. Douglas et al., 1990, investigated the idea of dissolving this product at the moment of its formation, i.e. to have the product dissolved in a solvent liquefaction reactor. This "solvent reactor" concept thereby combined two steps of a potential continuous wood liquefaction process, the liquefaction and the organic phase product extraction, into a single operation. While simple in concept, this idea was found difficult to put into practice because of the several constraints governing the choice of the reactor solvent:

(1) chemical non-reactivity to HI, I_2 and the product;
(2) a volatility permitting reactor operation around 100°C at atmospheric pressure;
(3) its solvent properties for the organic product;
(4) cost.

Some potential reactor solvents identified after an exhaustive search were tested directly in solvent liquefaction reactor experiments. Preliminary testing of phenol and acetic acid as a liquefaction solvent showed good characteristics, with zero yield of solvent insoluble product. However the reactivity of phenol and acetic acid with aqueous HI and iodine (Fuches, 1936; Konieczny and Harvey, 1979) eliminated them as potential liquefaction solvents. The product was found to dissolve partially in chlorobenzene and tetralin, which gave two phases when mixed with HI solution. Tetralin was eliminated because, with its hydrogen donor nature, it reacts with I_2 giving HI.

The only solvent of appropriate volatility found to satisfy the requirements of chemical non-reactivity in this highly reactive system was chlorobenzene. Solvent liquefaction reactor tests showed that the addition of chlorobenzene to the reactor did not change the chemistry of the liquefaction process. The chemical composition of the product was virtually unchanged. An advantage was that the I/C ratio of product dissolved in chlorobenzene was substantially lower than without this solvent. Unfortunately even chlorobenzene is not a particularly good solvent for the product, with the result that the size of a solvent liquefaction reactor would be substantially increased. Their conclusion was that although the solvent reactor concept has some attractive advantages, the constraints necessary in practice limited the application of this concept in the laboratory. They noted however that the search for an appropriate reactor solvent was a problem only for laboratory operation. For an industrial-scale process the ideal reactor solvent would be the more volatile fraction of the liquefaction product itself, which would automatically fulfil the constraints as to volatility, non-reactivity, product solubility and cost. Thus their solvent reactor concept may be reconsidered later using, as the reactor solvent, a fraction of the product itself.

(b) Hydrotropic salts

The approach of increasing the solubility of organic product in the aqueous phase through the effect of hydrotropic salts was also tested by Douglas, 1990. Hydrotropic salt solutions are aqueous solutions of salts that increase the solubility of slightly water-soluble substances, a phenomenon first noted by Neuberg in 1916. For example, concentrated solutions of alkali iodides are excellent solvents for numerous organic substances (McKee, 1946).

Preliminary testing of three salts, KI, NaI and LiI, in a system of the viscous organic product plus the aqueous HI solution gave complete dispersion of the organic phase product in the aqueous phase and no acetone-insoluble residue whatever. The reactor surface was quite clear of the usual adhering viscous organic product. The relative yields of the product as viscous liquid organic phase and as aqueous phase dissolved in the solution were however not changed by the hydrotropic salts. Neither the type of salt used or its concentration influenced the yields. This observation of a fine dispersion of the organic phase product in the aqueous solution by the hydrotropic salts could play a role in continuous laboratory reactor operation if the need to eliminate plugging of reactor effluent lines is encountered.

2.2.6 Chemistry of reaction of wood with aqueous HI

Examination of the chemistry of wood liquefaction with aqueous HI solution requires first a brief outline concerning the components of wood. Wood consists of three main constituents, cellulose, hemicellulose and lignin, and some minor ones, principally extractives and inorganic compounds (Goldstein, 1984). *Cellulose* is a glucan homopolymer, $(C_6H_{10}O_5)_x$, of high molecular weight (about 100,000), generally crystalline but also found in amorphous form, consisting of linear chains of β(1,4)-O-glucopyranose units. *Hemicelluloses* consist of amorphous branched chains (molecular weight < 30,000) comprising mixtures of polysaccharides containing D-glucose, D-mannose, D-xylose, D-galactose and L-arabinose and also some of their oxidation products. *Lignins* are amorphous three-dimensional networks of polymers of indeterminate molecular weight formed by free radical oxidative condensation of three phenylpropane units: p-hydroxyphenylpropane, guaiacylpropane and syringylpropane (Sarkanen and Ludwig, 1971). Lignin remains an enormous puzzle which is still quite incompletely understood in spite of long continuing intensive research. The overall formula of spruce milled wood lignin (MWL) was quoted by Wayman and Parekh, 1990, as $C_9H_8O_2(H_2O)_{0.4}(OCH_3)_{0.92}$, i.e. $CH_{1.17}O_{0.33}$.

Wood also contains a variety of extractives such as resins, phytosterols, fats and fatty acids. The composition of the extractives is highly species-specific. In addition wood contains very small amounts of ash, 0.3 – 1%, from inorganic compounds such as CaO, K_2O, Na_2O, MgO, SiO_2, Fe_2O_3 and P_2O_5.

The nature of cellulose is the same in all wood species, but hemicelluloses and lignins change in amount and in composition from species to species. The hemicelluloses of softwoods have a high proportion of mannose, while hardwood hemicelluloses have a high proportion of xylose. Softwood lignin is lower in methoxyl content, being about 15% compared to about 21% in hardwood lignin, implying that hardwood lignin has higher proportion of sinapyl alcohol. In summary, the distribution of wood components between softwoods (coniferous) and hardwoods (deciduous) differs as follows (Sjöström, 1981).

	Cellulose	Hemicellulose	Lignin	Extractives
Softwoods	42±2%	27±2%	28±3%	3±2%
Hardwoods	45±2%	30±5%	20±4%	5±3%

For consideration of reaction of lignocellulosic material with aqueous HI it is necessary to refer to the physical properties of aqueous HI solutions, densities, vapour pressure of HI, stability at the bubble point, and the vapor-liquid equilibrium data at atmospheric pressure, and these are recorded in Appendix A. T-x diagrams for the vapor-liquid equilibrium of the HI-H_2O system at atmosphere pressure appear as Figure 5.1.

Of all halogen acids, HI in aqueous solution has the most easily liberated proton, thus facilitating oxidation of I^- to I_2. This fact explains why biomass behaves so differently in aqueous HI than in other strong acids such as HCl, HBr or H_2SO_4. Moreover the presence of HI prevents I_2, which is produced by the attack of I^- on the molecular structure of a biomass, from reacting with organic compounds formed during liquefaction. Hence whatever organic iodides are in the product are the result of the original HI-wood reaction, not from subsequent reaction with I_2.

The reactions of wood with aqueous HI are mainly those of the three major macromolecular cell wall components - cellulose, hemicellulose and lignin. Three types of reaction of wood with aqueous HI are acidic hydrolysis, oxidation, and dehydration. Hydrolysis and oxidation are the most important degradative processes for depolymerizing the biomass. HI in aqueous solution acts as a chemical reagent, as a catalyst, and as a hydrogen donor in various reactions with wood, and not simply as an acid. Because of these important properties it is consistently referred to throughout the present work as "aqueous HI" rather than as "hydriodic acid" to underline the fact that the action of HI is not simply that of an acid.

Aqueous HI acts on lignocellulosic material in four ways:

- chemical cleavage reagent
- H^+ catalyst
- hydrogen donor medium
- iodinating agent

These types of chemical reactivity, Fengel and Wegener, 1984, are now considered from the perspective of the goals of good wood liquefaction with aqueous HI, listed below:

(1) Depolymerization of wood components to maximize yield of wood oil product

Hydrolysis of polymer linkages leads to depolymerization. Vulnerable to hydrolysis are acetal linkages in carbohydrates and aryl linkages in lignin. With the HI acting as a catalyst, the proton of HI interacts rapidly with glycosidic sugar units, depolymerizing them into their monomers. Lignin is not depolymerized to its monomers but is also affected by acid catalyzed hydrolysis through its aryl ether linkages to yield low molecular weight compounds.

Oxidation reactions occur simultaneously with hydrolytic degradation in acidic media. Hydroxyl groups and the end groups of polysaccharides and side chain groups of lignin may be subject to oxidation attack. Ring structures of polysaccharides and the three dimensional lignin structures can be preserved or may be destroyed by cleavage of the O−C or C−C bond.

(2) Reduction of oxygen content, desirable for the product as a fuel

Dehydration reactions occur under acidic conditions, causing decomposition of hydrolysed sugars. Acid catalyzed dehydration of monosaccharides leads to formation of furfurals or anhydro sugars by the elimination of water.

(3) Maximize the hydrogen:carbon ratio in the organic product and prevention of condensation reactions of initial or intermediate products of the liquefaction reactions.

Minimizing loss of hydrogen in the organic products and minimizing condensation reactions thereby minimizes the yield of insoluble residue, hence limits or eliminates the need for expensive hydrogenation to upgrade the biomass oil product. To avoid extensive condensation reactions it is common to add stabilizers that react with depolymerized units before they can undergo condensation. Hydrogen is frequently used for this purpose. In the system of wood liquefaction with aqueous HI, HI acts not only as a chemical reagent but also as a catalyst and as a hydrogen donor. Thus H^- provided from the aqueous HI solution protects the reaction intermediates against condensation reactions. The finding noted in Section 2.2.3 that the carbon-base yield of insoluble residue by liquefaction of wood in aqueous HI is typically from 0 to 10%, less than the yield of the more degraded product, char, from conventional biomass liquefaction processes indicates the effectiveness of depolymerization and suppression of condensation in biomass liquefaction with aqueous HI solution.

(4) Eliminate iodine content in the organic product

Organic iodides, produced as reaction intermediates in biomass conversion with aqueous HI, would be reduced by further reaction with HI, producing a compound of lower O/C ratio. Moreover HI would prevent I_2, produced by various reactions, from reacting with the organic products during wood liquefaction in aqueous HI solution.

2.3 Reduction of iodine to hydrogen iodide

As I_2 is produced in stoichiometric proportions by the reaction of biomass with aqueous HI, as recorded in the stoichiometric equations of Sections 2.2.2 and 2.2.3, the alternatives of dealing with this I_2 production are now presented.

2.3.1 Solvent extraction of I_2

Numerous publications treat the extraction of molecular iodine from aqueous solutions. The solubilities of I_2 in water, in HI solution and in some solvents appear in Appendix B. For application of any extraction strategy in the process of biomass liquefaction in aqueous HI solution the solvent for I_2 must be chemically non-reactive with HI and I_2, must be immiscible in aqueous HI, and must have a greater affinity for I_2 than does aqueous HI solution. The latter requirement alone is formidable: a litre of 57 wt% HI, weighting 1.7 kg, dissolves over 3.5 kg of I_2 (Powell and Campbell, 1947). In aqueous HI solution of this concentration of I_2 it is considered that each HI molecule sorbs four atoms of iodine, i.e. two molecules of I_2 per HI molecule, Appendix B.2. For typical conditions of wood liquefaction in aqueous HI solution, the aqueous phase after reaction contains about 6 – 7 gmol HI/litre, but only 0.5 gmol I_2/litre although this HI solution could sorb about 11 – 14 gmol I_2/litre. As no solvent is known which could compete with the HI solution as a solvent for I_2 it may be concluded that no I_2 extraction strategy would work.

2.3.2 Chemical reduction of I_2

Iodine, like other halogens, is active chemically (Kirk-Othmer, 1966). In acid solution it is a mild oxidizing agent. It readily oxidizes sulphite to sulphate, oxidizes sulphur dioxide to sulphuric acid, stannous and titanous salts to stannic and titanic salts, hydrogen sulphide/sulphur, nitrous acid/nitric acid, arsenious acid/arsenic acid, ferrous salts/ferric salts etc. ("Supplement to Mellor's Comprehensive Treatise", 1956; "Gmelins Handbuch", 1955). Sodium thiosulphate is a normal agent to determine I_2 concentration in dilute acid solution (Kalmann, 1887) with the reaction as

$$2\ Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2\ NaI$$

As I_2 is only a mild oxidizing agent most of the foregoing reactions are reversible under appropriate conditions. The fact that the aqueous phase after batch reaction contains about 6 – 7 moles HI per litre and only approximately 0.5 moles I_2 per litre therefore eliminates all the reducing agents noted above as being of too low reducing power. Reduction of I_2 with formic acid, oxalic acid and carbon monoxide is possible chemically but is too slow to be applicable in this wood liquefaction system.

The only reducing agent known to be sufficiently strong to fulfil all the chemical and kinetic requirements imposed by the liquefaction process is hypophosphorous acid, H_3PO_2. As noted earlier, aqueous HI is sold commercially with a small amount of H_3PO_2 to suppress the oxidation of HI to I_2. The reaction with I_2, given in "Supplement to Mellor's Comprehensive Treatise", 1971, is:

$$H_3PO_2 + I_2 + H_2O \rightarrow H_3PO_3 + 2\ HI$$

However on an industrial scale the cost of separating the H_3PO_3 and converting it back to H_3PO_2 would be prohibitive, so the route of chemical reduction of I_2 back to HI is not a practical alternative worth investigation.

2.3.3 Electrochemical reduction of I_2 to HI

Iodine in the presence of iodide ions is rapidly converted to the triiodide ion, I_3^-, (Kimura et al, 1990)

$$I_2 + I^- \rightarrow I_3^-$$

The I_2/I^- redox couple electrode reaction

$$I_3^- + 2e \rightarrow 3I^-$$

has been investigated by many researchers. The standard exchange current density of I_2/I^- on platinum, i. is claimed by Vetter, 1952, to be of the order of 0.4 A cm^{-2}, with the concentrations of I^- and I_2 are 1 M. Dané et al., 1968, found the exchange current density as 0.049 A/cm^2 for $[I^-] = 0.033M$ and $[I_2] = 0.0369M$ at 25°C. The high value of exchange current density shows that I_2 reduction to iodide is extremely fast, Wroblowa and Saunders, 1973, and that mass transfer control could be minimized until the very low I_2 concentration of 0.01 M, Gorbachev and Belyaeva, 1961.

Generation of HI by electrochemical reduction of I_2 was studied by Carlin, 1977. He patented the technique of producing aqueous hydrogen iodide solution in an electrolyte cell by feeding I_2 to an aqueous catholyte liquor, passing current through an electrically conductive anolytic liquor, a diaphragm or membrane, and an electrically conductive catholyte liquor, with formation of HI at the cathode. The catholyte liquor could be 1 to 55 wt% HI solution containing I_2 in concentration up to saturation. The anolytic liquor could be an aqueous acidic solution to provide the hydrogen ions, for example 5 – 40 wt% sulphuric acid, 2 – 38 wt% hydrochloric acid, or phosphoric acid, for which the respective co-product would be O_2, Cl_2, or O_2. The concentration of the anolyte acid should provide good electrical conductivity and minimize water transport from the anolyte to the catholyte.

Carlin separated the cathode and anode cells with a permionic membrane to allow hydrogen ions to pass from the anode to the cathode. His preferred permionic materials were duPont NAFION 425, a 0.005 inch thick film of 1200 equivalent weight perfluoroethylene copolymer, and duPont NAFION 390, a 0.004 inch thick layer of 1100 equivalent copolymer contacting the anolyte and a 0.0015 inch layer of 1500 equivalent weight copolymer contacting the catholyte. Carlin reported current densities of 0.1 – 1.0 A/cm^2 at such membranes.

Carlin's cathode and anode compartments consisted of two glass elbows, each with a 38 mm diameter by 102 mm long base and a 51 mm diameter by 76 mm vertical arm, with the membrane clamped between the horizontal arms. The anode was a stationary lead plate, 12.7 mm x 15.9 mm x 3.2 mm thick. Cathodes were thin square or circular plates of a titanium alloy, lead, 316 stainless steel or perforated steel. The anolytic liquor was 15 wt% aqueous sulphuric acid for O_2 production at the anode. The cells were unstirred and operated at room temperature. Carlin's interesting results are summarized in the Table 2.1.

With O_2 generation on a lead anode in H_2SO_4 solution the anode surface is covered first with $PbSO_4$, which oxidizes to a brown layer of PbO_2 when the electrode is polarized at higher potentials. When the conversion of $PbSO_4$ to PbO_2 is near completion, O_2 evolution starts on the PbO_2 surface. The initial $PbSO_4$ layer has a very high resistivity, whereas the PbO_2 layer is good conductor (Hine, 1985). The anodic overpotential for PbO_2 is very high, 0.6 – 0.7 V even at the very small current density of 10^{-7} A/cm^2 (Hoare, 1968). The effect of stirring has only a insignificant effect on the rate of oxygen evolution (Randle and Kuhn, 1979).

There are two crystalline forms of PbO_2, α-PbO_2 and β-PbO_2. When Pb is subjected to anodic oxidation in strong acids, β-PbO_2 is formed; in neutral and alkaline solutions normally α-PbO_2 occurs (Ruetschi et al., 1963). However both forms have been identified on the positive plates of lead acid batteries (Kirk and Othmer, 1980). As the overpotential is very dependent on the electrode surface, performance is difficult to reproduce. The polarization curves (overpotential vs. current density) for both forms of PbO_2 for oxygen evolution are given by Hoare, 1968. The overpotential of the strong acid form (β-PbO_2) is higher than the neutral and alkaline form of α-PbO_2. For β-PbO_2 the Tafel slope (defined in Appendix C.1) is 0.12 V and exchange current density is $6.2 \cdot 10^{-10}$ A/cm^2; for α-PbO_2 corresponding value are 0.05 V and $1.7 \cdot 10^{-16}$ A/cm^2.

The importance of Carlin's work is in establishing that for pure inorganic solutions of I_2 in aqueous HI it is practical to reduce the I_2 electrochemically to HI, and that I_2 concentration can thereby be maintained at very low levels.

Table 2.1 Electrochemical Reduction of I_2 by Carlin (1977)

Test	Anode	Cathode	Membrane NAFION	Spacing* (mm)	Voltage (V)	Cathode Current Density (A/cm^2)	[HI] wt%	[I_2] wt%	[I_2] M	I_2 Reduction Rate (g/min)
I	lead	Titanium alloy 12.7mm x 15.9mm x 1.6mm	425	19/12.7	4.08	0.495	55	1.5	0.1	0.08
II	lead	lead 12.7mm x 15.9mm x 1.25mm	425	12.7/19	4.25	0.495	55	0.8	0.05	0.08
IV	lead	316 stainless steel 12.7mm x 15.9mm x 1.5mm	390	12.7	3.77	0.155	40.4	0.03	0.002	0.11
V	lead	perforated steel diameter 31.8mm x 1.5 mm	390	12.7	3.78	0.222	42.2	0.02	0.001	0.11

* Spacing: Cathode/Membrane/Anode

2.4 Research strategy - the electrochemical liquefaction reactor

Biomass liquefaction reactions are fast in concentrated aqueous HI solution, in the order of a couple of minutes or less. During this direct liquefaction process, depolymerization and reduction of the biomass is accompanied by oxidation of I^- to I_2. A basic requirement for a continuous liquefaction reaction system is therefore for a companion process to close the iodine loop by reducing the I_2 back to HI for reaction with biomass in the liquefaction reactor.

The literature review shows that neither solvent extraction of I_2 or chemical reduction of I_2 to HI are practical, but that electrochemical reduction of I_2 to HI is fast and is reported not to be mass transfer controlled until very low I_2 concentration, in the order of 0.01 M, which is much lower than the levels of I_2 concentration in the aqueous HI solution reached in the wood liquefaction batch reaction experiments reviewed in Section 2.2.3. Electrochemical reduction of I_2 to HI has been demonstrated only in purely inorganic aqueous solutions of HI and I_2. However if it can be demonstrated that, even in the system of multicomponent viscous organic products from wood liquefaction in aqueous HI solution, I_2 can still be reduced electrochemically back to HI, the HI → I_2 → HI loop would thereby be closed. By carrying out the wood liquefaction reaction in the cathode compartment of an electrochemical cell, the I_2 produced by the liquefaction reaction may be converted immediately back to HI, thus providing the key to a continuous wood liquefaction reactor system. This novel concept is subsequently referred to as the **ECLR**, the **electrochemical liquefaction reactor.**

Thus the specific objectives of the present investigation are to design an electrochemical liquefaction reactor, an ECLR, for the direct liquefaction of wood in concentrated aqueous HI solution in the cathode cell so that the I_2 produced by the liquefaction reactions can simultaneously be reduced electrochemically back to the HI reactant, with an appropriate anode cell for generation of the H^+ ions required for regeneration of HI in the cathode cell; to determine the electrochemical performance characteristics of such an ECLR; to determine the characteristics of wood conversion in such an electrochemical liquefaction reactor.

CHAPTER 3

DESIGN OF ELECTROCHEMICAL LIQUEFACTION REACTOR

3.1 Introduction

In wood liquefaction by reaction with aqueous HI solution at atmospheric pressure and low temperature, the chemical reactions summarized in Section 2.2.6 include reduction of the components of wood and correspondingly oxidation of the iodide ion to I_2. As outlined in Section 2.3.3, electrochemical reduction of I_2 to HI is the most promising solution available for closing the HI → I_2 → HI loop. The basic concept of the electrochemical liquefaction reactor is to carry out the wood liquefaction in an electrochemical reactor with simultaneous reduction of the I_2 back to the HI reactant.

The electrochemical liquefaction reactor, the ECLR, is an electrolytic cell of two compartments separated by a membrane permeable only to hydrogen ions. The cathode cell is simultaneously the wood liquefaction reactor and the reactor for electrochemical reduction of I_2 to I^- ions. The anode cell must produce H^+ ions for transport through the semipermeable membrane to the cathode where I^- ions are generated, thus regenerating HI. Two options were considered for the anode cell electrolyte. With aqueous HCl as anolyte, H^+ and Cl_2 are generated at the anode whereas if aqueous H_2SO_4 is used, H^+ and O_2 are generated by water electrolysis. Due to environmental concerns and government regulations the trend is to reduce the use of chlorine for bleaching wood pulp, while the use of oxygen and oxygenated compounds for delignification and bleaching is correspondingly increasing. Attention was therefore focused on the hydrolysis of H_2O from concentrated H_2SO_4 solution in the anode cell to generate H^+ and O_2. Thus a unique electrochemical liquefaction reactor system was designed and built to incorporate the cathode and anode cells for wood liquefaction, I_2 reduction and O_2 production, as well as a continuous wood feeder and an HI gas supply system in order to control the HI concentration to the level desired for wood liquefaction in the electrochemical reactor.

3.2 Electrochemical aspects of the liquefaction reactor

3.2.1 Cathode compartment for I_2 reduction to HI

Extensive investigations of cathodic reduction of I_2

$$I_2 + 2e \rightarrow 2I^- \tag{3.1}$$

described in Section 2.3.3 establish that on a platinum electrode this reaction is extremely fast (Wroblowa and Saunders, 1973). The thermodynamic minimum potential can be calculated from the Nernst equation

$$V_c = \varepsilon^\circ_{I_2/I^-} + RT/2F \ln([I_2]/[I^-]^2) \tag{3.2}$$

which with the temperature correction term according to Plambeck, 1982, becomes

$$V_c = \varepsilon^\circ_{I_2/I^-} - 0.148\,(10^{-3})\,(T - 298.15) + RT/2F \ln([I_2]/[I^-]^2) \tag{3.3}$$

In Equation 3.3 the standard equilibrium potential $\varepsilon^\circ_{I_2/I^-} = 0.621$ V (Laitinen, 1975; Desideri et al., 1985), R is the gas constant, 8.314 J· mol· K, and F is the Faraday constant, 96487 $C \cdot mol^{-1}$. Typical reaction conditions in the cathode cell are 57 wt% HI catholyte, i.e. $[I^-] = 7.5$ M, iodine concentration $[I_2] = 0.01$ M, and temperature ≈ 120°C. For these conditions the thermodynamic minimum potential for reduction of I_2 is +0.46 V, the positive value indicating that cathodic reduction of I_2 to I^- is thermodynamically spontaneous with respect to the standard hydrogen electrode.

3.2.2 Anode compartment for H_2O hydrolysis to H^+ and O_2

For anodic oxidation of water at a lead surface in acidic conditions,

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e \tag{3.4}$$

reviewed in Section 2.3.3, the thermodynamic minimum required potential is

$$V_a = \varepsilon^o_{H_2O/O_2} - RT/2F\ (\ln\ ([H^+]^2\ p_{O_2}{}^{1/2})) \tag{3.5}$$

which again with the Plambeck temperature correction term is:

$$V_a = \varepsilon^o_{H_2O/O_2} - 0.846 \cdot 10^{-3}\ (T - 298.15) - RT/2F\ (\ln\ ([H^+]^2\ p_{O_2}{}^{1/2})) \tag{3.6}$$

The standard equilibrium potential is $\varepsilon^o_{H_2O/O_2} = -1.229$ V (Hoare, 1965; Milazzo et al., 1978). Typical anode conditions in the present study are 38 wt% H_2SO_4 anolyte, i.e. $[H^+] = 10.4$ M, at about 60°C because the anode cell is adjacent to the cathode wood liquefaction cell at about 120°C. For these conditions the thermodynamic minimum required potential becomes −1.29 V. The negative sign shows that hydrolysis of water at the anode is not spontaneous, i.e. it is necessary to apply sufficient voltage for this reaction to proceed.

3.2.3 Overall voltage for HI regeneration and O_2 production

The reactions are:

at the cathode	$I_2 + 2e \rightarrow 2I^-$	$V_c = +0.46$ V
at the anode	$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e$	$V_a = -1.29$ V
overall reaction	$I_2 + H_2O \rightarrow 1/2O_2 + 2H^+ + 2I^-$	$V_{min} = -0.83$ V

This -0.83 V is just the thermodynamic minimum required potential for the overall reaction to occur. To have electrochemical reaction at a finite rate there are in addition the overpotentials at both electrodes, $|\eta_c| + |\eta_a|$, plus the voltage drop from the electrical resistance of the entire system including for H^+ transport across the membrane, referred to as the ohmic voltage drop, V^{ohm}. Thus the total required voltage is

$$V_T = V_{min} - |\eta_c| - |\eta_a| - V^{ohm} \tag{3.7}$$

The cathodic overpotential, η_c for I_2/I^- conversion, and the anodic overpotential, η_a for H_2O/H^+-O_2 generation, are given in Appendices C.2 and C.3 for a platinum cathode and lead anode, electrode materials chosen for reasons discussed subsequently. At a cell current of 10A and for the present conditions, the upper limits are -0.19 V for the cathodic overpotential and 1.15 V for the anodic overpotential. At 10 A cell current the voltage drop by electrical resistance of the electrochemical circuit in the laboratory ECLR system is about 4.70 V (Appendix C.4). Therefore at 10 A the theoretical upper limit of the total applied voltage is $V_T = -6.87$ V, as shown below along with the relative contribution of the components to the total applied cell voltage.

	Percent contribution
$V_{min} = -0.83$ V	11%
$-|\eta_c| = -0.19$ V	3%
$-|\eta_a| = -1.15$ V	17%
$-V^{ohm} = -4.70$ V	69%
$V_T = -6.87$ V	100%

Thus the major component of the total required cell voltage is ohmic voltage drop

(4.70V), the source of 2/3 of the total cell voltage. As the initial design of a laboratory scale electrochemical liquefaction reactor, this first ECLR is undoubtedly remote from one that would minimize circuit ohmic drops. Of the 4.70 V ohmic voltage drop it is estimated that 40% of this drop is that required by the semipermeable membrane separating the cathode and anode compartments. Thus for the future there is substantial potential for reducing the ohmic voltage drop and hereby increasing cell energy efficiency.

At a very low cell current, 0.1 A, the cathodic overpotential, $\eta_c^{I\to 0}$, is -0.002V and the anodic overpotential, $\eta_a^{I\to 0}$, is 0.89 V, as given in Appendix C. Therefore at 0.1 A the total applied voltage,

$$V_T^{I\to 0} = -0.83 \text{ V} - |-0.002| \text{ V} - |0.89| \text{ V}$$

is -1.72 V. This is the estimated value of cell voltage which is just sufficient to produce a very small current in the electrochemical circuit.

In order to accommodate the maximum values of voltage and current estimated above, with capacity for a larger scale reactor in future, the cell voltage was supplied by a DC power supply of range 0 – 16 V and 0 – 100 A.

3.2.4 Competitive cathode reaction of H_2 evolution

The competitive reaction to iodine reduction, obviously one to be avoided, is cathodic evolution of hydrogen by reduction of the H^- ions which are transported from the anode cell through the semipermeable membrane.

$$2H^- + 2e \rightarrow H_2 \qquad (3.8)$$

The equilibrium reduction potential for H_2 evolution is

$$V_{H_2} = \varepsilon^{o}_{H^+/H_2} - RT/2F\ (\ln ([H^+]^2\ p_{H_2}^{1/2})) \qquad (3.9)$$

where by definition the standard equilibrium potential $\varepsilon^{o}_{H^+/H_2} = 0$ V. For typical cathode conditions as set by the requirements for wood liquefaction, 120°C with 57 wt% HI solution, i.e. $[H^+] = 7.5$ M, the thermodynamic minimum required potential is -0.068V. The overall minimum potential for H_2 evolution at the cathode and H_2O hydrolysis at the anode, with V_a for the latter as determined by Equation 3.6, becomes

$$V'_{min} = V_{H_2} + V_a = -0.068\ V + (-1.29\ V) = -1.36\ V$$

The overall cell voltage for H_2 generation and O_2 production is

$$V'_T = V'_{min} - |\eta_{H^+/H_2}| - |\eta_a| - V^{ohm} \qquad (3.10)$$

Using the cathodic Tafel equation and the data of Prentice, 1991, for the exchange current density for H_2 evolution at a platinum electrode, the overpotential for H_2 evolution at cathode is $\eta_{H^+/H_2} = -0.46$ V for a typical current for 10 A in the electrochemical cell, Appendix C.5. Fortunately with platinum as the cathode metal the absolute value of $\eta_{H^+/H_2} = 0.46$ V for the unwanted H_2 evolution is comfortably greater than the absolute value of $\eta_{I_2/I^-} = 0.19$ V for the desired I_2 reduction to I^-. Thus at 10 A cell current the predicted total cell voltage for H_2 and O_2 production is:

$$V'_T = -1.36 - |-0.46| - |1.15| - 4.70 = -7.67\ V$$

In order to obtain I_2 reduction to HI without generation of H_2 in the cathode cell the electrochemical circuit must be operated at a voltage lower than that which would generate H_2. For I_2 reduction, Equation 3.7 may be written as

$$V_T = V_{min} - |\eta_{I_2/I^-}| - |\eta_a| - V^{ohm} \qquad (3.11)$$

where, from Equation 3.11, the overall voltage $V_T = -6.87$ V for I_2 reduction.

Therefore by reference to Equations 3.10 and 3.11 it seen that with a platinum cathode there is a significant voltage range of $(-7.67 - (-6.87) =) -0.80$ V over which it should be possible to obtain I_2 reduction without H_2 production. The existence of this window of opportunity for obtaining I_2 reduction without H_2 generation is aided by the fact that on a platinum cathode the absolute value of the hydrogen overpotential (0.46 V) is over double that for I_2 reduction (0.19 V), hence enabling the latter to be obtained to the exclusion of the former.

3.3 Selection of electrodes and membrane

3.3.1 Cathode and anode

Three considerations regarding the choice of electrode are pre-eminent (Tilak and Weinberg, 1981): stability; conductivity and surface characteristics of the electrode material, i.e. overpotential of the electrode. Using these criteria, especially the requirement of high overpotential for hydrogen evolution, the electrode materials selected were platinum for the cathode (Wroblowa and Saunders, 1973) and lead for the anode (Carlin, 1977).

Cathode: The choice of platinum provides the critical requirement of an electrode of very high absolute value of hydrogen overpotential to favour I_2 reduction over H_2 production. Carlin, 1977, also used 316 stainless steel. However tests here established this to be a poor choice because it corrodes in the presence of I_2 and strong aqueous HI, forming precipitates through side reactions with HI. Any precipitates must avoided in the present wood liquefaction reaction system. An economical option for commercial use could be the use of an electrode electroplated with platinum.

The original platinum cathode, supplied by the Johnson Matthey/AESER Corp., was a thin wire mesh cylinder, 13 mm diameter, 50 mm long, of a mesh made of 0.15

mm diameter wire with the mesh openings about 0.36 mm square, of total surface area 55.9 cm^2. This electrode served successfully during the early development and evolution of the ECLR reactor but, being fragile, deteriorated during the innumerable assembling and disassembling operations and was therefore subsequently replaced.

The final platinum cathode, also manufactured by the Johnson Matthey/AESER Corp., was a cylinder, 25 mm diameter, 50 mm long, fabricated from 1 mm thick platinum sheet, of total surface area (both sides) 78.5 cm^2. This cylinder was mounted on a platinum shaft, 3 mm diameter x 100 mm long, with the shaft extending 10 mm beyond the end of the cylinder in order to fit in the bearing provided by a 59 mm diameter x 20 mm thick teflon support block. As cathode rotation was used to minimize mass transfer resistance, this support block served to prevent cathode oscillation. The upper end of the platinum shaft was screwed into a stronger shaft of 1/4" diameter, type 316 stainless steel, which was covered with heat shrinkable teflon tubing to prevent corrosion.

Anode: For H^+ and O_2 production by water hydrolysis from concentrated H_2SO_4, a good choice of anode metal is lead, inexpensive and easily shaped, as was used by Carlin, 1977. The actual anode surface is not lead but the lead dioxide, PbO_2, to which it is easily oxidized. Lead dioxide is a good electronic conductor, much better than lead, and is highly stable under the strongly oxidizing anodic conditions in acid media (Rifi and Covitz, 1974). For each electrochemical run, new pure lead plate was used to provide an excellent anode material, PbO_2, in H_2SO_4 solution for electrolysis of H_2O. The lead plate anode (50 mm square x 4 mm thick), cast in the McGill machine shop, was supported by a lead shaft bent to minimize inter-electrode spacing. Concentrated acid H_2SO_4 is used in the anode compartment to minimize water transfer with the H^+ transport from the anode to cathode cell.

3.3.2 Membrane

The cathode and anode compartments must be separated by a semipermeable membrane which allows H^+ ions generated at the anode to pass to the cathode compartment while preventing counter diffusion of the I^- ions to the anode cell. The permionic membrane selected was Nafion 324, 0.3 mm thick, a perfluorosulfonic acid cation exchange membrane. Nafion 324, which has good chemical resistance and low electrical resistance, is a reinforced composite membrane with 1500 and 1100 equivalent weight copolymer layers on the cathode and anode sides, respectively (Nafion perfluorinated membranes, Product Bulletin, by DuPont). Nafion 425 and 390 were used as cell membranes in Carlin's 1977 patent.

3.4 Design of electrochemical liquefaction reactor system

3.4.1 Electrochemical liquefaction reactor

The electrochemical liquefaction reactor was designed taking into account electrode current distribution and mass transfer effects (King, 1981; Savinell, 1983; Selman, 1981). Considerations of current distribution require that the cathode and anode face each other, while reduction of mass transfer effects at the cathode led to the use of a rotating cylindrical cathode. The ECLR design characteristics to obtain high I_2 reduction rate, high current efficiency, low ohmic resistance, high energy efficiency, and high I_2 reduction efficiency include:

(1) Large surface area of the electrodes, to give a high I_2 reduction rate, which controls directly the liquefaction rate and hence the wood feed rate.

(2) Large surface area of the membrane, matching the size of the electrodes, thereby reducing the membrane ohmic resistance.

(3) Small spacing between the cathode and anode surfaces, to reduce the cell ohmic resistance. The ohmic drop, discussed in Section 3.3, is the dominant factor controlling the applied cell voltage. Reducing the ohmic voltage drop increases the energy efficiency.

(4) Low mass transfer resistance at the cathode. Although the electrochemical reduction of I_2 to I^- is extremely fast, the reduction becomes mass transfer controlled at low $[I_2]$. As low levels of $[I_2]$ are desired for the wood liquefaction reaction, this lower limit on I_2 concentration can be reduced by reducing the mass transfer resistance at the cathode, conveniently obtained by the use of a rotating thin-walled cylindrical cathode.

The ECLR must be a two compartment electrolytic cell with the cathode and anode compartments separated by a cationic membrane permeable only to H^+ ions, Figure 3.1, to avoid mixing the HI solution catholyte and the H_2SO_4 solution anolyte, as discussed in Sections 3.2.1 and 3.2.2. In the cathode compartment, which is also the wood liquefaction reactor, wood is fed into aqueous HI solution generally at its bubble point between 100 – 125°C for the HI concentration range used. Thus two reactions occur simultaneously in the cathode cell, the wood liquefaction and the electrochemical reduction of the reaction product I_2 back to the reactant HI. In the anode compartment the electrolytic hydrolysis of water in H_2SO_4 solution produces both the H^+ ions necessary for the cathode cell and O_2 as the associated product.

The cathode compartment is a vertical glass cylinder of diameter 60 mm ID, 180 mm high, connected by a horizontal flange, located 20 mm from the bottom of the cathode cell, to a matching flange on an end of the horizontal cylindrical body of the anode compartment, Figure 3.1. As the height of both cathode and anode is 50 mm, the connection between the cells that carries the semipermeable membrane was slightly larger. Thus these connecting flanges were 57 mm ID, thereby aiding uniform current distribution between the cathode and anode. The anode cell is an L-shaped container with a vertical glass cylinder, 60 mm ID, 180 mm high, joined to a horizontal glass cylinder, 90 mm ID, which carries the 57 mm ID flanged connection to the cathode cell. The 57 mm flanges carry the permionic membrane, mounted in silicone rubber seals, which separates the compartments. The cells were joined tightly at the two flanges with a teflon clamp.

To reduce the electrical resistance the distance between the two electrodes was

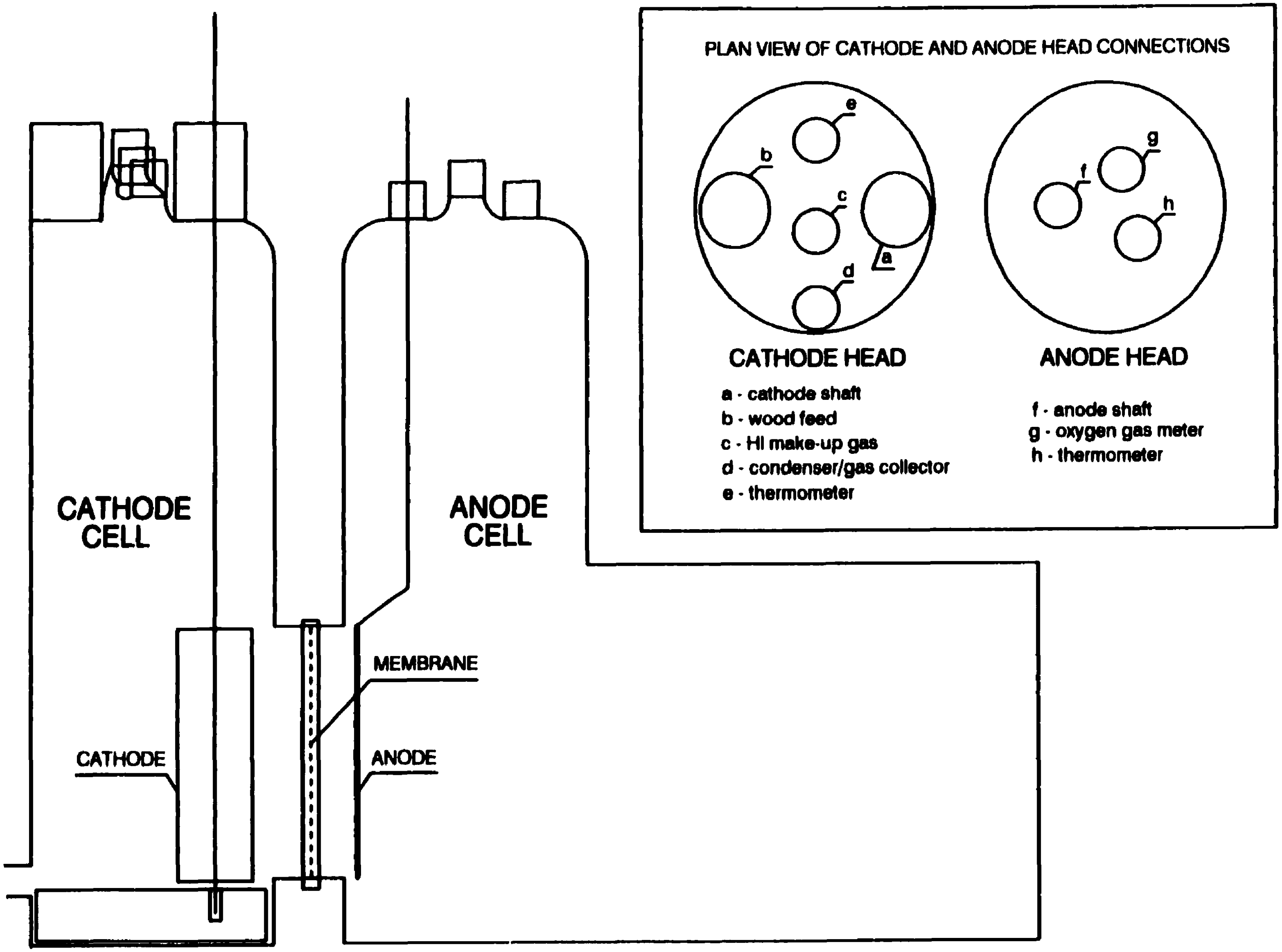


Figure 3.1 Schematic Diagram of ECLR Design

minimized to 38 mm, but for tests described in Chapter 4 this spacing was varied by repositioning the lead anode electrode. The large size of the anode compartment was to accommodate sufficient anolyte for long uninterrupted runs. The level of catholyte and anolyte solutions was maintained just above the top of the flanged connection, thereby maintaining the electrodes just completely submerged. The volumes of catholyte and anolyte solution typically charged were 220 ml and 1300 ml respectively. A teflon block, 59 mm diameter x 20 mm thick, with the support bearing for the shaft of the rotating cathode was located at the bottom of the cathode cell, Figure 3.1.

The top connection of cathode cell was a 60/50 standard taper joint, mounted directly on the top of the 150 mm high cylinder. The glass head of the cathode cell was particularly challenging, with no less than five openings which are identified in the same way below and on Figure 3.1:

(a) rotating cathode shaft and cathode electrical connection, with a 24/40 standard taper joint, off-centre to reduce the spacing between the cathode and anode
(b) wood feeder connection, with a 24/40 standard taper joint
(c) HI make-up gas inlet line, with size 7 ring seal plug
(d) connection, via a 10/19 standard taper joint, for flow of vapour from the reactor to 160 mm high condenser and its return after condensation
(e) thermometer connection with size 7 ring seal plug

The anode head was mounted on the 60 mm ID vertical cylinder which extended for 60 mm above the top of the horizontal anode cell cylinder. The glass head of the anode compartment was less complex, with three connections, identified also in the same way on Figure 3.1 as below:

(f) anode electrical connection, size 7 ring seal plug
(g) O_2 gas outlet, size 7 ring seal plug
(h) thermometer connection, size 7 ring seal plug

The gas outlet of the anode head was connected to a wet test meter to measure the O_2 production. With the final version of the ECLR, a gas product collector was connected to the top of the cathode cell water cooled vapour condenser. The glass blowing for this design of ECLR was carried out by La Salle Scientific Inc, Montreal.

3.4.2 Continuous wood feeder

The feeder which introduces dry wood flour into the boiling aqueous HI solution in the reactor, Figure 3.2, was fabricated in the McGill machine shop. The detailed view of the wood feeder, Figure 3.3, shows its two parts, the wood reservoir and metering screw. The stainless steel conical wood flour supply tank, 75 mm ID diameter, of capacity 100 g wood flour (oven dried for 2h at 80°C), is covered to isolate the wood flour from air humidity and has a motor driven wiper to prevent bridging at the bottom of the cone. The stainless steel horizontal metering screw in a 25.4 mm diameter cylinder carries wood flour to the reactor. The wood feed rate is determined by the speed of the metering screw through calibrations given in Appendix D.

The horizontal metering screw is connected to the glass head of the cathode compartment through a teflon adaptor. This connection is provided with a vertical teflon cleaning rod, 120 mm long, fitted closely into a teflon cylinder which in turn fits into a glass 24/40 standard taper joint. The teflon cleaning rod serves periodically to clear any wood flour sticking to the inside surface of teflon connection into the liquefaction reactor.

3.4.3 HI make-up supply system

The HI make-up supply system is shown by a photograph, Figure 3.4, and a schematic diagram, Figure 3.5. The make-up is required in order to maintain HI concentration at the exact level desired for wood liquefaction. The HI supply cylinder, supplied by Matheson Gas Products Corp., is permanently stored in a freezer at −23°C

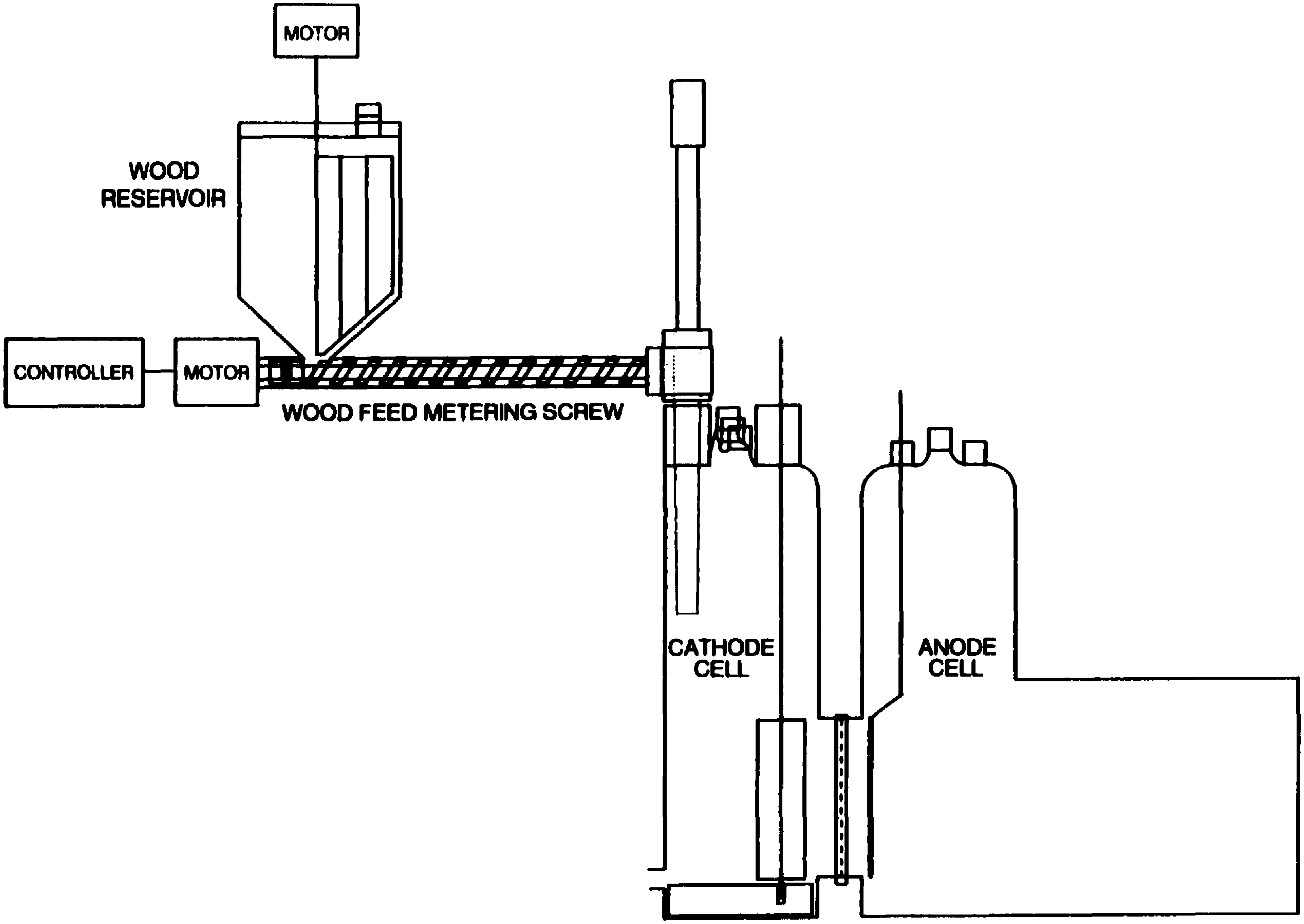


Figure 3.2 Schematic Diagram of ECLR and Wood Feeder

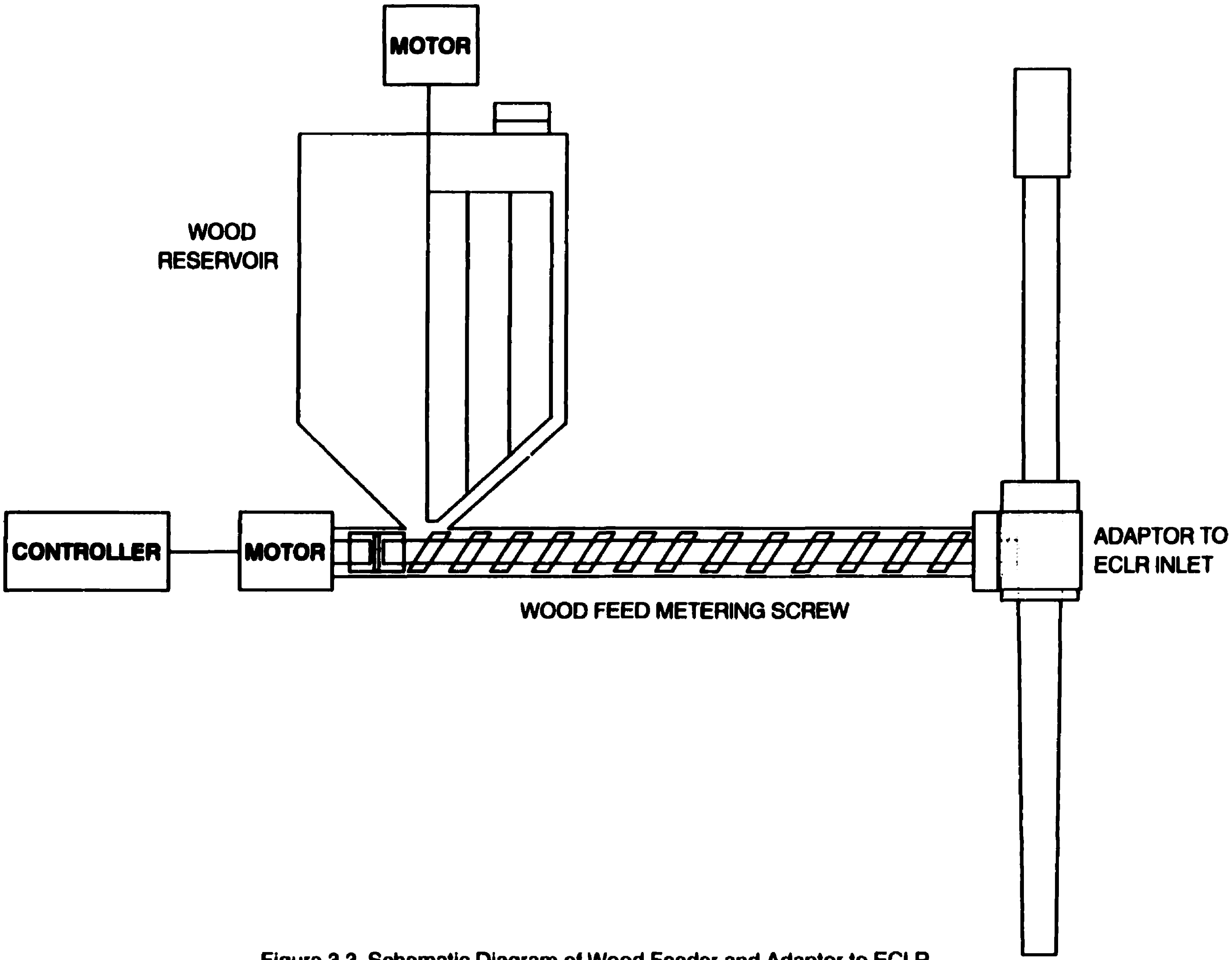


Figure 3.3 Schematic Diagram of Wood Feeder and Adaptor to ECLR

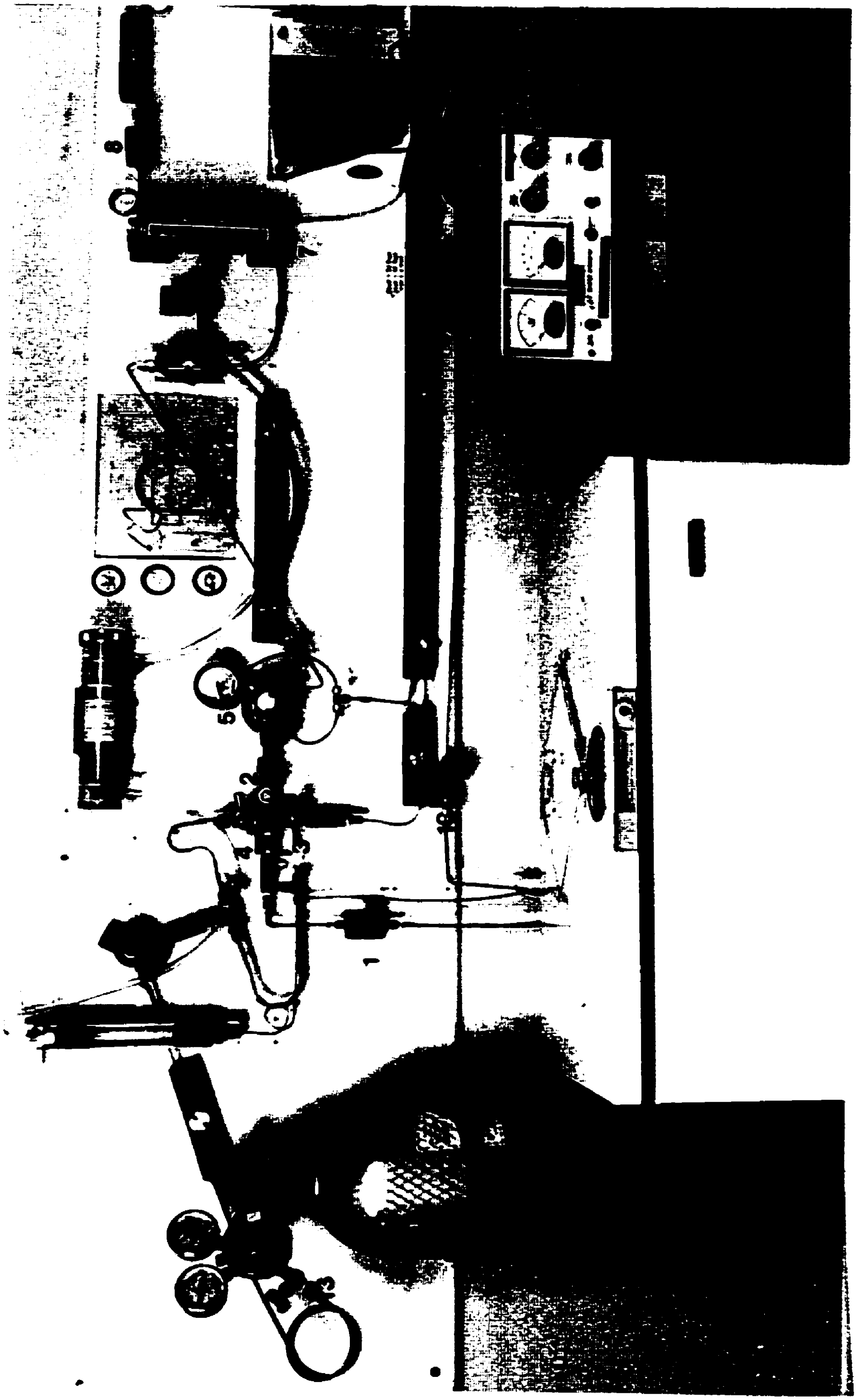


Figure 3.4 HI Gas Make-up Supply System

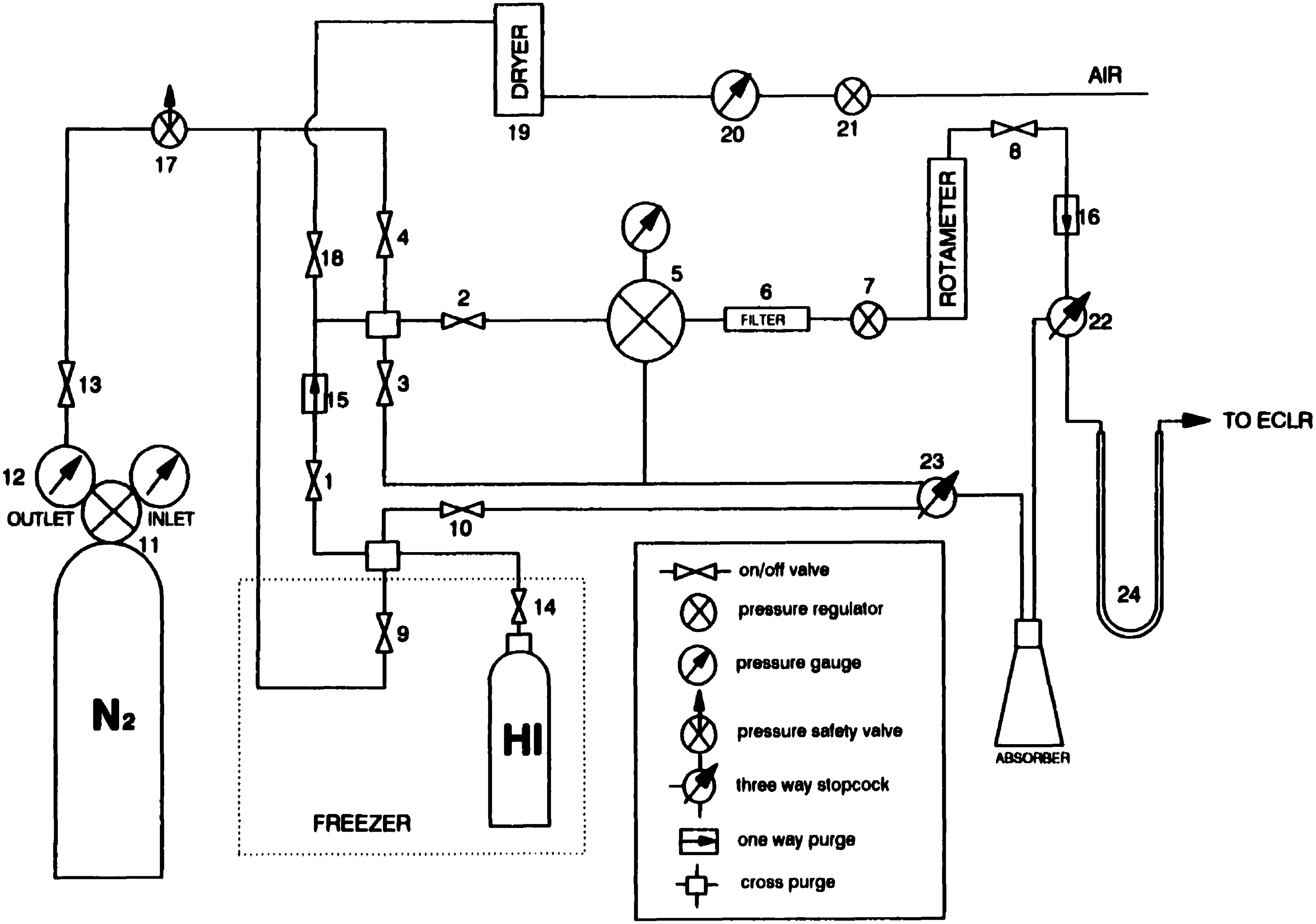


Figure 3.5 Schematic Diagram of HI Supply System

to reduce to a negligible level the rate of HI decomposition to I_2. The vapour pressure of HI at −23°C is 25 psig (Mellor, 1930), while the boiling point of HI at atmospheric pressure is −35.3°C (Kirk-Othmer, 1963). The installation contains four main parts:

(a) HI gas supply system for make-up during wood liquefaction consists of HI cylinder, cylinder shut-off valve 14, valves 1 and 2, main regulator 5, filter 6, flowmeter 7, shut-off valve 8, two one-way purges 15 and 16, a three way on/off valve 22, and a U-tube to prevent flow of aqueous solution into the HI main supply line and HI cylinder.

(b) HI gas purging lines for emergency purposes, consisting of valve 3, valve 10 and a three way on/off valve 23. These two lines can be used if there is excess pressure in the main HI gas supply line during wood liquefaction or at the moment stopping the wood liquefaction. The line with valve 10 is used also to flush HI through the HI cylinder exit line in order to prevent corrosion deposits from accumulating and plugging the main HI cylinder valve.

(c) nitrogen gas purging system, consisting of N_2 cylinder (extra dry), main cylinder valve 11, two stage regulator 12, shut-off valve 13, relief valve to prevent high pressure in the system 17, and shut-off valves 4 and 9. This line is used to prevent corrosion of the main HI supply system by purging the HI out with nitrogen before and after a liquefaction experiment. When wood liquefaction is not being carried out, dry nitrogen is kept in all lines to avoid corrosion.

(d) dry air purging system, consisting of shut-off valve 18, dryer column 19, pressure gauge 20, and regulator 21. The dry air purging system is used to eliminate humidity and prevent corrosion in the main HI supply system by purging with dry air before and after a liquefaction experiment. After each purging of this system with dry air, the line is then purged with dry nitrogen. When not in use the system is always maintained in a dry nitrogen atmosphere.

The operation of the HI gas supply system is recorded in Appendix E.

CHAPTER 4

ELECTROCHEMICAL PERFORMANCE CHARACTERISTICS

4.1 Introduction

A series of experiments was performed to determine the characteristics of the electrochemical liquefaction reactor (ECLR) when used for electrochemical reduction of I_2 in aqueous HI solution but without wood liquefaction in the cathode compartment. Thus these tests were performed with the cathode compartment charged with 55 – 57 wt% aqueous HI solutions maintained at their bubble point temperature of about 125°C, and containing known concentrations of I_2. With both cylindrical platinum cathodes, i.e. the original mesh cathode, 13 mm diameter x 50 mm long x 0.15 mm mesh thickness, and the subsequent sheet metal cathode, 25 mm diameter x 50 mm long x 1 mm sheet thickness, the electrochemical reactor was characterized for O_2 production in the anode compartment with the lead plate anode, 50 mm square x 4 mm thick, and 38 wt% H_2SO_4 solution as anolyte.

4.2 Basis for electrochemical characteristics

The electrochemical reactions for this system are:

Cathode: $I_2 + 2e = 2I^-$

Anode: $H_2O = 1/2\ O_2 + 2\ H^+ + 2e$

Overall: $I_2 + H_2O = 2\ H^+ + 2\ I^- + 1/2\ O_2$

The electrochemical characterization involved determining the form of interdependence relating the parameters of current - voltage - cathode rpm - I_2 concentration - I_2 reduction rate - cathode current efficiency (Appendix F). The H^+ and I_2 concentrations were analyzed by the methods recorded in Appendix H.1.

For calculation of the important electrochemical characteristic, cathode current density, a value is required for the cathode area that is effective for electrochemical reaction. "Effective area" is that with view of the anode. With a cylindrical cathode the inside surface and the half of the external surface which faces away from the anode have no view of the anode and thus do not participate much in the electrochemical circuit. Thus current density in those regions is low. Excluding that less ineffective area leaves 1/4 of the total surface area, i.e. the 1/2 of the external surface facing the anode. Although all this area sees the anode it is not all equally effective because both electrode separation distance and viewing angle between cathode and anode vary substantially. At the point where the cylindrical cathode surface is parallel to the anode, the inter-electrode spacing is smallest and the viewing angle is perfect. At 90° on either side of that position not only is the spacing at a maximum but the cathode angle of view of the anode drops to zero. With such an electrode geometry the current density drops off from the maximum at the point where the cathode surface is closest and parallel to the anode, to a low current density when the viewing angle is zero. The theoretical solution giving the variation in current density with position is dependent on the specific electrochemical system as well as the geometry, and in any case is very uncertain. As an approximation it is assumed here that, of the cathode cylinder external surface that to a variable extent sees the anode, the effective area is 3/4 of that circumferential area. On this basis the effective area of cathode would be 1/4 x 3/4 of its total surface area, i.e. 10.4 cm^2 for the original platinum mesh cathode and 14.7 cm^2

for the subsequent cathode made from a continuous sheet. These are the values used for all calculations of cathode current density.

The iodine reduction rate was determined from measured solution volumes and iodine concentrations by the relation

$$r_{I_2\,red.} = \frac{[I_2]_i\, V_i - [I_2]_f\, V_f}{t}\, M_{I_2} \text{ (g/min)} \tag{4.1}$$

where

$r_{I_2\,red.}$: I_2 reduction rate, g/min
$[I_2]_i$, $[I_2]_f$: initial and final iodine concentrations, mol/l
V_i, V_f : initial and final solution volumes in the cathode cell, l
M_{I_2} : molecular weight of I_2, 253.8
t : reduction time, min

Current efficiency, E, is the yield relative to the electrical charge passed during electrolysis, i.e. relative to the electron as a reactant (Pletcher and Walsh, 1990). Thus

$$E = \frac{\text{Charge used forming product}}{\text{Total charge passed}} \tag{4.2}$$

For the cathode reaction

$$I_2 + 2e = 2\,I^-$$

the cathode current efficiency is

$$E_c = \frac{\textit{Charge used reducing } I_2}{\textit{Total charge passed}} = \frac{2nF}{It} \tag{4.3}$$

or, in terms of measured quantities and with n = 1,

$$E_c = \frac{2\ F}{60\ I_{ave}\ M_{I_2}}\ r_{I_2\,red.} \tag{4.4}$$

where

E_c : cathode current efficiency, fraction

F : Faraday constant, 96487 C mol^{-1}

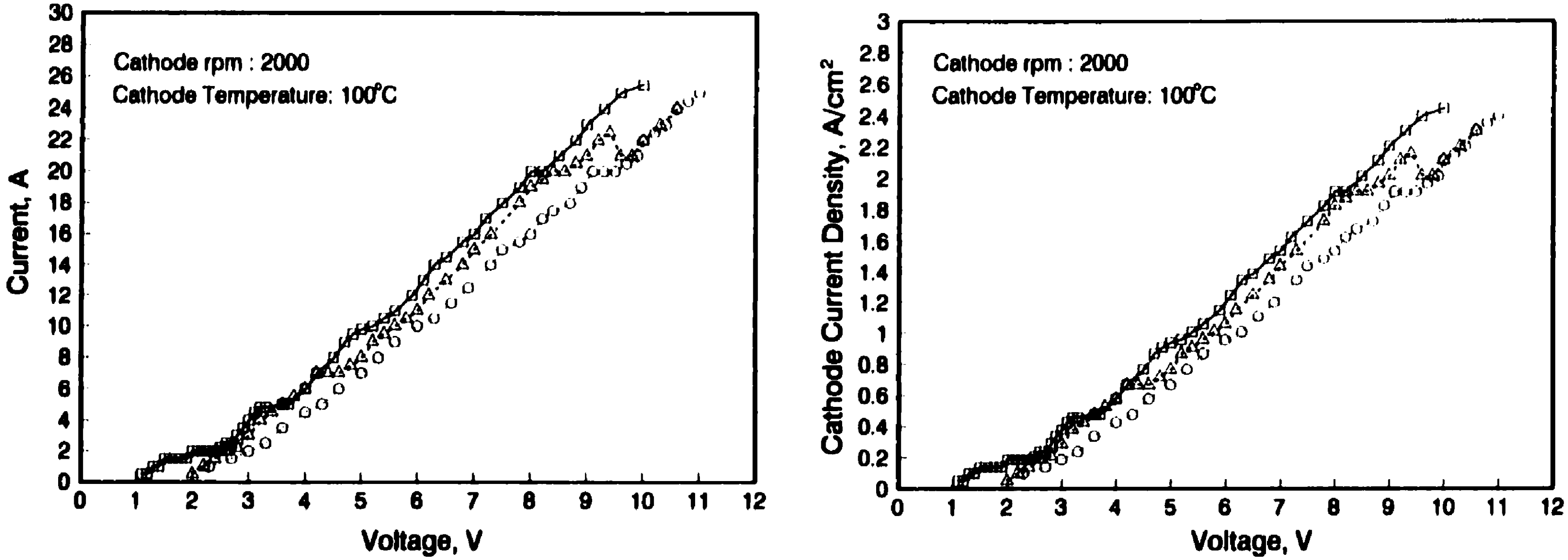
I_{ave} : average current during I_2 reduction, A

n : number of electrons, g equivalent

4.3 Performance characteristics with the mesh cathode

With the platinum mesh cathode, voltage - current - cathode current density characteristics determined at various levels of I_2 concentration in the aqueous HI solution are shown in Figure 4.1. Each test was carried out with the voltage being increased from zero to the maximum value shown in Figure 4.1, then repeated, with three such cycles being required to reduce essentially all the I_2 to HI. Thus during the first cycle, which took 15 min, the I_2 concentration decreased from 0.14 M to 0.02 M. During the second cycle (8 min) the I_2 concentration decreased from 0.02 M to 0.002 M, while in this case for the third cycle (5 min) almost no I_2 remained to be reduced. As it was shown in Section 3.2.3 that the ohmic drop accounts for about 70% of the minimum cell voltage while the Nernst potential of the cathode and anode accounts for

Figure 4.1 Voltage - Current - Cathode Current Density Relations : Mesh Cathode



Voltage - Current Relation

Voltage - Cathode Current Density Relation

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	Cycle 1 : 15 min	Cycle 2 : 8 min	Cycle 3 : 5 min
	$V_{I=0}$ = 2.1 V	$V_{I=0}$ = 2.0 V	$V_{I=0}$ = 2.3 V
Initial Values	$[I_2]$ = 0.14 M	$[I_2]$ = 0.02 M	$[I_2]$ = 0.002 M
	$[H^+]$ = 7.39 M	$[H^+]$ = 7.41 M	$[H^+]$ = 7.46 M
	[HI] = 56.2 wt%	[HI] = 56.2 wt%	[HI] = 56.5 wt%
Final Values	$[I_2]$ = 0.02 M	$[I_2]$ = 0.002 M	$[I_2]$ = 0.0015 M
	$[H^+]$ = 7.41 M	$[H^+]$ = 7.46 M	$[H^+]$ = 7.54 M
	[HI] = 56.2 wt%	[HI] = 56.5 wt%	[HI] = 56.8 wt%

Cathode: Pt; 13 mm diam. x 50 mm
Anode: Pb; 50 mm x 50 mm
Catholyte: 56 wt% HI
Anolyte: 38 wt% H_2SO_4

only about 10%, it is not surprising that the current and cathode current density decrease only slightly with decreasing the I_2 concentration at a fixed voltage.

Performance characteristics at fixed values of cell voltage, 8 V, and cathode rotation speed, 2000 rpm, are illustrated in Figures 4.2 – 4.4. The iodine reduction rate and cathode current efficiency decrease only slightly with the I_2 concentration over the range down to about 0.02 M, then drop very sharply for lower $[I_2]$. This break point in the curves of Figures 4.2 – 4.4 indicates that the onset of mass transfer control of I_2 reduction occurs for these conditions at $[I_2]$ of about 0.01 – 0.02 M. This value checks well with the work of Gorbachev and Belyaeva, 1961, discussed in Section 2.3.3, who found that I_2 reduction becomes mass transfer controlled at an I_2 concentration of about 0.01 M.

4.4 Performance characteristics with the sheet cathode

4.4.1 Current - voltage relations

The test cycles as described for Figure 4.1 were carried out also for the cathode cylinder made from a solid sheet of platinum, as used for the later experiments. The levels of cathode current density are similar for the two cathodes, but cannot be compared precisely because of the indeterminant effectiveness of the small scale curved surfaces of the mesh cathode. At very low circuit current, near zero, the voltage is about 2 V, Figure 4.5. The theoretical calculation in Section 3.2.3 indicated the voltage as 1.62 V at the very low circuit current of 0.1 A. The ~0.4 V difference from the measured value can be attributed to the assumptions made for that calculation. For example it was assumed that the anode would behave as β-PbO_2, but in the anodic solution there may be a mixture of α-PbO_2 and β-PbO_2, Ruetschi et al., 1963.

When I_2 concentration becomes very low, ~ 0.01 M, H_2 generation was observed for applied voltage higher than 9.2 V. This observation shows that in this

Cathode: Pt; 13 mm diam. x 50 mm
Anode : Pb; 50 mm x 50 mm

Catholyte : 56 wt% HI
Anolyte : 38 wt% H_2SO_4

Cathode Temp. : 100°C
Anode Temp. : 60°C

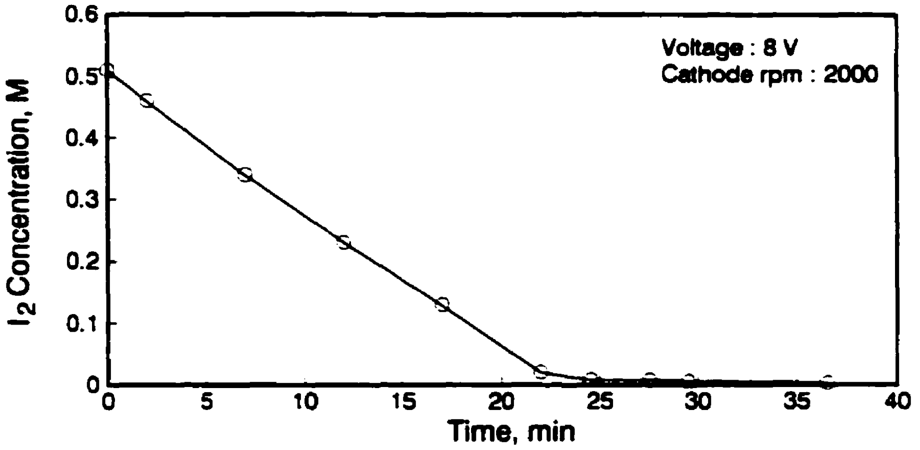


Figure 4.2 I_2 Concentration - Time Relation

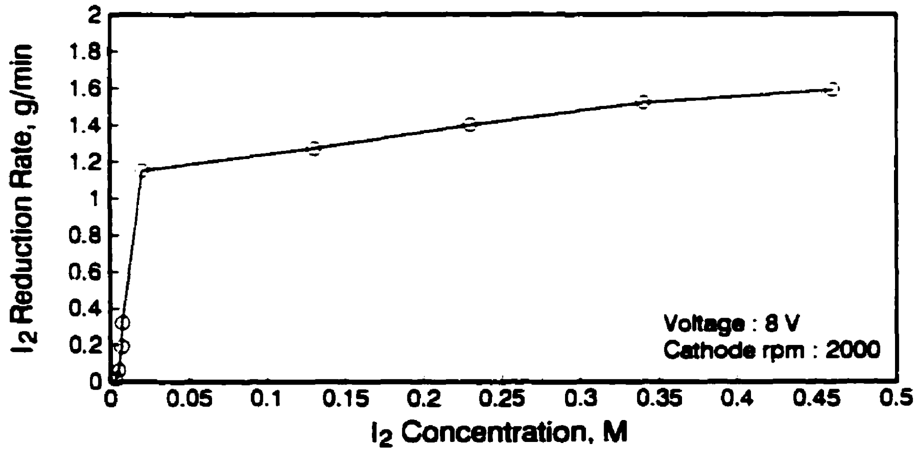


Figure 4.3 Effect of I_2 Concentration on I_2 Reduction Rate

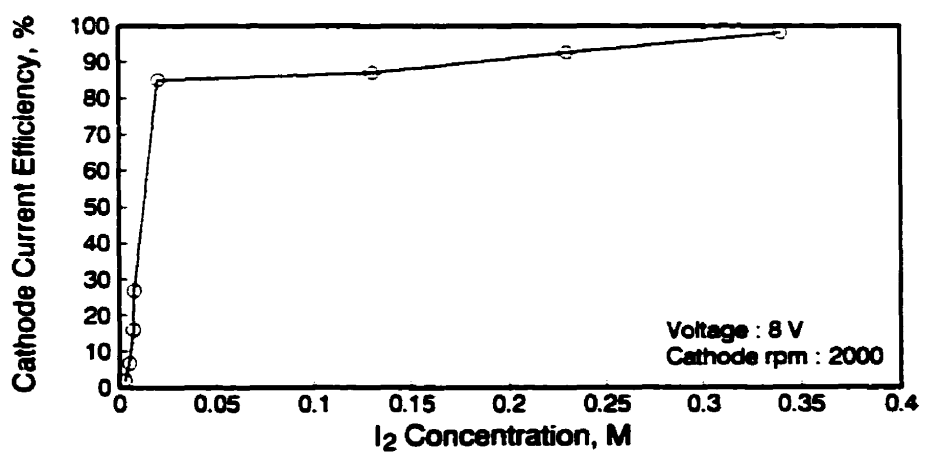
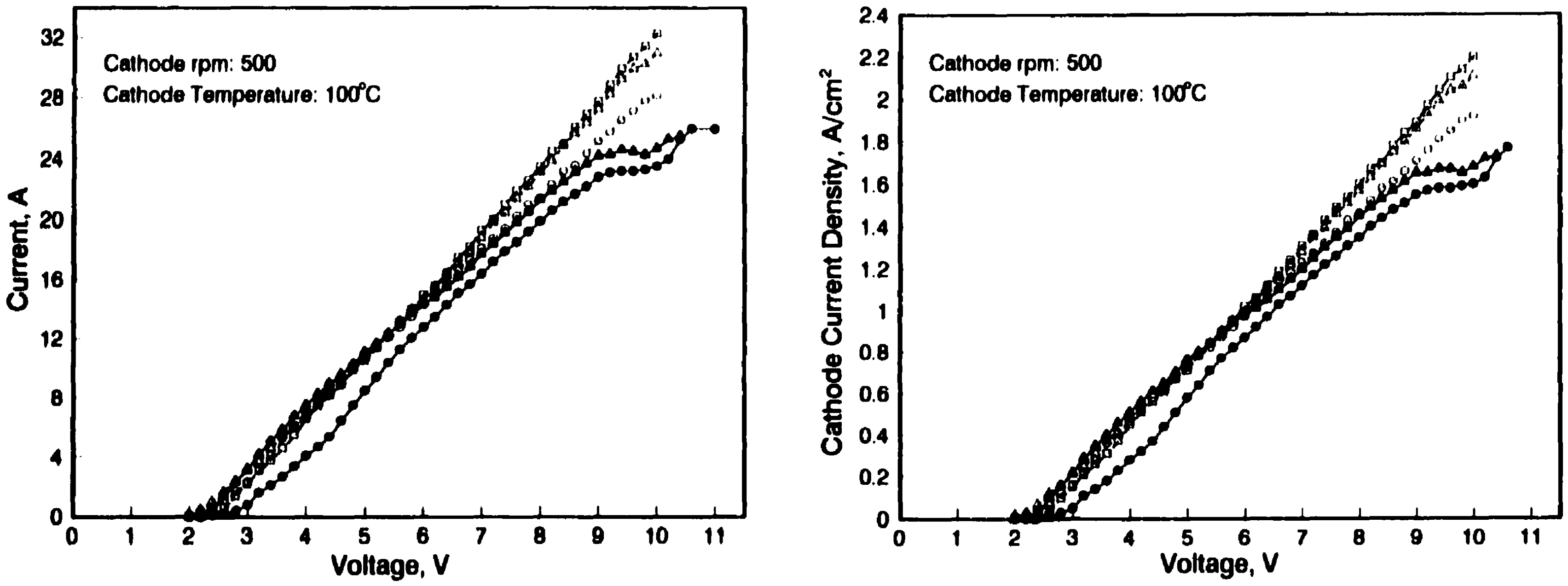


Figure 4.4 Effect of I_2 Concentration on Cathode Current Efficiency

Figure 4.5 Voltage - Current - Cathode Current Density Relations : Sheet Cathode



Voltage - Current Relation

Voltage - Cathode Current Density relation

	- - -□- - -	······△······	○	—▲—	—●—
	Cycle 1 : 8.2 min	Cycle 2 : 7.3 min	Cycle 3 : 6.5 min	Cycle 4 : 7 min	Cycle 5 : 7.3 min
	$V_{I=0}$ = 2.2 V	$V_{I=0}$ = 2.0 V	$V_{I=0}$ = 2.0 V	$V_{I=0}$ = 2.3 V	$V_{I=0}$ = 2.4 V
Initial Values	$[I_2]$ = 0.52 M $[H^+]$ = 7.23 M [HI] = 55.4 wt%	$[I_2]$ = 0.37 M $[H^+]$ = 7.27 M [HI] = 55.6 wt%	$[I_2]$ = 0.22 M $[H^+]$ = 7.56 M [HI] = 56.9 wt%	$[I_2]$ = 0.18 M $[H^+]$ = 7.71 M [HI] = 57.6 wt%	$[I_2]$ = 0.006 M $[H^+]$ = 7.73 M [HI] = 57.6 wt%
Final Values	$[I_2]$ = 0.37 M $[H^+]$ = 7.27 M [HI] = 55.6 wt%	$[I_2]$ = 0.22 M $[H^+]$ = 7.56 M [HI] = 56.9 wt%	$[I_2]$ = 0.18 M $[H^+]$ = 7.71 M [HI] = 57.6 wt%	$[I_2]$ = 0.006 M $[H^+]$ = 7.73 M [HI] = 57.6 wt%	$[I_2]$ = 0.004 M $[H^+]$ = 7.50 M [HI] = 56.6 wt%

Cathode: Pt; 25 mm diam. x 50 mm
Anode: Pb; 50 mm x 50 mm
Catholyte: 56 wt% HI
Anolyte: 38 wt% H_2SO_4

electrochemical wood liquefaction reactor the I_2 concentration could not be maintained at a level as low as 0.01 M. However, as $[I_2]$ reaches 0.7 M – 1.2 M with nonelectrochemical batch liquefaction of wood in aqueous HI, a limiting value of $[I_2] = 0.01$ M could correspond to the only about 1% of the I_2 concentration levels experienced without I_2 conversion back to HI, hence constitutes no significant limitation. Carlin, 1977, reported a cathode current density of about 0.5 A/cm^2 for parallel flat plate electrodes at 4 V and with I_2 concentration about 0.1 M. For the necessarily approximate value of effective cathode area between the cylindrical cathode and flat plate anode in the present experiments, Figure 4.5 shows that at 4 V and for $[I_2]$ in the range of 0.006 – 0.5 M, the cathode current density obtained here is likewise in the order of $i = 0.5$ A/cm^2. With all the dissimilarities from Carlin's experiments and the approximations required, it is remarkable to obtain such similar cathode current densities. Thus fortunately the evidence is that this is a quite robust, stable electrochemical system.

The resistance of the electrolyte cell is calculated by the relation

$$V - V_{I \to 0} = IR \tag{4.5}$$

where

V : voltage, V

I : current, A

$V_{I \to 0}$: maximum voltage at $I \to 0$ A, V

R : resistance, ohm

and is shown in Figure 4.6. It is apparent that there is initially a nonlinear voltage-current relation region at very low current, this region being larger at very low I_2 concentration. Nonlinear voltage-current behaviour indicates phenomena other than simple ohmic resistance. At very high voltage there is occurrence of other phenomena such as H_2 generation. Excluding those extreme regions it is apparent from Figure 4.6

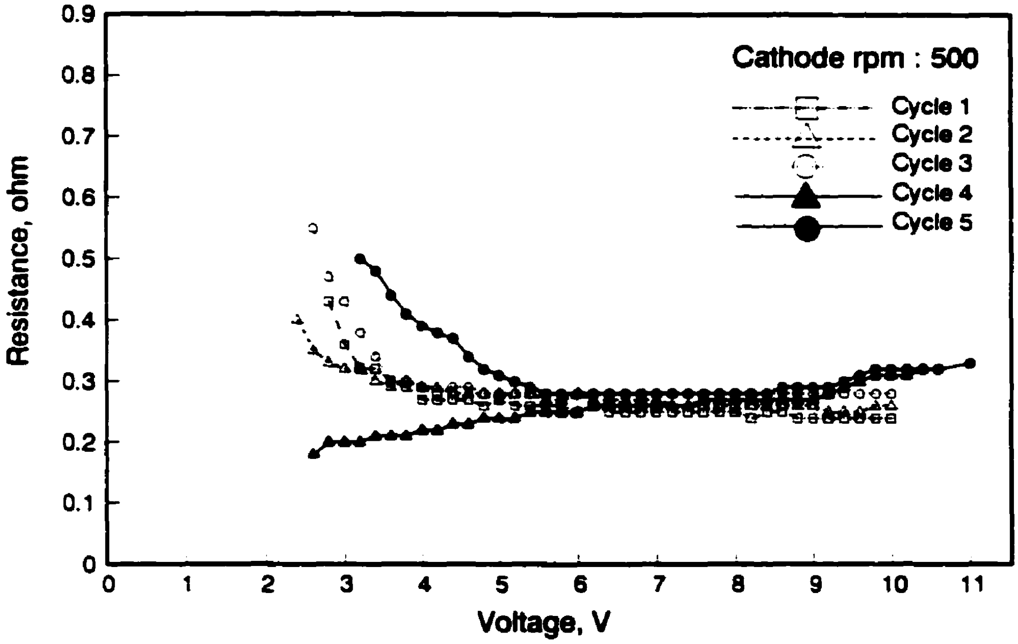


Figure 4.6 Electrical Resistance of the System

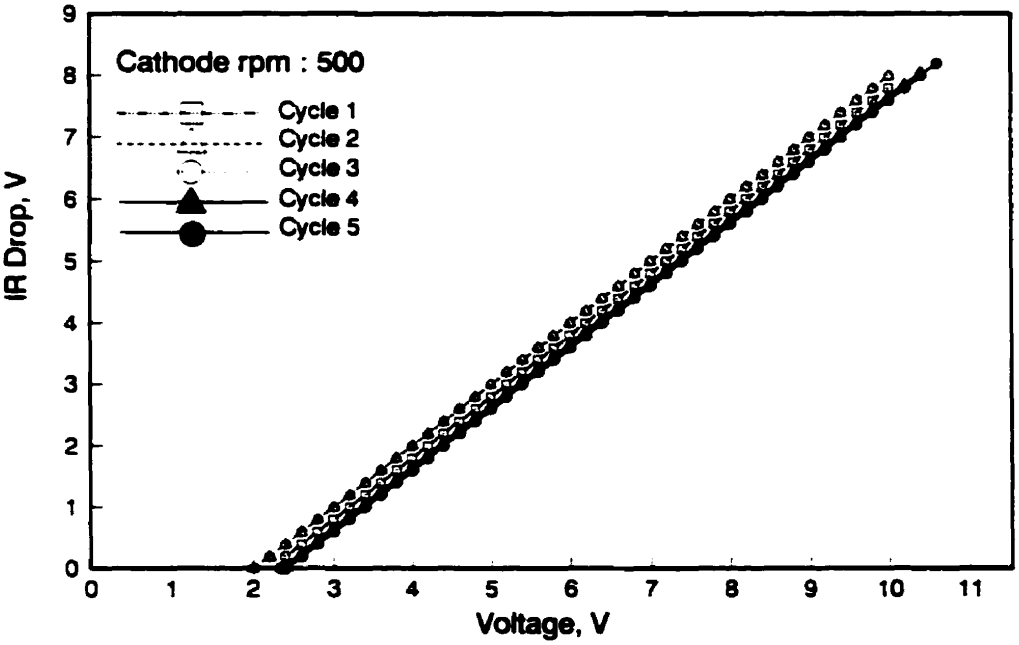


Figure 4.7 Relation of Voltage and IR Drop

that the overall cell ohmic resistance is about 0.27 ohm.

The IR drop must increase linearly with voltage, as shown by the data represented in Figure 4.7. It was estimated in Section 3.2.3 that the IR drop due to the electrical resistance of the system would be 4.70 V at 6.80 V, which is confirmed by the measurements for $[I_2]$ of 0.52 M – 0.18 M shown in Figure 4.7.

4.4.2 Effect of voltage and I_2 concentration

The electrochemical characteristics were determined at 3 levels of cell voltage, 3 V, 6 V and 7 V, with the cathode rotation speed fixed at 500 rpm. The current and cathode current density decrease relatively little as $[I_2]$ approaches zero, Figures 4.8 and 4.9, because of the dominant role of cell ohmic resistance, about 70% of the total, and the small role of the Nernst potential of electrodes, only about 10% of the total cell voltage as noted in Section 3.2.3. By contrast the I_2 reduction rate and cathode current efficiency, Figures 4.10 and 4.11, drop off precipitously at low values of $[I_2]$. The value of $[I_2]$ at which the I_2 reduction rate begins to drop significantly with decreasing $[I_2]$ is dependent on the cell voltage. These critical values for $[I_2]$ are approximately 0.16 M for 7 volts, 0.08 M for 6 volts, and 0.02 M for 3 volts. Likewise cathode current efficiency begins to drop for $[I_2]$ less than about 0.08 M at 6 or 7 volts, but not until $[I_2]$ is about 0.01 M at 3 volts. Below these threshold values of $[I_2]$ the iodine reduction rate and cathode current efficiency drop because the electrochemical cell performance becomes affected by the rate of mass transfer of I_2 from the bulk of the solution to cathode surface.

It is highly favourable to the ECLR concept to have found that there is a wide region of operability for I_2 concentration and cell voltage over which cathode current efficiency is in the range 90 – 100%. A value of $[I_2] = 0.08$ M is about 10% of the I_2 concentration levels obtained for wood liquefaction without conversion of I_2 back to HI, suggesting that it may be possible to reduce these levels of $[I_2]$ by about 90% in an ECLR.

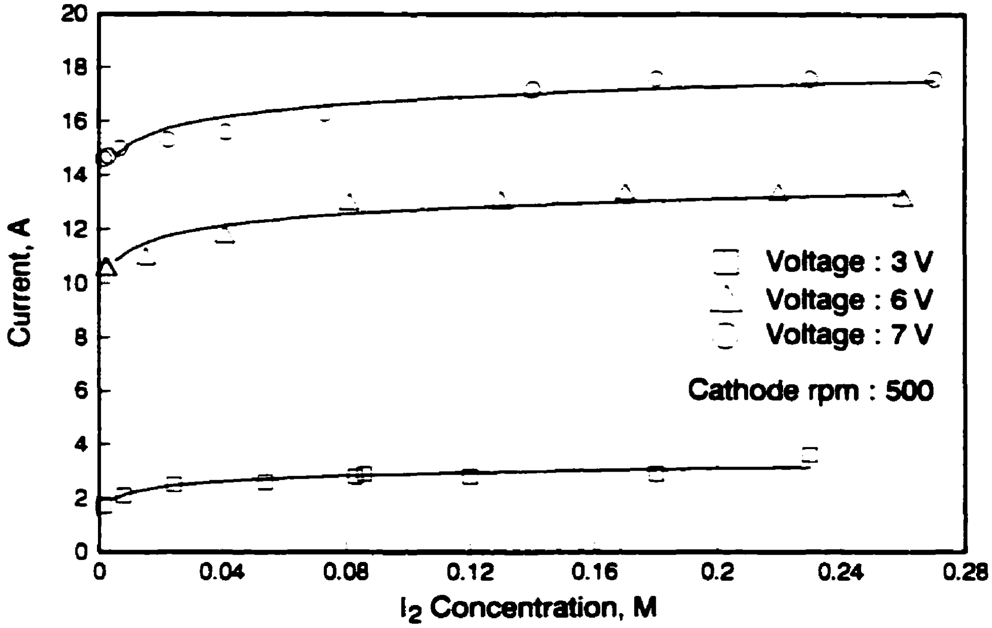


Figure 4.8 Effect of I_2 Concentration on Current at Various Cell Voltage

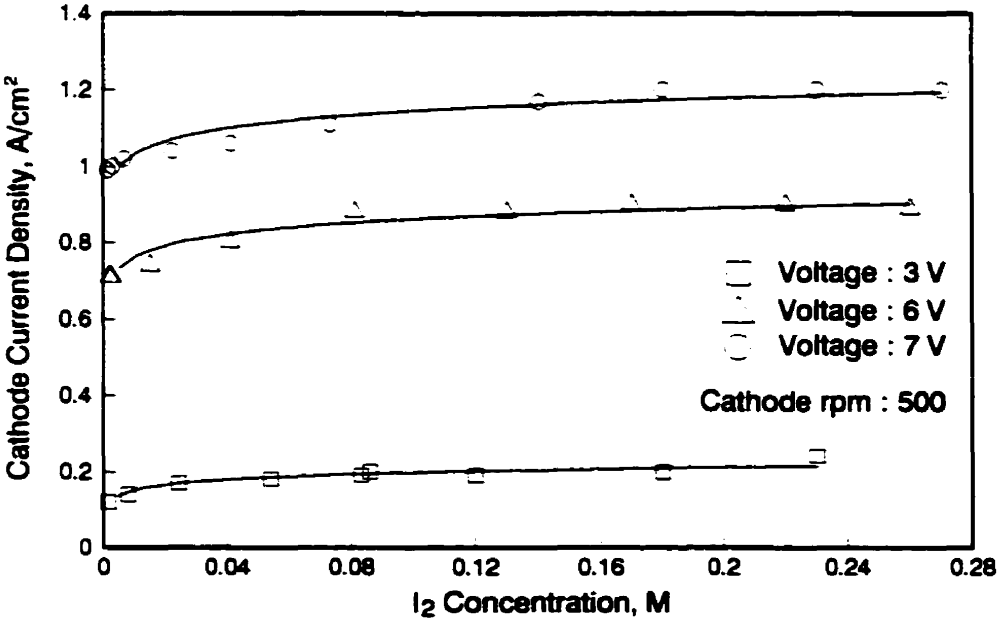


Figure 4.9 Effect of I_2 Concentration on Cathode Current Density at Various Cell Voltage

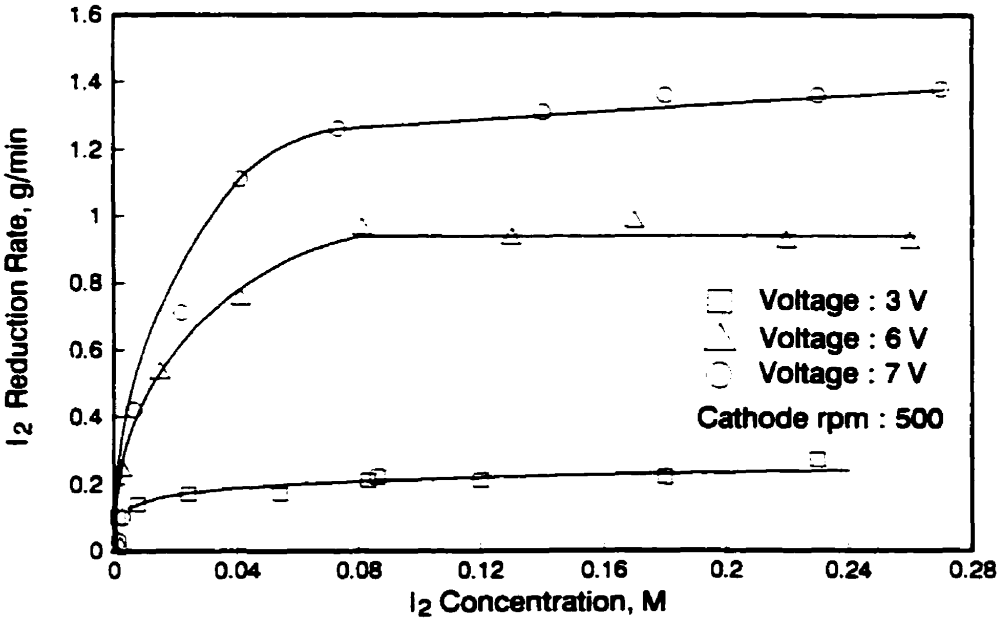


Figure 4.10 Effect of I_2 Concentration on I_2 Reduction Rate at Various Cell Voltage

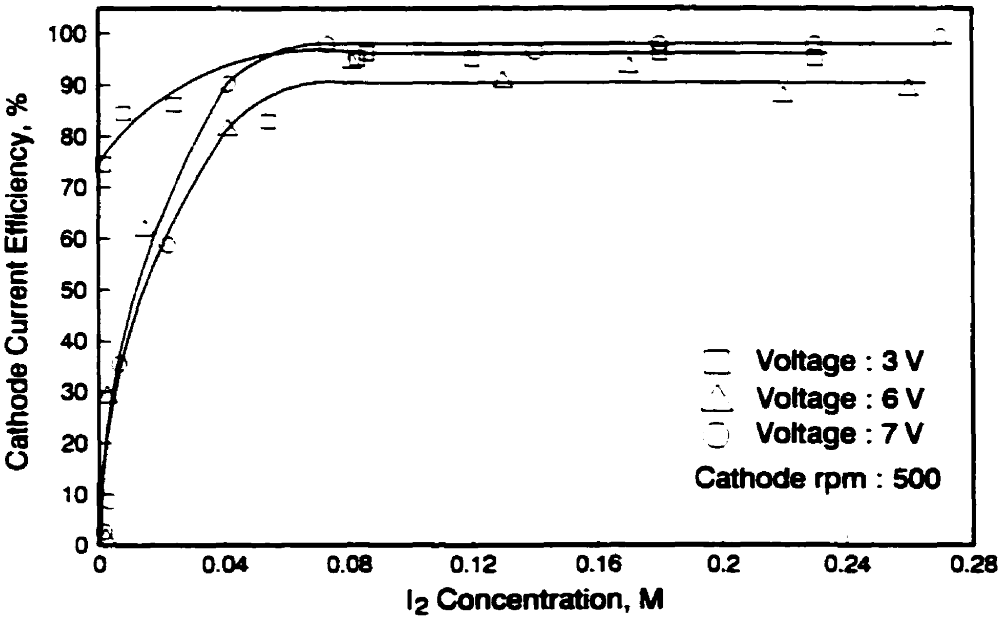


Figure 4.11 Effect of I_2 Concentration on Cathode Current Efficiency at Various Cell Voltage

4.4.3 Effect of cathode rotation and I_2 concentration

The electrochemical characteristics were next determined at 3 levels of cathode rpm, 0, 500 and 1000 rpm, for a constant cell voltage of 6 V. Figures 4.12 to 4.15 show patterns similar to those discussed in Section 4.3.2. The higher the cathode rotation speed, the lower the critical value of $[I_2]$ at which I_2 reduction rate, Figure 4.14, and cathode current efficiency, Figure 4.15, begin to drop off. This effect results from the higher cathode rotation speed reducing the mass transfer resistance for I_2 transport to the cathode surface. For I_2 reduction rate and cathode current efficiency these threshold values of $[I_2]$ are about 0.15 M, 0.08 M and 0.04 M for cathode rotation speed of 0, 500 and 1000 rpm, respectively. In the range of I_2 where diffusion of I_2 to the cathode surface is not mass transfer controlled, cathode current efficiency is 95 – 100% for the highest cathode rotation speed, 1000 rpm, but even with a stationary electrode the current efficiency is about 90%.

Thus it is found that at easily obtainable cathode rotation rpm, mass transfer control starts at values of $[I_2]$ an order of magnitude less than the values of $[I_2]$ existing in a nonelectrochemical liquefaction reactor, typically 0.7 M – 1.4 M as will be detailed in Chapter 5. It is fortunate for the overall objective of this investigation that the electrochemical cell may be operated in the range where mass transfer is not a major restriction in determining the rate of reduction of I_2 which, in the ECLR concept, determines the wood liquefaction rate. Although cathode rotation was used in the present study to reduce mass transfer effect in the reactor, it is encouraging to note from Figures 4.14 and 4.15 that even with no flow of the aqueous HI solution over a stationary electrode, cathode current efficiency starts to drop below the plateau value of about 90% only when the I_2 concentration drops below 0.15 M, an order of magnitude below the levels of 0.7 M – 1.4 M occurring in a batch wood liquefaction reactor without I_2 reduction. In an industrial design of ECLR, fluid flow over a stationary cathode could perform the same function of reducing the boundary layer thickness and thereby improving the cell current efficiency above the lower limit of 90% found here for a stationary cathode in non-flowing solution.

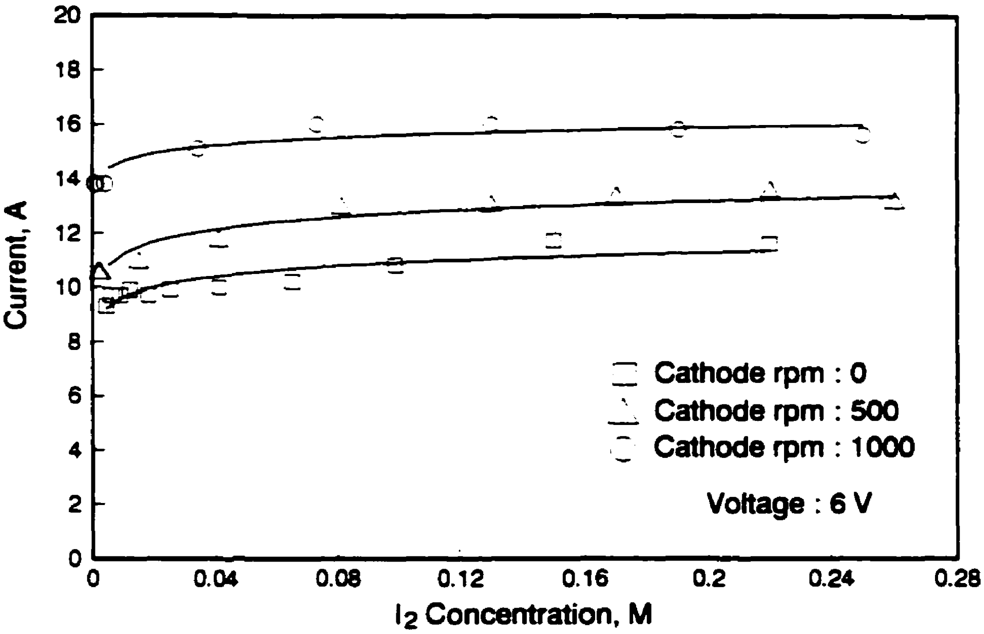


Figure 4.12 Effect of I_2 Concentration on Current at Various Cathode Rotational Speed

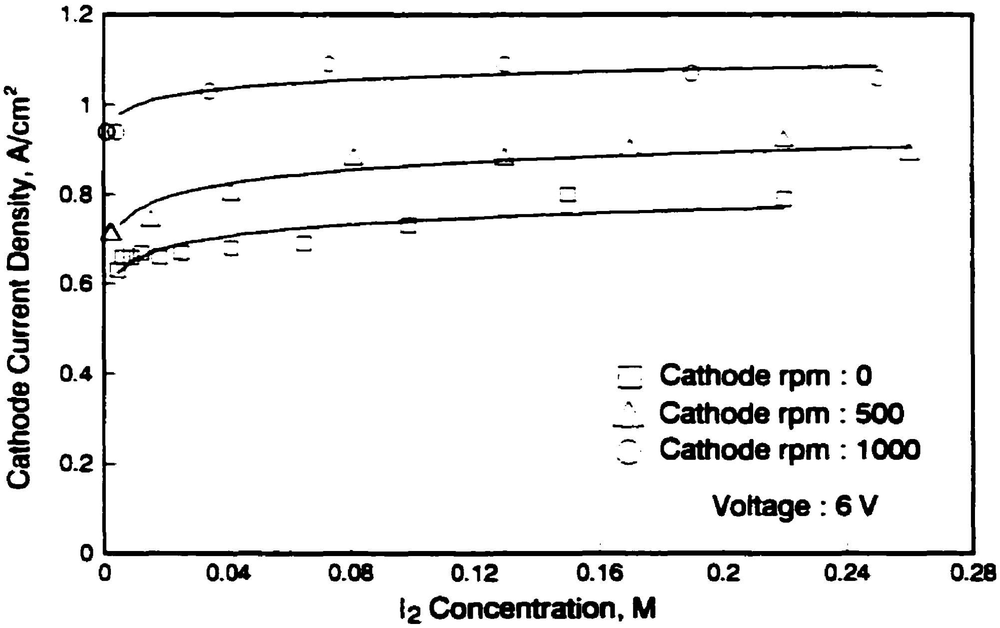


Figure 4.13 Effect of I_2 Concentration on Cathode Current Density at Various Cathode Rotational Speed

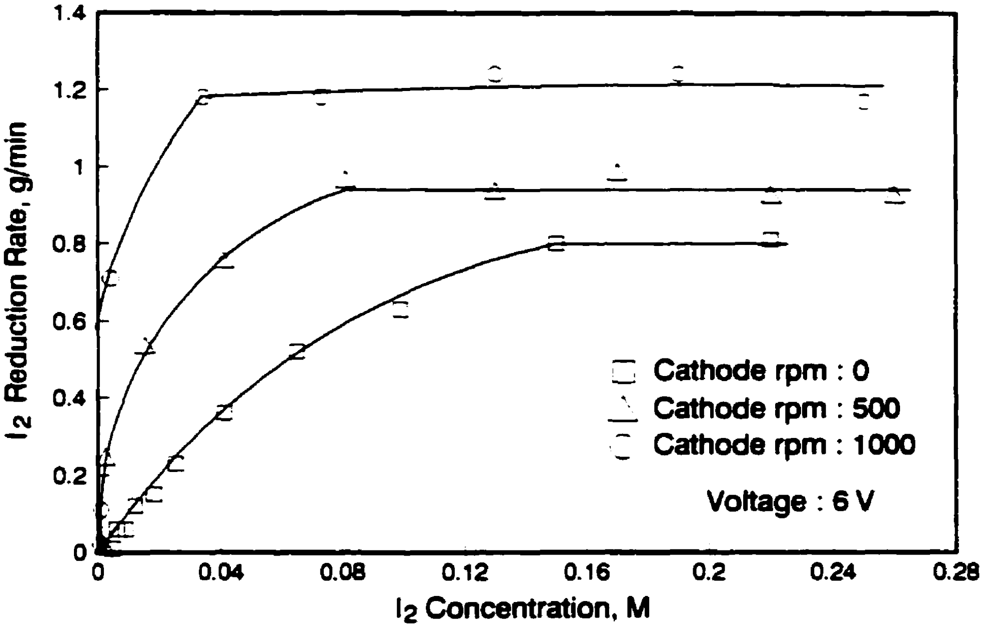


Figure 4.14 Effect of I_2 Concentration on I_2 Reduction Rate at Various Cathode Rotational Speed

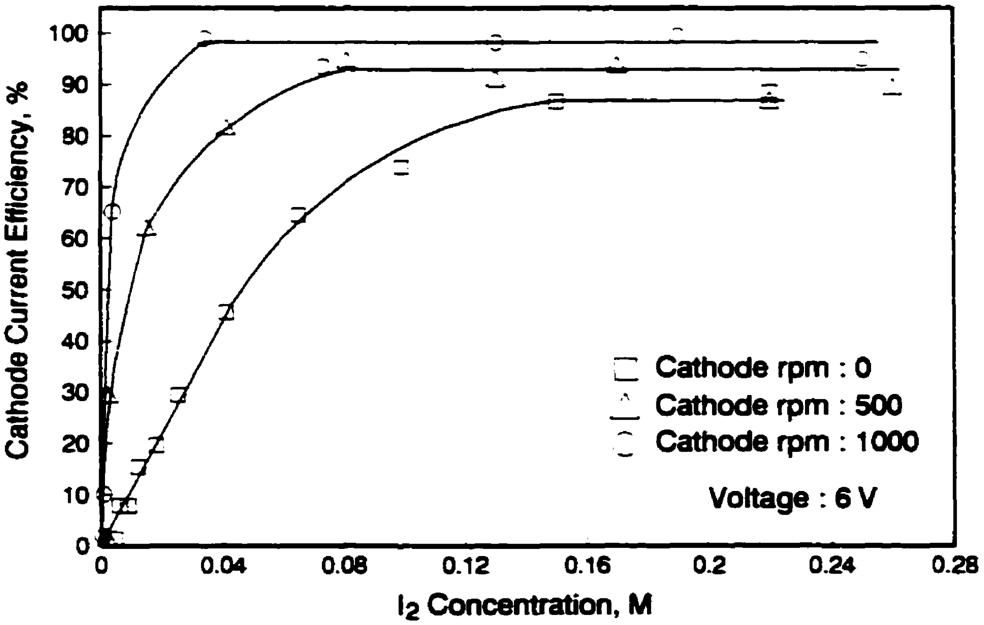


Figure 4.15 Effect of I_2 Concentration on Cathode Current Efficiency at Various Cathode Rotational Speed

4.4.4 Effect of spacing between electrodes

A test was made of the sensitivity of the electrochemical characteristics to the spacing between cathode and anode. The normal inter-electrode spacing was 40 mm, i.e. a 20 mm closest point distance between cathode and membrane, and 20 mm from anode to membrane. This 40 mm spacing was increased to 50 mm by increasing the anode-to-membrane distance from 20 mm to 30 mm. The test was made at a cell voltage of 7 volts and cathode rotation speed of 500 rpm. For this approximately 30% increase in inter-electrode spacing Figures 4.16 and 4.17 show that the I_2 reduction rate and cathode current efficiency both are decreased by only about 10%. This demonstration indicates that performance characteristics are not particularly sensitive to electrode spacing. This finding indicates that a large scale ECLR could be designed without severe constraints as to inter-electrode spacing.

4.4.5 Water transfer between cells

With ECLR operation, significant water transport could occur in association with the transport of H^+ as H_3O^+ from the anode to the cathode compartment. The fairly concentrated solution of H_2SO_4, 38 wt%, used in the anode cell helps limit this water transport by lowering the thermodynamic potential for water transport from the anode cell. Tests were performed to measure the extent of this effect. For the base case with no electrochemical current, with 57 wt% HI solution in the cathode compartment and 38 wt% of H_2SO_4 solution in the anode compartment, it was found that during 4h there was 5 ml increase in the cathode compartment and 5 ml decrease in the anode compartment, i.e. 1.25 ml/h H_2O transfer rate. With electrochemical reduction of I_2 in the 57 wt% HI solution for 3h 45 min there was 46 ml solution volume increase in the cathode cell and 60 ml solution volume decrease in the anode cell. Thus with electrochemical reduction the water transport rate is much greater (46 ml/3.75h=) 12.3 ml/h. The net loss of solution volume (60 − 46) = 14 ml is due to water hydrolysis to H^+ and O_2. The phenomena of water transport during wood liquefaction in the ECLR

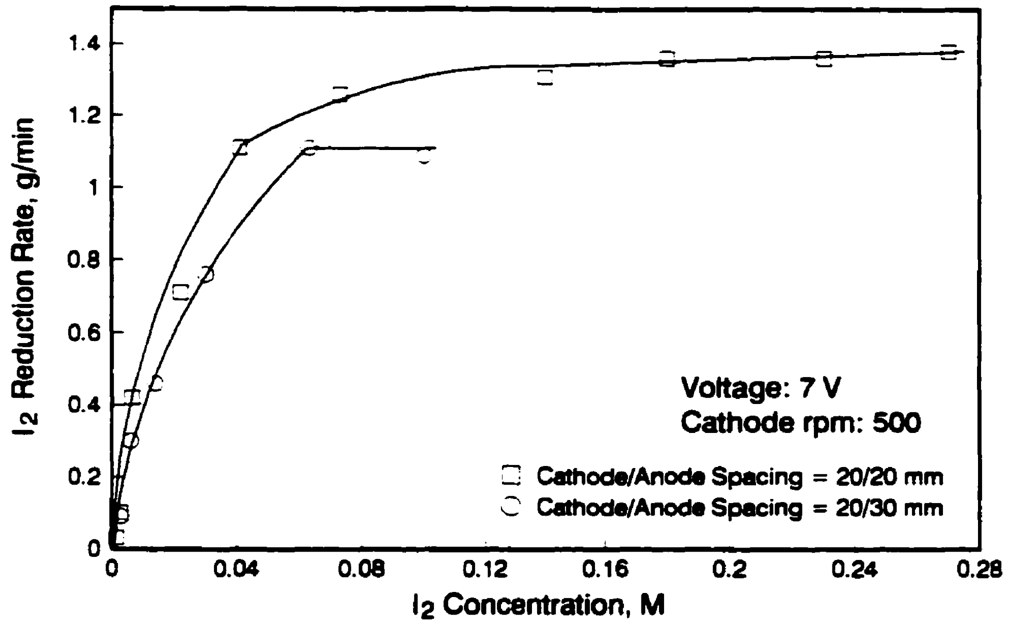


Figure 4.16 Sensitivity of I_2 Reduction Rate to Inter-electrode Spacing

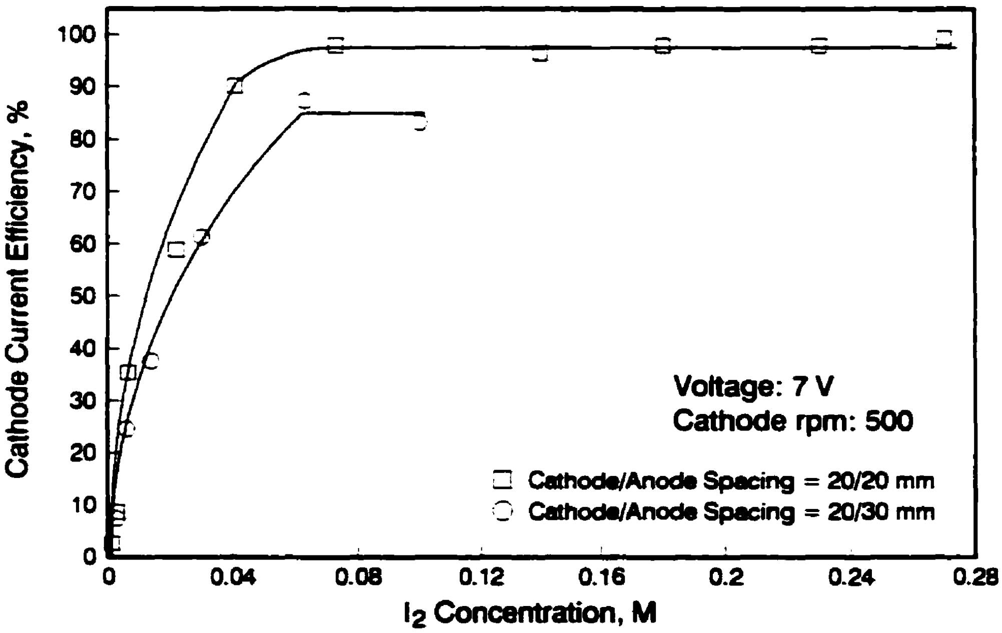


Figure 4.17 Sensitivity of Cathode Current Efficiency to Inter-electrode Spacing

is discussed in Section 7.9.

4.5 Summary

The performance characteristics for electrochemical reduction of I_2 in the ECLR design of this laboratory but in the absence of wood liquefaction have been documented. Because of the unknown effects of wood liquefaction on the electrochemical performance of this ECLR design, it was essential first to determine these characteristics quantitatively with the presence of just the inorganic constituents of the system I_2 - HI - H_2O. The following characteristics were determined.

(1) Hydrogen is produced when the voltage is 9.2 volts or more. Thus cell voltage would always be set below this value in order to avoid hydrogen generation at the cathode.

(2) In the range of I_2 concentration that would be experienced for ECLR wood liquefaction, current begins with the electrochemical circuit at a cell voltage of about 2 V. In the region of stable operating characteristics the total resistance of the ECLR circuit is about 0.27 ohms. At a cell voltage of 6.80 V, a realistic value, the IR drop in the electrochemical circuit was measured as 4.70 V. These measured values confirm those calculated in advance in Chapter 3 in connection with the design of the ECLR.

(3) The electrochemical performance characteristics, i.e. current, current density, I_2 reduction rate, and current efficiency, have been determined as a function of cell voltage, I_2 concentration, cathode rotational speed and inter-electrode spacing.

(4) Over a broad range of operating conditions the cathode current efficiency is high, in the range 90 – 100%, and is stable with respect to cell voltage, cathode rotational speed and I_2 concentration.

(5) The I_2 concentration at which cathodic current efficiency starts to drop because of mass transfer control was determined as a function of cell voltage, cathode rotational speed and inter-electrode spacing. Depending on these electrochemical

parameters this threshold I_2 concentration is in the range of 0.04 M – 0.08 M, concentrations which are very low relative to typical levels of $[I_2]$ about 0.7 – 1.4 M for non-electrochemical batch wood liquefaction.

CHAPTER 5

NONELECTROCHEMICAL WOOD LIQUEFACTION

5.1 Experimental approach

5.1.1 Introduction

Prior to beginning study of electrochemical liquefaction a limited investigation was made of the corresponding nonelectrochemical process, i.e. the liquefaction of wood at low severity conditions, atmospheric pressure and low temperature, by batch reaction in aqueous HI solution. The effects of four parameters were investigated - short reaction times, concentration of HI in the aqueous phase, HI:wood stoichiometric ratio, and the individual behaviour of the principal components of wood - cellulose, hemicellulose and lignin.

5.1.2 Procedures

The experimental batch reactor was a one-litre, three-neck round bottom flask. One neck carried a thermometer, another the water-cooled overhead condenser to return HI-H_2O vapour and low boiling point product vapour as condensate to the flask. The centre neck was enlarged to facilitate charging the wood flour at the start of each batch reaction. Agitation by a magnetic stirrer was provided to achieve temperature uniformity, minimize mass transfer effects and disperse the product.

Previous work in this laboratory established that wood liquefaction can be obtained in 50 – 57 wt% aqueous HI solution at 115 – 127°C. By a fortunate coincidence this temperature range corresponds to the bubble point line for the liquid phase for HI-H_2O vapor-liquid equilibrium at compositions just below the atmospheric pressure azeotrope at 56.5 wt% HI and 127°C. Most of the T-x phase diagram for the HI-H_2O system at atmospheric pressure, Figure 5.1, was determined by Carriére et Ducasse, 1926. The numerical data are recorded in Appendix A. Thus an atmospheric pressure reactor operating at the bubble point of the aqueous HI solution, Figure 5.1, conveniently provides reactor temperatures in the range 100 – 127°C for HI concentrations from 0 – 64 wt% HI. The present study extended the concentration of the HI solution in the batch reactor to values both above and below those studied previously. The maximum HI concentration used in the present experiments is 68.5 wt% for which the bubble point is about 40°C.

For investigation of the effect of initial HI concentration in the range 15 – 61 wt% HI the batch reactor experiments were performed by adding wood flour to boiling aqueous HI solution which, over these concentrations, is in the range 102 – 127°C. After the required amount of aqueous HI solution was brought to its bubble point temperature an amount of wood satisfying the desired HI/substrate ratio, R, was added. Wood flour, oven dried for 2h at 80°C, wrapped in "kimwipes" tissue paper (paper 1 – 2 wt% of the amount wood used) was introduced quickly (<10s) and the reaction allowed to proceed for the desired reaction time t, generally 15 min. At the desired reaction time the reaction was quenched by reducing of the temperature to about 60°C within a few seconds by immersing the reactor in a bath of crushed dry-ice in ethanol, which provided an initial rate of temperature drop of about 3°C/s.

For experiments with an initial HI concentration solution of 68 wt% a different procedure was used because the bubble point of this concentration HI solution is only about 40°C. Thus wood flour was mixed in the reactor with 68 wt% HI solution at room temperature, then heated to 90°C in about 6 min. As the biomass liquefaction reactions consume HI and produce H_2O, as given quantitatively in Sections 2.2.2 and 2.2.3, these effects cause HI concentration in a batch reactor to decrease, and explain why it is possible to increase the reactor temperature above the bubble point, about

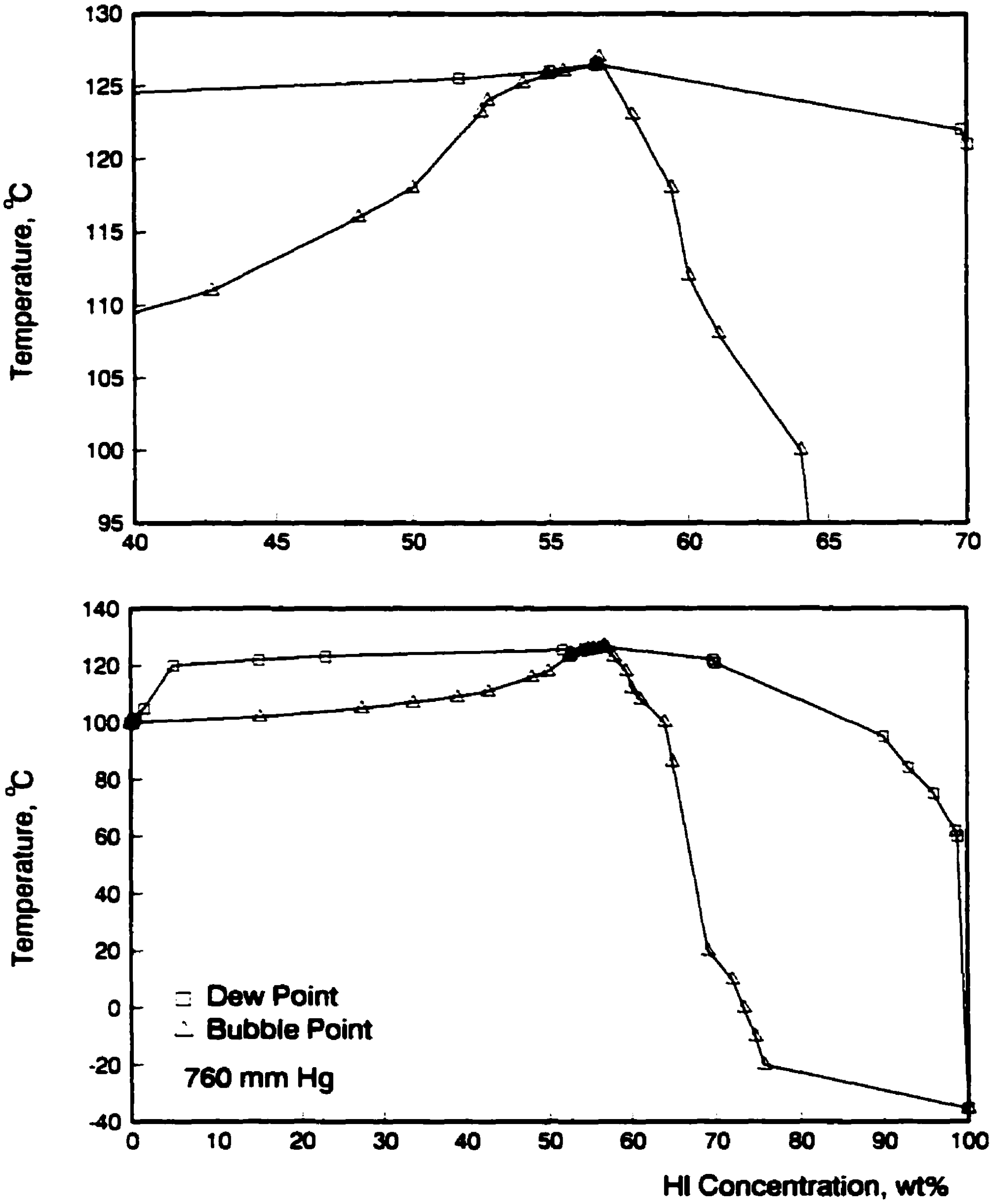


Figure 5.1 Vapor - Liquid Phase Equilibrium For HI-H_2O System

40°C on Figure 5.1, of the 68 wt% HI solution charged to the reactor. As reaction rates are low at the lower temperatures, the time when the reactor temperature reached 90°C was taken as the effective start of reaction. Thus reaction was continued for 15 min after reaching the temperature of 90°C. This approximation is not important because for reaction times in the order of 15 min the wood liquefaction reactions are relatively insensitive to reaction time.

In the reactor the total organic product is automatically partitioned by the aqueous HI solution acting also as a solvent, yielding an aqueous phase soluble product fraction, AP, and an organic phase fraction, OP. In batch reactor liquefaction of wood the yield of the OP fraction is typically about five times the yield of the AP product fraction. In the steps of purification of the OP this fraction is partitioned again by solvent extraction with acetone into an acetone-soluble fraction, OA, and the organic residue not soluble in either aqueous HI or acetone, designated ON. The insoluble ON, the undesired product fraction, might loosely be considered as a char-type product.

After batch reaction the aqueous solution was removed from the reactor and the part of the OP product fraction dispersed in it was separated by filtration. All the OP product fraction was dried in an oven at 80°C for 2h to obtain it in a water-free, HI-free state. For elemental analysis a small amount, about 5 wt% of the OP product fraction, was not subjected to acetone extraction. The remainder of the OP fraction was subjected to an acetone extraction as described above. The ON insoluble residue fraction was separated by filtration from the solution of OA product in acetone. For determination of the yield and elemental analysis of the OA product fraction, first the acetone was removed by distillation, then the material subjected to 3 days of atmospheric evaporation and finally dried in an oven at 80°C for 2h. Although the acetone-soluble product fraction OA obtained in this way should be in an acetone-free, water-free, HI-free state, in fact the OA product composition may have been influenced by contact with acetone. Therefore the elemental composition of the OP product recorded in Tables 5.1 – 5.3 is that measured directly for the OP not contacted with acetone rather than being taken as the sum of the OA and ON product fractions.

The yields of all product fractions are defined on a carbon basis. The small yield of the aqueous phase product AP was generally obtained by difference because this fraction is difficult to determine directly. This procedure was validated by direct determinations for the AP product fraction from two experiments reported in Section 5.2. The OP, OA, and ON product fractions were analyzed for carbon, hydrogen and oxygen by Pregl type microcombustion using the elemental analysis facility of the McGill Department of Chemical Engineering. The iodine content was determined separately by the microcombustion method described in Appendix H.2. Before and after reaction the aqueous solutions were analyzed for HI and I_2 concentrations using 0.15 M NaOH solution and 0.03 M $Na_2S_2O_3$ solution by the methods recorded in Appendix H.1. The analysis methods for the substrates and products appear in Appendix H.2. The experimental conditions and results for this series of experiments, Nos.36−39, 56−57, 59−60, 62−68, 72−87, 89−99, 101 and 105 are appeared in Appendix I and J.

5.1.3 Materials

Standard hybrid poplar wood (particle size d_p = 0.22 mm), from FORINTEK Canada Corp., was used, of elemental composition reported by NRC in 1985 to be $CH_{1.59}O_{0.70}$. The NRC wood certificate information is recorded in Appendix G.

The microcrystalline cellulose, $(C_6H_{10}O_5)_n$, i.e $CH_{1.67}O_{0.83}$, was obtained from A&C Chemical Products Inc.

Xylan was purchased from Aldrich Chemicals Corp. The analysis of this xylan was determined here to be $CH_{1.61}O_{0.79}$, while the elemental composition of hemicellulose is reported to be approximately $(C_5H_8O_4)_n$, or $CH_{1.60}O_{0.80}$. Xylan is considered to be representative of hemicellulose.

Alkali lignin from Sigma Chemical Corp. was determined here to have the elemental composition of $CH_{1.15}O_{0.33}$.

A supply of "Alcell" lignin from the experimental alcohol pulping process of Repap Inc., of elemental composition determined in this laboratory as $CH_{1.15}O_{0.31}$, was obtained from Repap.

Appendix G records the composition of the substrates used - hybrid poplar, cellulose, xylan, and alkali and Alcell lignins.

The 55 – 57 wt% aqueous HI solution, without H_3PO_2 stabilizer, was supplied by ACP Chemical Inc. The lower concentration HI solutions, < 57 wt%, were prepared by dilution with distilled water. Solutions of > 57 wt% HI were prepared by purging pure HI gas into 57 wt% HI solution. A cylinder of pure HI was obtained from Matheson Gas Products Corp. and stored in a freezer at −23°C.

5.1.4 Definition of yields

Yields of the various product fractions on a carbon basis are indicated by $Y_{C/j}$, where j indicates the particular fraction of product i.e. OP (OA and ON) and AP. Yields of the OA and ON fractions on a carbon basis are related to the yield by weight, W_j, and weight fraction carbon content, $Z_{C/j}$, of that fraction as follows, where the subscript s refers to the substrate:

$$Y_{C/OA} = (W_{OA} \cdot Z_{C/OA}) / (W_s \cdot Z_{C/s}) \qquad (5.1)$$

$$Y_{C/ON} = (W_{ON} \cdot Z_{C/ON}) / (W_s \cdot Z_{C/s}) \qquad (5.2)$$

Yields of the OP and AP fractions are:

$$Y_{C/OP} = Y_{C/OA} + Y_{C/ON} \qquad (5.3)$$

As reviewed in Section 2.2.1 and to be discussed in Section 7.3, the methoxy (CH_3O-) group in lignin should be converted quantitatively by HI to methyl iodide, CH_3I. By the method recorded in Appendix H.2 the methoxy carbon content of hybrid poplar was determined to be 4.7%. The direct measurement of yield of CH_3I produced by hybrid poplar reaction with 57 wt% HI solution was 4.9% as recorded in Section 7.3, thus providing excellent agreement between these two methods. If methyl iodide is represented as MI, the complete material balance for carbon may be expressed as:

$$Y_{C/OP} + Y_{C/AP} + Y_{C/MI} = 1 \tag{5.4}$$

The H/C, O/C, and I/C atomic ratios and the hydrogen retention and oxygen removal values of the OP, OA, and ON product fractions are related to the elemental analysis of corresponding product fractions and substrates, as:

$$(H/C)_j = (Z_{H/j} \,/\, Z_{C/j}) \cdot (A_C \,/\, A_H) \tag{5.5}$$

$$(O/C)_j = (Z_{O/j} \,/\, Z_{C/j}) \cdot (A_C \,/\, A_O) \tag{5.6}$$

$$(I/C)_j = (Z_{I/j} \,/\, Z_{C/j}) \cdot (A_C \,/\, A_I) \tag{5.7}$$

$$(\text{Hydrogen Retention})_j = (Z_{H/j} \,/\, Z_{C/j}) \,/\, (Z_{H/s} \,/\, Z_{C/s}) \tag{5.8}$$

or $$(\text{Hydrogen Retention})_j = (H/C)_j \,/\, (H/C)_s$$

$$(\text{Oxygen Removal})_j = 1 - (Z_{O/j} \,/\, Z_{C/j}) \,/\, (Z_{O/s} \,/\, Z_{C/s}) \tag{5.9}$$

or $$(\text{Oxygen Removal})_j = 1 - (O/C)_j \,/\, (O/C)_s$$

where

j : OA, ON, OP, and AP product fractions
s : substrate, i.e. hybrid poplar, cellulose, xylan, alkali lignin, Alcell lignin
A_C : atomic weight of carbon, 12.01

A_H : atomic weight of hydrogen, 1

A_I : atomic weight of iodine, 126.9

A_O : atomic weight of oxygen, 16

$(H/C)_j$: H/C atomic ratio of product j

$(I/C)_j$: I/C atomic ratio of product j

$(O/C)_j$: O/C atomic ratio of product j

$(H/C)_s$: H/C atomic ratio of substrate

$(O/C)_s$: O/C atomic ratio of substrate

W_j : weight of product fraction j, g

W_s : weight of substrate used, g

$Y_{C/j}$: carbon base yield for product fraction j, fraction or %

$Z_{C/j}$: weight fraction carbon in product fraction j

$Z_{H/j}$: weight fraction hydrogen in product fraction j

$Z_{I/j}$: weight fraction iodine in product fraction j

$Z_{O/j}$: weight fraction oxygen in product fraction j

$Z_{C/s}$: weight fraction carbon in the substrate

$Z_{H/s}$: weight fraction hydrogen in the substrate

$Z_{O/s}$: weight fraction oxygen in the substrate

All weights and compositions are on a moisture-free basis, and where relevant, on an HI-free and I_2-free basis.

5.2 Stoichiometric equations for liquefaction reactions

5.2.1 General stoichiometric equations

The reaction stoichiometric equation may be written as:

$$CH_{ks}\,O_{ls} + a\,HI = \Sigma Y_{C/j}\,(CH_k\,O_l\,I_m)_j + b\,H_2O + c\,I_2 \qquad (5.10)$$

or

$$\begin{aligned} CH_{ks}\,O_{ls} + a\,HI &= Y_{C/OP}\,(CH_k\,O_l\,I_m)_{OP} + Y_{C/AP}\,(CH_k\,O_l\,I_m)_{AP} + Y_{C/MI}\,(CH_3I) \\ &\quad + b\,H_2O + c\,I_2 \\ &= Y_{C/OA}\,(CH_k\,H_l\,I_m)_{OA} + Y_{C/ON}\,(CH_k\,H_l\,I_m)_{ON} \\ &\quad + Y_{C/AP}\,(CH_k\,H_l\,I_m)_{AP} + Y_{C/MI}\,(CH_3I) \\ &\quad + b\,H_2O + c\,I_2 \qquad (5.11) \end{aligned}$$

Where

k, l, m : H/C, O/C, I/C atomic ratio of a product fraction

ks, ls : H/C, O/C atomic ratio of the substrate, i.e. hybrid poplar, cellulose, xylan, alkali lignin or alcell lignin

Therefore when all the product fraction yields, $Y_{C/j}$, and elemental compositions, $(CH_k\,O_l\,I_m)_j$, have been determined the stoichiometric coefficients a, b and c may be calculated by successive balances for H, O and I from application of the following three equations:

$a = \Sigma[(Y_{c/j})(k)_j] + 2\,b - ks$, gmol HI reacted per gmol C in substrate

$b = ls - \Sigma[Y_{C/j})(l)_j]$, gmol H_2O produced per gmol C in substrate

$c = 0.5\,\{a - \Sigma[(Y_{C/j})(m)_j\}$, gmol I_2 produced per gmol C in substrate

With the stoichiometric ratio of HI to substrate, R, defined as gmol HI supplied/gmol C in substrate, it follows that the ratio HI reacted/HI supplied, i.e. the fractional conversion of HI, designed X_{HI}, is

$$X_{HI} = a / R \qquad (5.12)$$

The hydrogen retention of a product fraction j relative to the substrate, Equation 5.8, is k_j / ks. The oxygen removal for fraction j relative to the substrate, Equation 5.9, is $(1 - l_j / ls)$.

An ideal model stoichiometric equation may be described for the following specific assumptions:

(1) All oxygen in the substrate is converted to water, with production of an oxygen-free hydrocarbon product.

(2) All hydrogen in the substrate remains in the organic product, which has the same H/C atomic ratio as the substrate.

(3) All HI supplied is converted, and all I^- oxidized to I_2, i.e. an organic product without iodine content.

With these assumptions for ideal liquefaction to produce hydrocarbon product the general Equation 5.10 may be rewritten as:

$$CH_{ks}O_{ls} + 2(ls)\ HI = CH_{ks} + ls\ H_2O + ls\ I_2 \qquad (5.13)$$

where the model stoichiometric coefficients are

$$a_{model} = 2(ls)$$
$$b_{model} = ls$$
$$c_{model} = ls$$

The model stoichiometric ratio of HI/substrate, R_{model}, is

$$R_{model} = a_{model}$$

for which the model HI conversion, $X_{HI,\ model}$, is

$$X_{HI,\ model} = a_{model} / R_{model} = 100\%$$

The ratio of actual to model stoichiometric ratio of HI/substrate, R/R_{model}, indicates the effectiveness of the HI supplied in a liquefaction reactor.

For the substrates of hybrid poplar, cellulose, xylan, alkali lignin, and Alcell lignin, the above model stoichiometric coefficients are as follows:

Substrate	Composition	a_{model}	b_{model}	c_{model}	R_{model}
Hybrid Poplar	$CH_{1.59}O_{0.70}$	1.40	0.70	0.70	1.40
Cellulose	$CH_{1.67}O_{0.83}$	1.66	0.83	0.83	1.66
Xylan	$CH_{1.61}O_{0.79}$	1.58	0.79	0.79	1.58
Alkali Lignin	$CH_{1.15}O_{0.33}$	0.66	0.33	0.33	0.66
Alcell Lignin	$CH_{1.15}O_{0.31}$	0.62	0.31	0.31	0.62

Because the yield of the product AP dissolved in the aqueous HI phase is not easily determined, $Y_{C/AP}$ is generally obtained by difference. Likewise the composition of AP, i.e. $(CH_k O_l I_m)_{AP}$, is difficult to determine reliably. Therefore it was not generally possible to apply fully the rigorous method based on balancing the stoichiometric Equation 5.11. An alternate method to determine the reaction stoichiometric coefficients a and c is by material balance before and after reaction by titration for $[H^+]$ and $[I_2]$. This material balance alternative leads to the following expressions determining the coefficients a and c:

$$a = \frac{(gmol\ H^+)_{before\ reaction} - (gmol\ H^+)_{after\ reaction}}{gmol\ C\ of\ substrate} \tag{5.14}$$

$$c = \frac{(gmol\ I_2)_{after\ reaction} - (gmol\ I_2)_{before\ reaction}}{gmol\ C\ of\ substrate} \tag{5.15}$$

By this method it is not possible to obtain the stoichiometric coefficient b, gmol H_2O produced/gmol C in substrate.

When as described in Sections 5.2.2 and 5.2.3 both the yield and the composition of the AP fraction is determined directly, the stoichiometric reaction Equation 5.11 can be solved for the stoichiometric coefficients, a, b and c.

5.2.2 Stoichiometric equation for wood liquefaction

The application of the reaction stoichiometric Equations 5.10 and 5.11 when complete yield and composition information is available is now compared with the procedure using Equations 5.14 and 5.15 when this information on the AP product fraction is not available. The abbreviated version with Equations 5.14 and 5.15 is demonstrated with the results of wood liquefaction for Experiment 78 at R = 4.4 gmol HI/gmol C in wood with initial concentration of solution 57 wt% HI for 15 min reaction time. The reaction stoichiometric coefficients a and c as determined by Equations 5.14 and 5.15, recorded in Appendix I.3, are

a = 0.72 gmol HI reacted/gmol C in wood
c = 0.33 gmol I_2 produced/gmol C in wood

The yield of the OP (OA + ON) product fraction, $Y_{C/OP}$, was 83.3%. The elemental composition of the OP fraction by direct elemental analysis for carbon, hydrogen, oxygen, and iodine content as detailed subsequently in Tables 5.1 and 5.2 was determined as $CH_{1.16}O_{0.16}I_{0.12}$. The carbon-base yield of CH_3I was determined to be 4.9%, Section 7.3. Therefore allowing for 4.9% yield of CH_3I, the carbon base yield of AP product obtained by difference from Equation 5.4 would be 11.8%.

The comparison case using the complete Equations 5.10 and 5.11 is demonstrated with the wood liquefaction results from Experiment 99, a replicate of Experiment 78 but for which the yield and elemental composition of the AP product fraction were determined directly. The aqueous solution after reaction was treated by 0.03 M $Na_2S_2O_3$ solution to reduce I_2 in the aqueous solution, which then was extracted by methylene chloride to obtain the organic product fraction AP. The CH_2Cl_2 phase was very slowly separated from the aqueous phase with a separatory funnel. In the distillation column that was used to remove the CH_2Cl_2 (b.p. 47.7°C) the methyl iodide (b.p. 42.4°C) produced from reaction of HI with methoxy groups in the lignin would also be removed. In order to obtain AP product free of CH_2Cl_2, HI and H_2O the material was evaporated for about 3 days under atmospheric conditions, then for 2h in a 50°C oven to constant weight.

The carbon base yield of the AP product fraction by this direct measurement was 15.9%, which compares reasonably to the AP yield of 11.8% obtained by difference from Equation 5.4 along with the estimated 4.9% yield of CH_3I. With this confirmation of satisfactory agreement for a yield which is very difficult to determine, the values of $Y_{C\,AP}$ for all other experiments were determined by difference using Equation 5.4.

The composition of the AP product by direct elemental analysis was determined to be $CH_{1.57}O_{0.20}I_{0.04}$. Therefore the reaction stoichiometric Equation 5.11 can be written for hybrid poplar liquefaction as

$$\begin{aligned} CH_{1.59}O_{0.70} + a\,HI = 0.833\ CH_{1.16}O_{0.16}I_{0.12}\ (OP) + 0.118\ CH_{1.57}O_{0.20}I_{0.04}\ (AP) \\ + 0.049\ CH_3I + b\,H_2O + c\,I_2 \qquad (5.16) \end{aligned}$$

All values in Equation 5.16 are those determined directly with the exception of the yield of the AP product fraction, 0.118, which is the value determined by difference. As the direct measurement of the AP fraction yield involves the most complex procedures and is then the determination most subject to error, the AP yield by difference is taken as a reasonable estimate in Equation 5.16 and is in fact the only basis available for all other sets of wood liquefaction experimental results.

By balancing Equation 5.16 for H, O, and I, as described earlier for Equation 5.11, the reaction stoichiometric coefficients are determined as:

$a = 0.79$ gmol HI reacted/gmol C in wood

$b = 0.54$ gmol H_2O produced/gmol C in wood

$c = 0.32$ gmol I_2 produced/gmol C in wood

By comparison, for ideal reaction with hybrid poplar as substrate producing a pure hydrocarbon product the stoichiometric coefficients gave in Section 5.2.1 are $a = 1.40$, $b = 0.7$ and $c = 0.7$. Thus for hybrid poplar liquefaction, the actual stoichiometric coefficient a, representing the extent of HI reaction with the substrate, is 56% of that for the ideal model, with stoichiometric coefficients b and c also substantially lower than those ideal values.

Therefore Equation 5.16 can be written as follows, with all stoichiometric coefficients now determined:

$$CH_{1.59}O_{0.70} + 0.79\ HI = 0.833\ CH_{1.16}O_{0.16}I_{0.12}\ (OP) + 0.118\ CH_{1.57}O_{0.20}I_{0.04}\ (AP) + 0.049\ CH_3I + 0.54\ H_2O + 0.32\ I_2 \qquad (5.17)$$

These values of the reaction stoichiometric coefficients, a and c, are close to the values of 0.72 and 0.33 obtained by Equations 5.14 and 5.15.

5.2.3 Stoichiometric equation for cellulose liquefaction

This comparison of application of the complete stoichiometric Equations 5.10 and 5.11 when complete yield and composition information is available, with the partial solution, Equations 5.14 and 5.15, when only partial data exists is demonstrated now for cellulose as substrate. For Experiment 86 at the same reaction conditions of R = 4.4 gmol HI/gmol C in cellulose, 57 wt% initial HI solution and 15 min reaction time, the reaction stoichiometric coefficients a and c determined by Equations 5.14 and 5.15, recorded in Appendix I.3, for the partial solution are a = 1.02 gmol HI reacted/gmol C in cellulose

c = 0.49 gmol I_2 produced/gmol C in cellulose

The yield of the OP (OA + ON) product fraction of cellulose liquefaction, Y_{COP}, was 72.7%. The elemental composition of the OP fraction by direct elemental analysis, listed subsequently in Table 5.3, was $CH_{1.49}O_{0.14}I_{0.19}$. In the absence of the methoxy groups of lignin, no methyl iodide is produced from cellulose and the yield of the AP product fraction by difference from Equation 5.4, is therefore Y_{CAP} = 27.3%.

For the comparison case of complete solution using Equations 5.10 and 5.11 the aqueous phase product fraction AP for a replicate test, Experiment 105, was obtained by treatment of the HI aqueous phase with $Na_2S_2O_3$ solution followed by methylene chloride extraction of the AP product. The yield of AP product fraction was thereby determined to be 29.2%, very close to the 27.3% yield obtained by difference from Equation 5.4. The elemental composition of AP product from cellulose was determined to be $CH_{1.63}O_{0.24}I_{0.03}$. Therefore the reaction stoichiometric Equation 5.11 can be written for cellulose liquefaction as

$$CH_{1.67}O_{0.83} + a\ HI = 0.727\ CH_{1.49}O_{0.14}I_{0.19}\ (OP) + 0.273\ CH_{1.63}O_{0.24}I_{0.03}\ (AP) + b\ H_2O + c\ I_2 \qquad (5.18)$$

Balancing Equation 5.18 for H, O and I gives:

$$CH_{1.67}O_{0.83} + 1.18\ HI = 0.727\ CH_{1.49}O_{0.14}I_{0.19}\ (OP) + 0.273\ CH_{1.63}O_{0.24}I_{0.03}\ (AP) + 0.66\ H_2O + 0.52\ I_2 \qquad (5.19)$$

Thus the reaction stoichiometric coefficients are:

a = 1.18 gmol HI reacted/gmol C in cellulose

b = 0.66 gmol H_2O produced/gmol C in cellulose

c = 0.52 gmol I_2 produced/gmol C in cellulose

By comparison with coefficients given in Section 5.2.1 for the ideal reaction with cellulose liquified to a pure hydrocarbon product, i.e. values of a, b and c of, respectively 1.66, 0.83 and 0.83, it is seen that the actual value of the stoichiometric coefficient "a" representing reactivity of the substrate with HI is 71% of that this ideal limit. The greater reactivity of HI with cellulose than with wood is shown by the stoichiometric coefficient "a" being 71% of the ideal limit with cellulose compared to 56% with wood as noted in Section 5.2.2. These reaction stoichiometric equations for both hybrid poplar and cellulose are in the range of those found by the previous work for hybrid poplar by Douglas et al., 1985, reviewed in Section 2.2.3 and for cellulose by Douglas and Sabade, 1984, reviewed in Section 2.2.2.

5.3 Evolution of wood liquefaction during short reaction time

The relations of reaction time - temperature - HI solution concentration during the liquefaction reaction with hybrid poplar were examined for short reaction times using initial HI concentrations of 57, 61 and 68 wt% HI. During batch reactor liquefaction the HI concentration drops because of HI reaction with wood as well as the production of H_2O of reaction, as discussed in Section 5.1.2 and shown in stoichiometric Equations 5.10 and 5.11. Reaction temperature varies corresponding to HI concentration when, for atmospheric pressure operation, reaction temperature is the bubble point of the liquid phase for the HI-H_2O system, Figure 5.1.

With 57 wt% initial concentration HI solution (Experiment 101 at R = 4.4 gmol HI/gmol C in wood) the initial temperature is that of the azeotrope, 127°C. Figure 5.2 shows that after only about 20s the reaction with HI is already effectively complete because the reaction temperature has dropped to 125°C with little further temperature

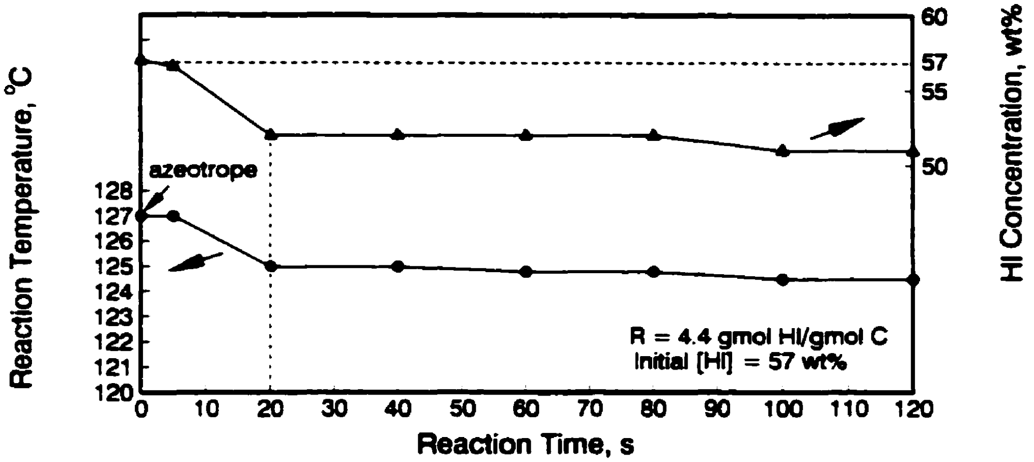


Figure 5.2 Reaction Temperature and HI Concentration During Reaction: Initial HI Concentration 57 wt%

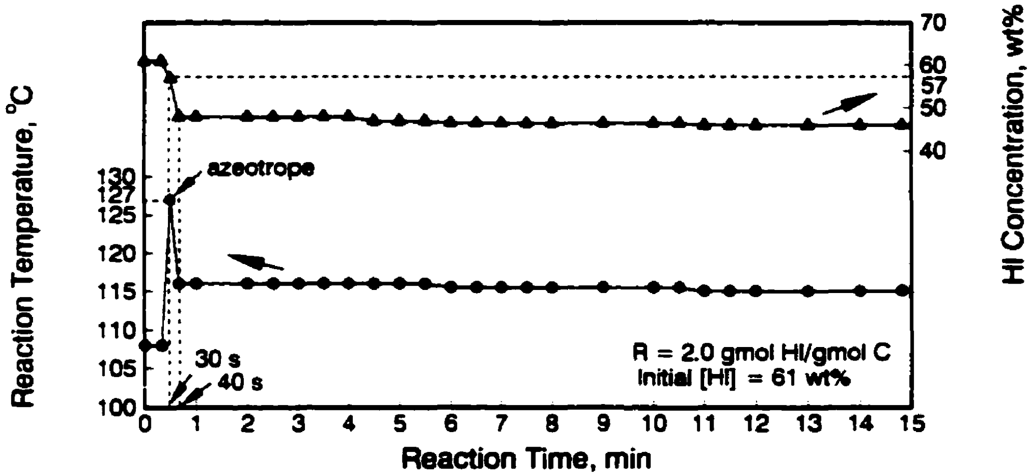


Figure 5.3 Reaction Temperature and HI Concentration During Reaction: Initial HI Concentration 61 wt%

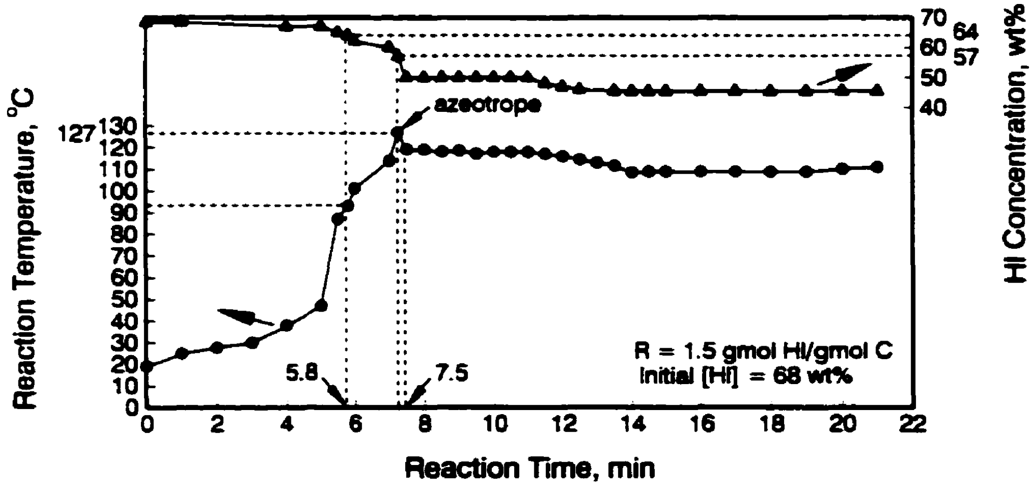


Figure 5.4 Reaction Temperature and HI Concentration During Reaction: Initial HI Concentration 68 wt%

decrease up to 120s reaction time. Specifically, after dropping 2°C in the first 20s of reaction, the reaction temperature decreased only 0.5°C in the next 100s. Thus the HI concentration dropped from the initial 57 wt% to about 52 wt% in 20s, to about 51 wt% after 120s reaction time. The values of HI concentration shown on Figure 5.2 are those from the T-x diagram, Figure 5.1, for the precisely measured temperature, except the initial and final values which were determined by analysis. The excellent agreement between HI concentration by the two methods confirms the correctness of using reactor temperature to monitor reactor HI concentration even though the aqueous HI solution after reaction contains a small amount of dissolved I_2 and aqueous phase soluble product.

As the reaction of HI with wood is largely completed in 20s with initial 57 wt% HI solution, it follows that all the I_2 produced in 15 min reaction is from wood reaction with HI in 20s reaction time with little I_2 produced by further reactions involving conversion of aqueous product AP into organic product OP in the following 14 min 40s. Therefore the rate of I_2 production from Equation 5.10 can be estimated by the amount of I_2 before and after reaction, Appendix I.6, with the relation

$$r_{I_2\,pro.} = \frac{(I_2,\, g)_{after\ reaction} - (I_2,\, g)_{before\ reaction}}{1/3\ \text{min}} \tag{5.20}$$

to be 113 g I_2/min or, alternately, by the stoichiometric coefficient c and amount of wood used with relation

$$r_{I_2\,pro.} = \frac{c\, M_{I_2}\, W_{wood} \,/\, M_{wood}}{1/3\ \text{min}} \tag{5.21}$$

to be 124 g I_2/min, where

c : stoichiometric coefficient, 0.32 gmol I_2/gmol C, Equation 5.16
M_{I_2} : molecular weight of I_2, 253.8
M_{wood} : formula weight of wood, $CH_{1.59}O_{0.70}$, 24.92
$r_{I_2\ pro.}$: I_2 production rate, g/min
W_{wood} : 12.68 g (1 − 0.0026) = 12.64 g,
(0.26% moisture in wood, Appendix I.1)

The rate of I_2 production determined by direct measurement of I_2 agrees well with that by the reaction stoichiometric coefficient. In 20s reaction about 40 g I_2 was produced by wood reaction with 57 wt% HI solution.

Figure 5.3 shows that with the initial HI concentration about 61 wt% (Experiment 77 at R = 2.0 gmol HI/gmol C in wood) the initial temperature was 108°C, which is consistent with the T-x diagram, Figure 5.1. At about 30s reaction time the reaction temperature had increased to the azeotrope temperature of 127°C, indicating that HI concentration had dropped from 61 wt% to the azeotrope temperature composition of 57 wt%. By 40s reaction the reaction temperature had now dropped to 116°C where it stabilized, indicating that by 40s HI concentration had dropped, according to Figure 5.1, to 46 wt%. When the reactor is charged with solution of HI content higher than the azeotrope and the reactor is operated at the bubble point temperature, the temperature - time profiles show very clearly how reaction temperature passes through a maximum as the bubble point passes through the HI-H_2O azeotrope composition, after which reaction temperature drops. In this case where in the space of 40 s reaction temperature passes from 108°C to 127°C and back to 116°C, the temperature - time profiles show that reaction with HI was effectively completed in about 40 s during which the 61 wt% initial HI solution was diluted by reaction to about 46 wt% HI.

With an initial HI concentration of about 68 wt%, (Experiment 76 at R = 1.5

gmol HI/gmol C in wood), for which the bubble point is about 40°C, Figure 5.4 shows that it required about 5.8 min of very slow reaction with HI in order to drop the HI concentration to about 64 wt% HI, corresponding to bringing the bubble point temperature to about 93°C from the room temperature, 20°C. This reaction time, although long compared to the cases of Figures 5.2 and 5.3 because of the lower reaction rate at lower temperature, none the less shows that at the higher HI concentration of 68 wt% and even at the exceptionally low stoichiometric ratio of R = 1.5 gmol HI/gmol C in wood used in this experiment, liquefaction reaction rates remain substantial even down to 40°C. The highest wood liquefaction reaction rate occurred in the 2 minute interval between 5.5 and 7.5 minutes, during which the reaction temperature went from about 90°C to the azeotrope temperature of 127°C, then back down to 120°C while HI concentration decreased from about 68 wt% to the 57 wt% azeotrope composition to 50 wt% HI. Thereafter the reaction temperature changed only slowly to 113°C, corresponding to 45 wt% HI concentration, while it was monitored for a total of 21 min reaction time. Thus this set of three experiments indicates that with aqueous HI at an initial concentration of 57 – 65 wt% HI, a reaction time of 1 – 2 min at most, and as little as 20 – 40s in some cases is sufficient for completion of the liquefaction reaction with HI.

Because of the coupling between reaction rate - reaction time - reaction temperature - HI concentration, with these all variable in batch reactor experiments, more precise conclusions are not possible. However in spite of these limitations the findings from this interesting set of batch reactor experiments have important implications for future optimization of the process variables of reactor residence time - reaction temperature - HI concentration for continuous wood liquefaction reactors operating at steady state conditions.

5.4 Effect on wood liquefaction of initial HI concentration: 15 – 68 wt%

The limits of aqueous phase HI concentration may be appreciated by examination of the T-x diagram for the HI-H_2O system, Figure 5.1. When operated at the bubble point temperature, reactor temperature decreases as reactor HI concentration is either increased or decreased from the value of 56.5 wt% at the maximum boiling azeotrope of 127°C. From batch reactor experiments starting with solution of initial concentration 56 – 57 wt% HI, Douglas et al., 1985 and Ng, 1985, established that the liquefaction reactions were not greatly affected by reaction temperature down to about 85 – 90°C, with the wood being effectively completely reacted in short reaction time. For HI concentrations below that of the azeotrope, Figure 5.1 shows that the reduction in bubble point temperature is not serious because at all HI concentrations on the dilute side of the azeotrope the temperature remains above 100°C. By contrast the bubble point temperature for HI-H_2O drops very sharply at compositions only slightly above that of the azeotrope, which limits the maximum HI concentration for operation at atmospheric pressure. For the present study the highest HI concentration tested was 68 wt% HI, for which the bubble point is about 40°C.

In batch reaction liquefaction of hybrid poplar the effect caused by varying both initial HI concentration and the HI/wood stoichiometric ratio, R, was investigated over the ranges of 15 – 68 wt% HI and 1.0 – 4.4 gmol HI/gmol C in wood. Reaction time was fixed at $t = 15$ min in order to correspond to conditions used in earlier work from this laboratory, Douglas et al., 1985, and Ng, 1985. For initial HI concentrations at and above the azeotrope composition the relations between initial and final reaction temperatures are shown on Figure 5.5. With 57 wt% initial HI concentration the reaction temperature drops continuously during reaction, starting from the azeotropic temperature of 127°C. The lower the stoichiometric ratio, R, naturally the larger is this temperature drop. Thus at values of R of 4.4, 3.5 and 2.0 gmol HI/gmol C in wood, the drop from initial to final temperature is respectively 5, 7 and 14°C. For liquefaction starting with [HI] of 61 or 68 wt% HI, Figures 5.3 and 5.4 showed that the reaction temperature starts below the azeotropic temperature, increases to a maximum at the azeotrope concentration, then drops. This double-valued reaction temperature history

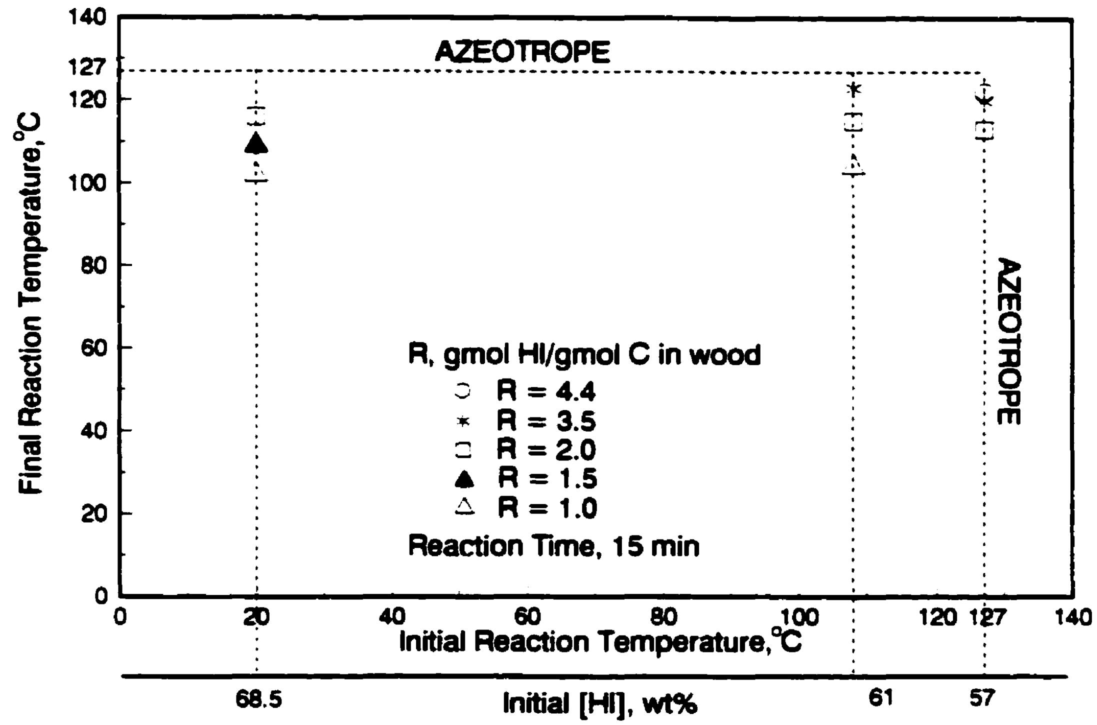


Figure 5.5 Relation between Initial and Final Reaction Temperature

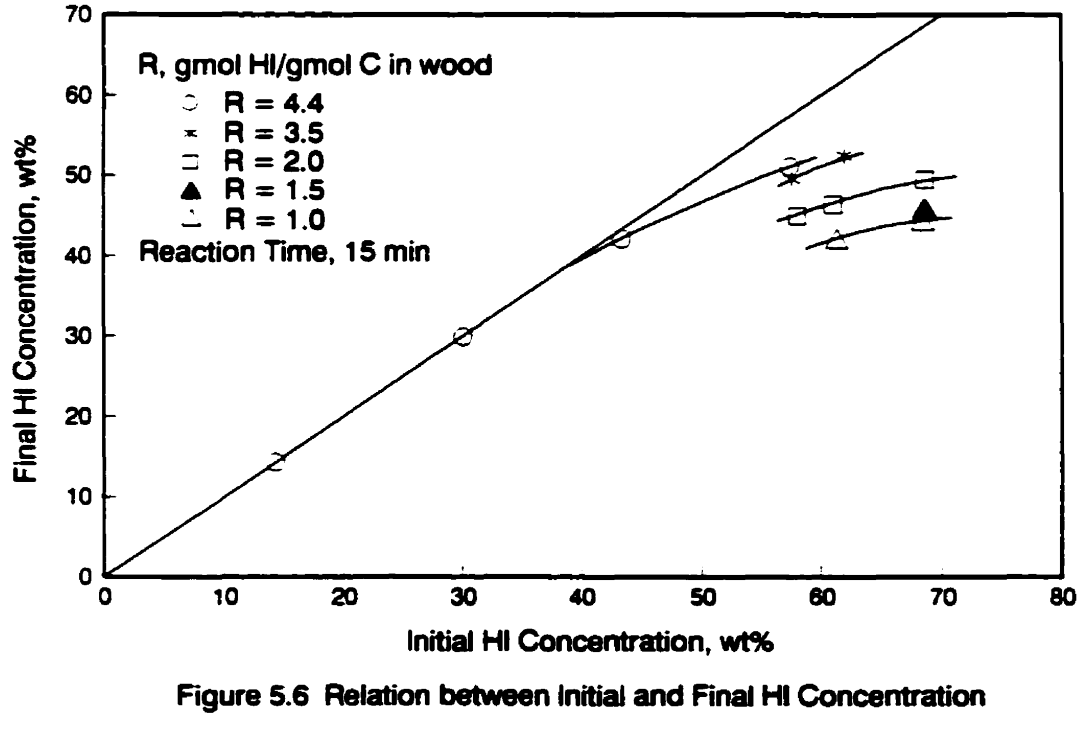


Figure 5.6 Relation between Initial and Final HI Concentration

occurs because the HI concentration drops continuously as H_2O is produced and HI consumed by the liquefaction reaction, so the reaction temperature follows the bubble point temperature from one side of the azeotrope composition to the other. Figure 5.5 shows just the initial and final values of the reaction temperature monitored continuously in Figures 5.2 – 5.4. These changes in reaction temperature and HI concentration are naturally more pronounced at lower R, for which the change in HI concentration is correspondingly higher, as shown in Figure 5.6. For initial concentration 45 wt% HI or less, the reactivity of HI acting as reducing agent becomes very small, as indicated by the negligible change in HI concentration.

Application of reaction stoichiometry Equations 5.10 and 5.11, or their partial solution as Equations 5.14 and 5.15, leads to the relations shown in Figures 5.7 and 5.8. At a particular value of stoichiometric ratio R the stoichiometric coefficients a and c increase with increasing initial HI concentration, as does HI conversion also, over the wide range from [HI] = 30 wt% below which there is negligible reactivity of HI acting as the reducing agent, up to the maximum concentration tested, 68 wt% HI. Figure 5.7 shows that, judged by the reaction stoichiometric coefficients a and c, wood-HI reactivity increases very sensitively with HI to wood stoichiometric ratio at low levels of R but approaches independence from stoichiometric ratio at higher values. Specifically, as R is increased from 1 to 2 to 3.5 to 4.4 gmol HI/gmol C in wood, those stoichiometric coefficients show increases first by about one-half, then by much less than that, then by a negligible change. As R_{model} = 1.4 gmol HI/gmol C in wood for "ideal" liquefaction to a pure hydrocarbon with wood as substrate, Section 5.2.1, these results indicate that a value of R/R_{model} of only (2.0/1.4 =) 1.4 times this theoretical value is sufficient to obtain about 90% of the maximum reactivity between HI and wood, while (3.5/1.4 =) 2.5 times this theoretical value gives the maximum HI-wood reactivity beyond which further increases in R provide no further increase in HI-wood reactivity.

Methyl iodide is produced quantitatively from wood when the HI concentration is 57 wt% or greater, and to a lesser extent at low HI concentration. Therefore the

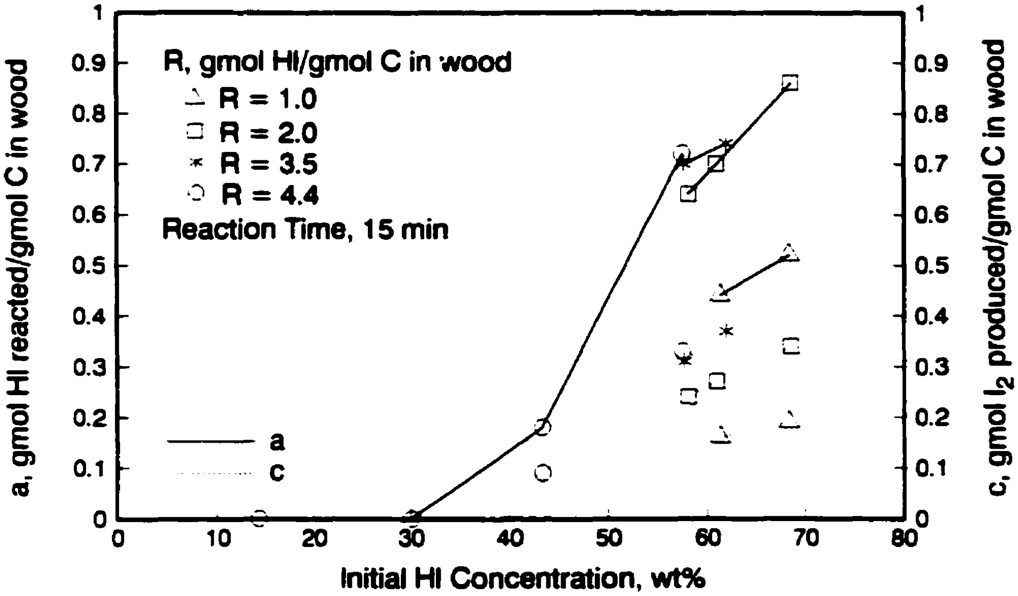


Figure 5.7 Effect of Initial HI Concentration on Stoichiometric Coefficients

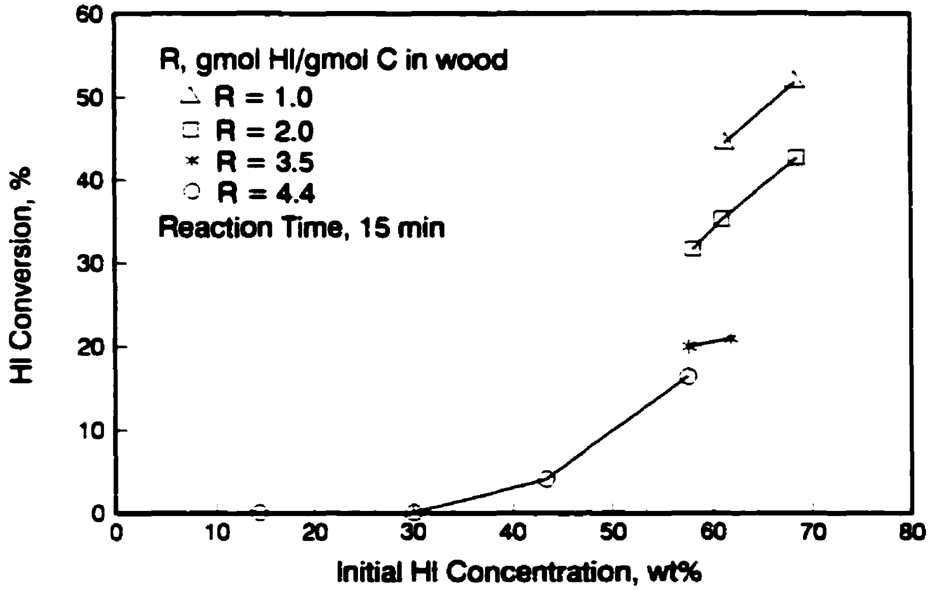


Figure 5.8 Effect of Initial HI Concentration on HI Conversion

yields of CH_3I and the AP product fraction are combined in Figure 5.9. This figure shows that at a constant value of the stoichiometric ratio R, increasing the initial HI concentration has the effect of increasing the yield of the desirable product fraction OA, at the expense of decreasing that of the undesirable product fraction ON, and of the aqueous phase soluble product fraction AP. When using 57 wt% initial HI concentration, R = 3.5 gmol HI/gmol C in wood is sufficient to eliminate production of ON. Figure 5.9 indicates that when the initial HI concentration is increased only to about 64 wt% HI, the yield of ON can be suppressed totally with R = 2 gmol HI/gmol C in wood, where this value of R is only 43% higher than R_{model} value of 1.4 gmol HI/gmol C in wood. Determination by this study that the yield of the most desirable and least desirable product fractions, OA and ON, are very sensitive to HI concentration represents a significant contribution. These results open the possibility of determining the optimum combination of R and aqueous phase HI concentration for a continuous liquefaction reactor where there is no need to operate at the azeotropic composition.

For the severity of conditions just sufficient to eliminate any production of the undesired ON product fraction, it is of interest to consider the final rather than the initial HI concentration. Thus the conditions noted above of R = 3.5 gmol HI/gmol C in wood and initial [HI] = 57 wt% corresponds according to Figure 5.6 to final HI concentration of about 49 wt%, while R = 2 gmol HI/gmol C in wood and initial [HI] = 64 wt% corresponds to final HI concentration of about 48 wt%. These observations suggest that any combination of R and initial HI concentration which results in final HI concentration of around 48 – 49 wt% of HI or higher would be sufficient to eliminate completely the undesired acetone-insoluble ON product fraction. As any practical wood liquefaction would be operated as a continuous not a batch reactor, it is a potentially important finding that just under 50 wt% HI at the exit of a continuous reactor may be sufficient to completely suppress production of any char-like product in this liquefaction process.

As HI initial concentration is increased from 57 to 68 wt%, the yield of OP approaches 100% as the yields of the AP and ON fractions approach zero, Figure 5.9,

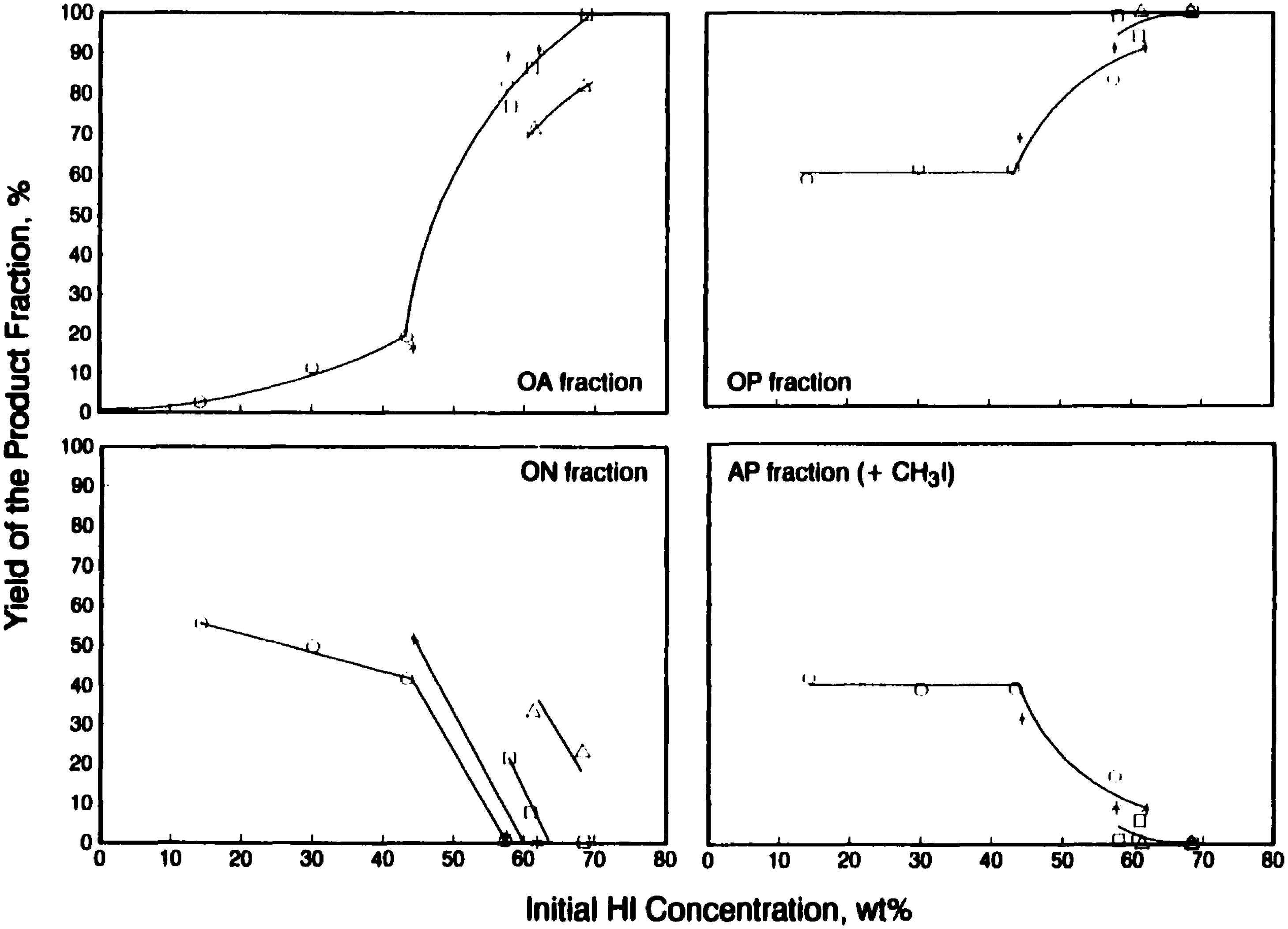


Figure 5.9 Effect of Initial HI Concentration on Yield of Product Fractions

R, gmol HI/gmol C in wood, △ R = 1.0 ♦ R = 3.5
□ R = 2.0 ○ R = 4.4

Reaction Time, 15 min

even at the very low value of R of 2.0 gmol HI/gmol C. This low value of R may be judged by the limiting value for "ideal" reaction to a pure hydrocarbon where, for hybrid poplar as substrate, R_{model} = 1.4 gmol HI/gmol C. It should be recalled from Figure 5.6 that for R fixed at 2.0 gmol HI/gmol C, increasing initial HI concentration from 57 to 68 wt% increases the final concentration from 45 to 49 wt% HI. Aside from changes in product solubility with HI concentration, the finding that at R = 2.0 gmol HI/gmol C the yield of the acetone-insoluble residue fraction ON decreases from 22% to zero as initial HI concentration is increased from 57 to 68 wt% shows that the reaction chemistry has changed, with no more acetone-insoluble product. With both the reaction chemistry and product solubility in the aqueous phase changing with HI concentration it is not possible to identify to what extent the changes in results are due to changed chemistry or changed solubility. However the total elimination of the insoluble residue product, ON, at higher HI concentration suggests that changes in reaction chemistry are dominant.

Figure 5.9 also shows that when the initial HI concentration is lower than 45 wt% at R = 4.4 gmol HI/gmol C, the yields of OP and AP become constant at about 60% and 40%. This organic phase product OP is however of very low quality, mostly the acetone-insoluble residue, ON, which in fact is approaching unreacted wood as will be indicated by the compositions in Table 5.1. The relatively high yield of AP product at the lower HI acidity condition, initial [HI] < 45 wt%, indicates that wood is easily converted to an aqueous phase soluble product at relatively weak reaction conditions. Douglas and Sabade, 1984, Douglas et al., 1985, and Ng, 1985, concluded that cellulose and wood were converted initially to an aqueous phase product then subsequently, at a lower reaction rate, to an organic phase product. The present data provides experimental evidence in support of that earlier hypothesis, based on limited information, that the wood hydrolysis reaction catalyzed by H^{+} is fast and is the first step of wood liquefaction with HI solution.

Figure 5.10 shows that for a wide range of HI stoichiometric ratio, R of 2.0 to 4.4 gmol HI/gmol C in wood, the extent of deoxygenation of the OP product is

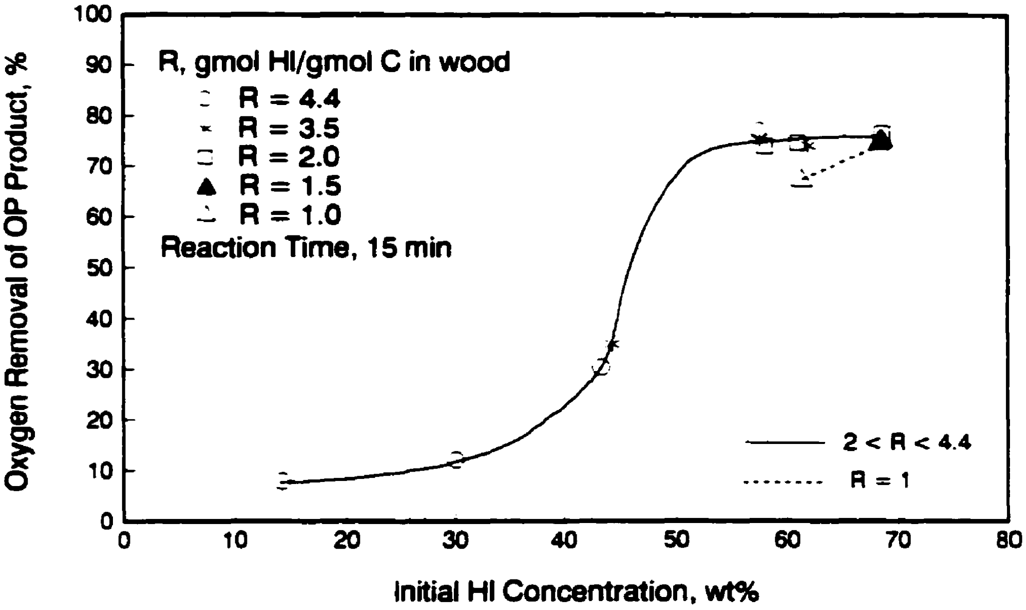


Figure 5.10 Effect of Initial HI Concentration on Oxygen Removal of OP Product

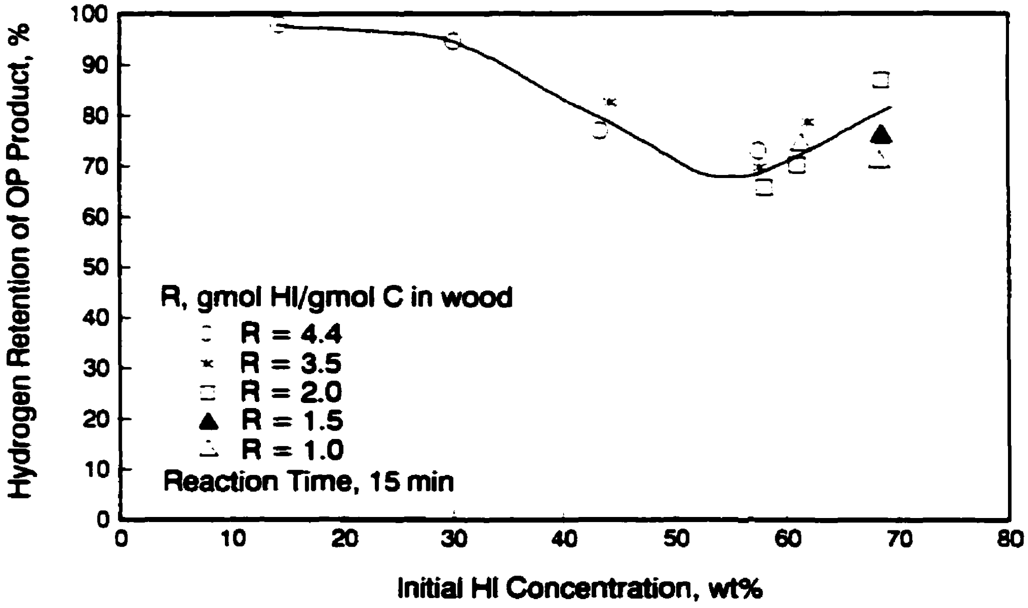


Figure 5.11 Effect of Initial HI Concentration on Hydrogen Retention of OP Product

insensitive to initial HI concentration from 68 wt% down to 57 wt%, but deoxygenation of OP drops off precipitously at some concentration not much less than 57 wt%. Figure 5.11 shows that the hydrogen retention of OP improves for initial HI concentration above 57 wt%, perhaps by a hydrogen donor effect with the more concentrated HI solution minimizing the loss of hydrogen from the principal product, as reviewed in Section 2.2.6. Whatever the reaction mechanism, clearly initial HI concentrations above 57 wt% change the reaction chemistry, as was indicated also in Figure 5.9 by the elimination of acetone-insoluble residue fraction. The fact that hydrogen retention increases for HI concentrations less than 45 wt% is of no practical interest because Figure 5.10 shows that oxygen removal correspondingly becomes negligible. The AP fraction from reaction with initial HI concentration lower than 45 wt% HI was not obtained for analysis. The complete product composition data from which Figures 5.10 and 5.11 derive are shown in Table 5.1.

With respect to the composition of the ON fraction, it is seen in Table 5.1 that for initial [HI] below 45 wt% the nature of ON simply approaches that of only lightly reacted wood, hence the high H/C and O/C ratios, nearly those of wood, and very low I/C ratio, nearly zero. For initial [HI] higher than 45 wt% the low H/C ratio of the ON fraction distinguishes this char-type product from the desirable OA fraction with its high H/C ratio.

The values of I/C in the OP product fraction are dependant on I_2 concentration in the aqueous solution, Figure 5.12. The final I_2 concentration in the solution is in turn related to initial HI concentration and to HI/wood stoichiometric ratio R, Figure 5.13, in a type of relation paralleling that for the stoichiometric coefficient c for I_2 production in Figure 5.7.

These yield and elemental composition data establish that wood reacts only weakly with HI at low levels of initial HI concentration, < 45 wt%. Also it appears that as initial HI concentration decreases below 57 wt%, dehydration reactions drop off very sharply while wood hydrolysis continues to the lowest levels of HI concentration tested, 15 wt% HI. However a clear trend is established for both a more favourable distribution

Table 5.1 Effect on Product Composition of Initial HI Concentration: 14 to 68 wt%

R, gmol HI/gmol C	1.0	1.5	2.0	3.5	4.4
			OA Fraction		
$[HI]_{initial}$, wt%					
14					$CH_{1.48}O_{0.293}I_{0.071}$
30					$CH_{1.25}O_{0.251}I_{0.085}$
44				$CH_{1.16}O_{0.249}I_{0.052}$	$CH_{1.15}O_{0.237}I_{0.048}$
57			$CH_{1.45}O_{0.129}I_{0.106}$	$CH_{1.31}O_{0.164}I_{0.084}$	$CH_{1.31}O_{0.146}I_{0.075}$
61	$CH_{1.36}O_{0.160}I_{0.105}$		$CH_{1.28}O_{0.153}I_{0.095}$	$CH_{1.37}O_{0.100}I_{0.075}$	
68	$CH_{1.39}O_{0.115}I_{0.090}$	$CH_{1.31}O_{0.122}I_{0.105}$	$CH_{1.35}O_{0.122}I_{0.101}$		
			ON Fraction		
$[HI]_{initial}$, wt%					
14					$CH_{1.54}O_{0.655}I_{0.003}$
30					$CH_{1.46}O_{0.638}I_{0.005}$
44				$CH_{1.41}O_{0.530}I_{0.005}$	$CH_{1.43}O_{0.541}I_{0.004}$
57			$CH_{1.01}O_{0.197}I_{0.032}$	$CH_{1.07}O_{0.196}I_{0.020}$	
61	$CH_{1.17}O_{0.214}I_{0.031}$				
68	$CH_{1.21}O_{0.244}I_{0.039}$	$CH_{0.99}O_{0.143}I_{0.050}$			
			OP Fraction		
$[HI]_{initial}$, wt%					
14					$CH_{1.56}O_{0.645}I_{0.007}$
30					$CH_{1.50}O_{0.616}I_{0.031}$
44				$CH_{1.31}O_{0.456}I_{0.023}$	$CH_{1.22}O_{0.488}I_{0.021}$
57			$CH_{1.04}O_{0.182}I_{0.169}$	$CH_{1.11}O_{0.172}I_{0.135}$	$CH_{1.16}O_{0.161}I_{0.124}$
61	$CH_{1.18}O_{0.230}I_{0.130}$		$CH_{1.12}O_{0.178}I_{0.170}$	$CH_{1.25}O_{0.181}I_{0.140}$	
68	$CH_{1.13}O_{0.178}I_{0.196}$	$CH_{1.21}O_{0.175}I_{0.214}$	$CH_{1.38}O_{0.165}I_{0.211}$		

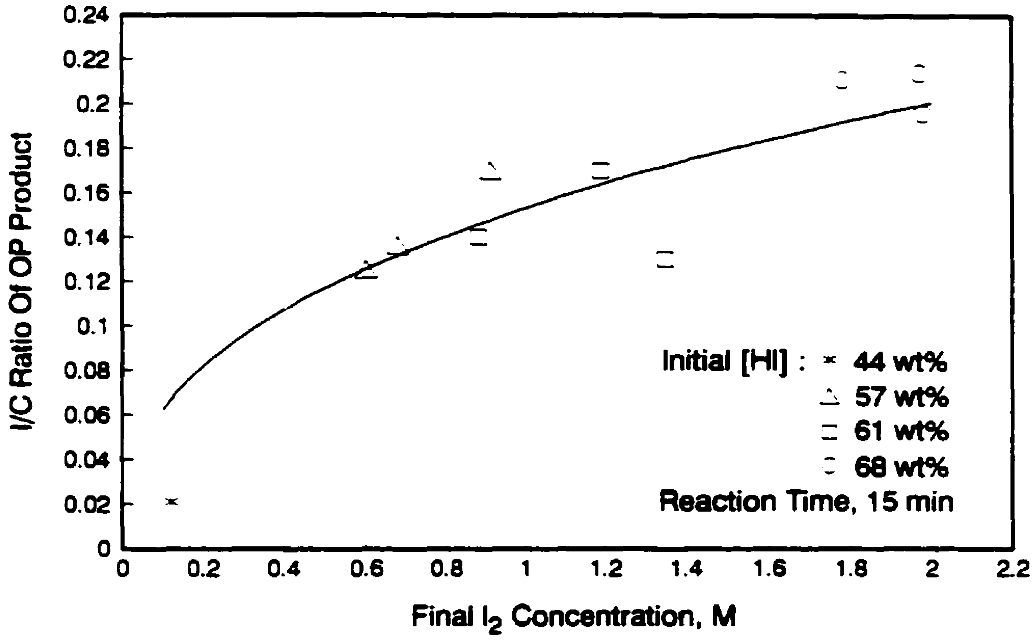


Figure 5.12 Effect of Final I_2 Concentration on I/C Ratio of OP Product

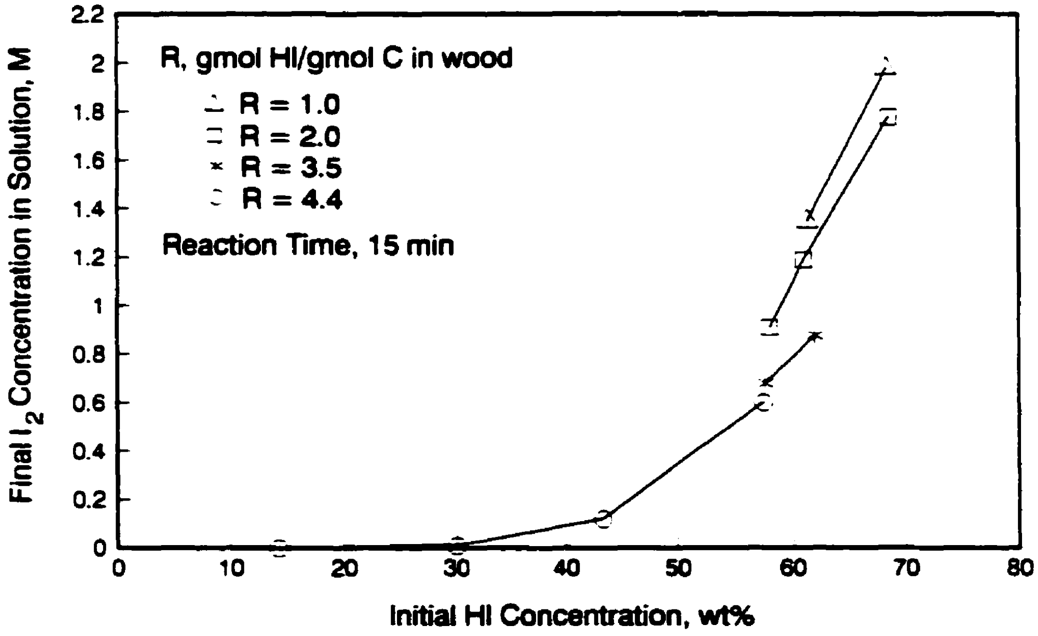


Figure 5.13 Effect of Initial HI Concentration on the Final I_2 Concentration

in yield between desirable and undesirable product fractions, and an improved hydrogen retention and improved oxygen removal as initial HI concentration is increased from 45 wt% through what has in previous work been the typical level, 57 wt% of HI, to the maximum concentration tested, 68 wt% of HI. These results thus open new possibilities for future optimization of the conditions of this wood liquefaction process in a continuous flow reactor operating at steady state conditions.

The data of Section 5.4 are detailed in Appendices I and J.

5.5 Effect on wood liquefaction of initial HI concentration: 57 – 68 wt%

As the results presented in section 5.4 establish that wood liquefaction is ineffective at the initial HI concentration as low as 45 wt% and is effective at the final concentration just below 50 wt%, additional experiments with the stoichiometric ratio extended up to 13 gmol HI/gmol C in wood were carried out. Reaction time was maintained the same, at t = 15 min. Reaction temperature, a dependent variable with the research technique used here, was maintained at the bubble point of the aqueous phase, Figure 5.1.

The interacting effects of R and initial and final HI concentrations are shown on Figures 5.14 – 5.19. The extent of the liquefaction reactions, as measured by the coefficients a and c of the stoichiometric Equation 5.10, is seen on Figure 5.14 to increase with R and initial HI concentration, particularly in the low range of HI/wood stoichiometric ratio. At R = 2 gmol HI/gmol C in wood it is impressive that the HI coefficient, a, increases by 1/3 when initial HI concentration is increased from 57 to 68 wt%. Although this coefficient increases with both R and [HI], it increases much more sensitively with HI concentration than with R. Therefore the fraction HI converted (X_{HI} = a/R), in fact decreases strongly with R, as is shown by Figure 5.15.

As the results of section 5.3 establish the reaction of HI with wood to be completed typically in less than a minute, and as final HI concentration is a function

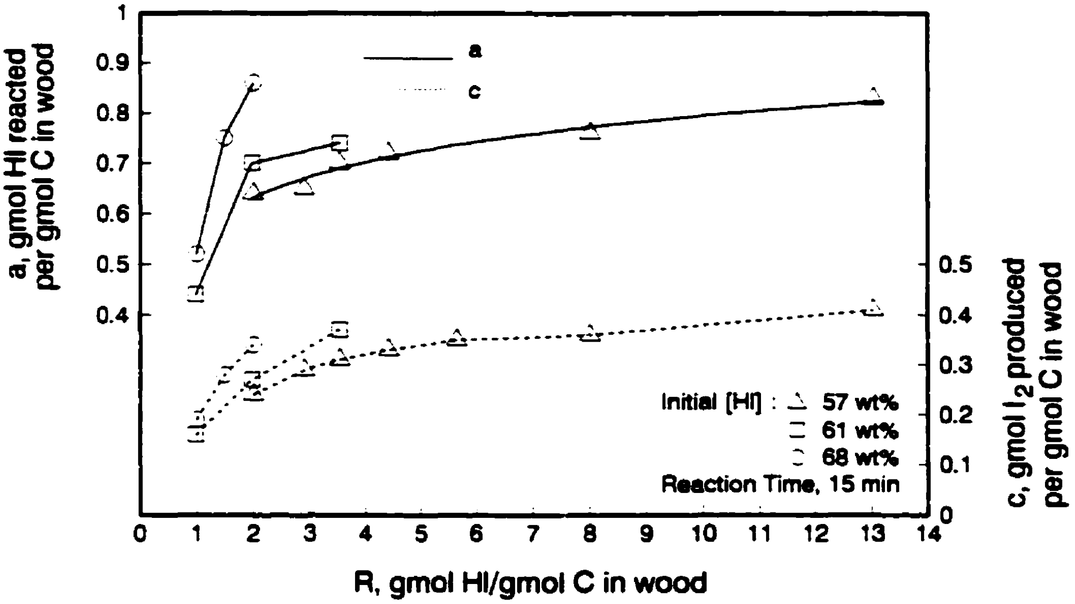


Figure 5.14 Effect of HI/Wood Stoichiometric Ratio on Stoichiometric Coefficients

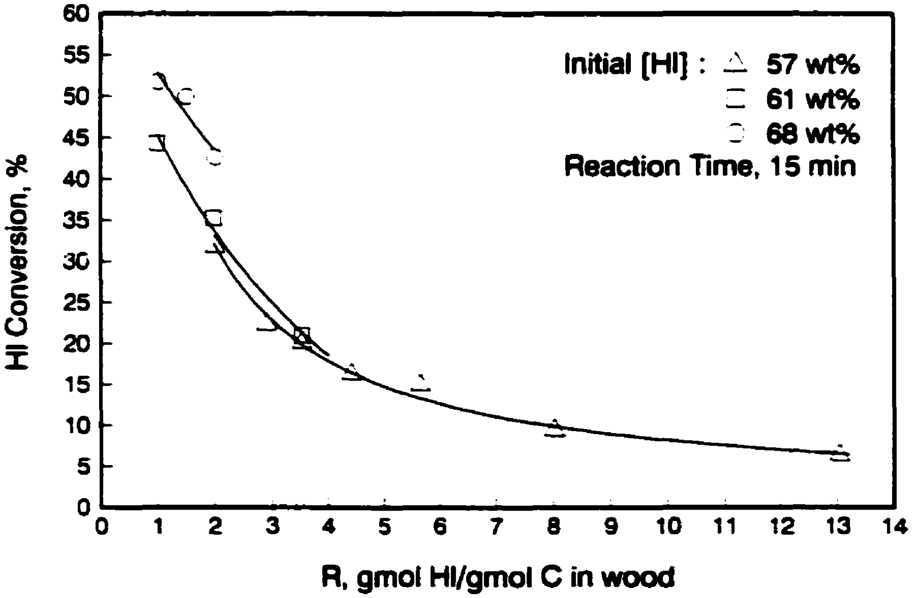


Figure 5.15 Effect of HI/Wood Stoichiometric Ratio on HI Conversion

of initial HI concentration and the stoichiometric ratio R, this suggests relating reaction characteristics directly to final HI concentration. The relationship between R and initial and final HI concentrations, displayed first as Figure 5.6, is now give with the additional data as Figure 5.16. When the reaction stoichiometric coefficients a and c of Figure 5.14 are related to final HI concentration, Figure 5.17 shows that no additional parameter such as stoichiometric R is required. This demonstration of the dominant role of final HI concentration in determining these reaction characteristics of the HI-wood reaction constitutes a new perspective on this technique of wood liquefaction.

At 3 levels of initial HI concentration the effect of HI:wood ratio R on yield of the various product fractions is displayed on Figure 5.18, where, as noted in connection with Figure 5.9, the yield of AP product and CH_3I are combined. The combination of higher values of HI:wood stoichiometric ratio and initial HI concentration is seen to be highly effective in reducing the yield of the undesirable fraction, ON, and correspondingly increasing the yield of the OA fraction.

As Figure 5.17 demonstrated that the stoichiometric coefficients may be related to a single variable, final HI concentration, rather than to the two variables, initial HI concentration and R, this approach was tested further by expressing the yield data of Figure 5.18 as a function of final HI concentration on Figure 5.19. The only product fraction yield that appears to be a unique function of final HI concentration is that for the ON product. Thus Figure 5.19 indicates that this undesired product fraction can be eliminated by any combination of initial [HI] and R which give final [HI] of 50 wt% or greater. Figures 5.18 and 5.19 show that the yield of the OA product fraction is clearly dependent on two of the three variables, stoichiometric ratio R and initial or final HI concentration. Figure 5.18 is more informative concerning yields of the product fractions OA, OP and AP because it is evident that as R is increased the yield of the AP fraction dissolved in the aqueous HI phase must increase, which necessarily decreases the yields of the OP and OA product fractions.

Over the range $1 < R < 3.5$ gmol HI/gmol C in wood, by increasing the initial [HI] from 57 to 68 wt% the hydrogen retention of the OP product fraction can be

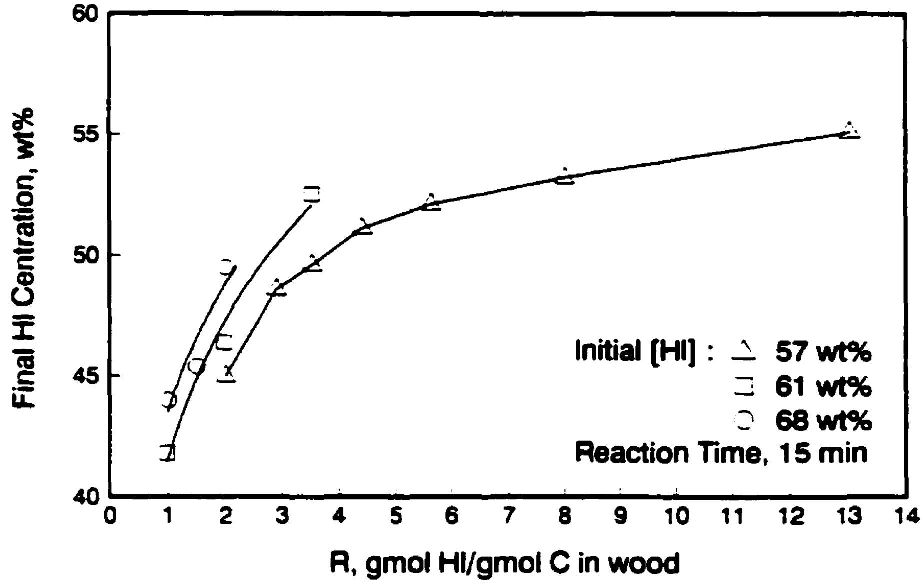


Figure 5.16 Effect of HI/Wood Stoichiometric Ratio on Final HI Concentration

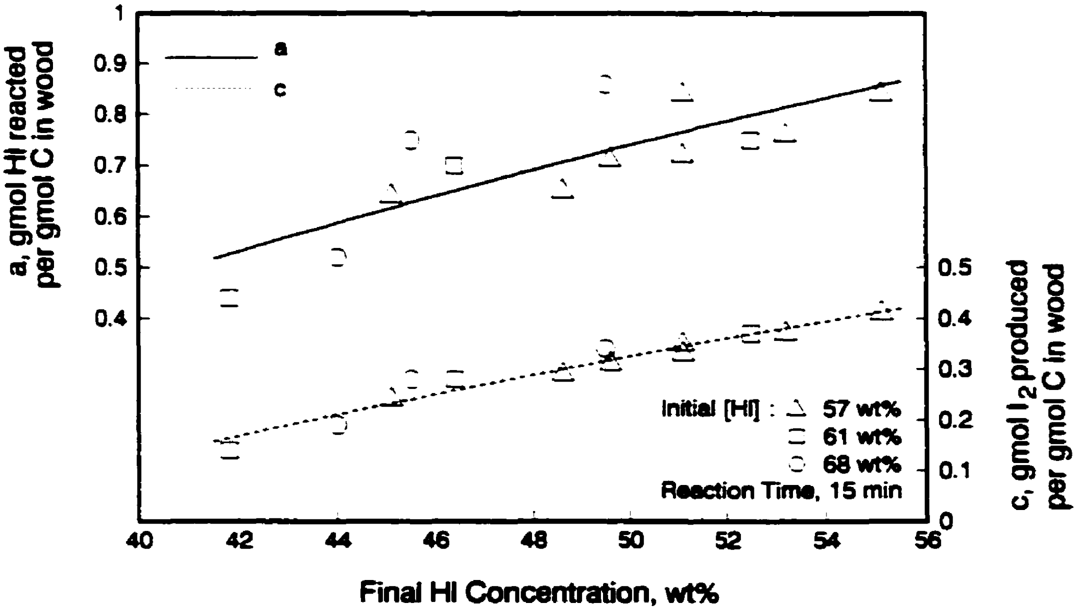


Figure 5.17 Effect of Final HI Concentration on Stoichiometric Coefficients

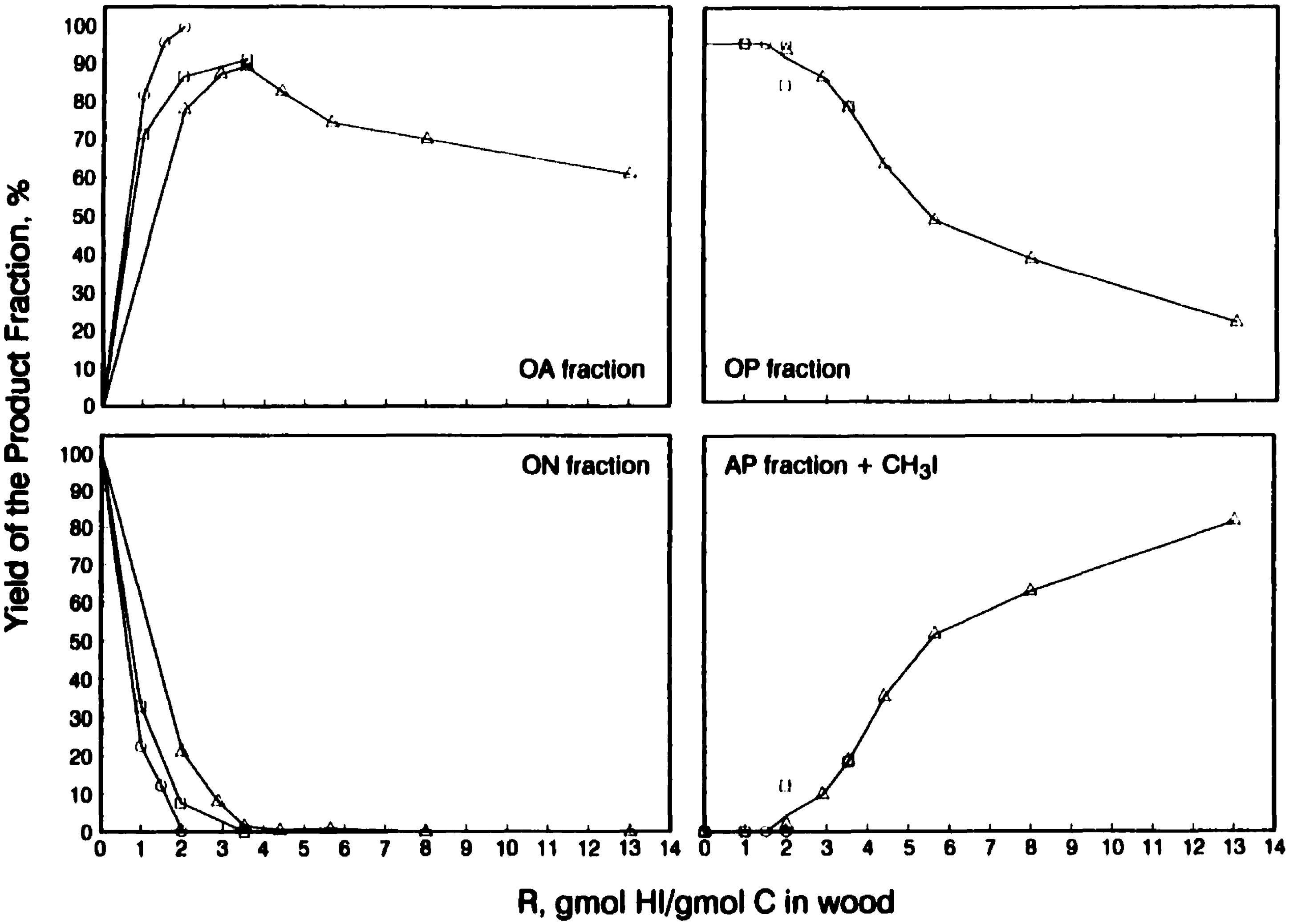


Figure 5.18 Effect of HI/Wood Stoichiometric Ratio on Yield of Product Fractions

Initial [HI] : △ 57 wt%
□ 61 wt%
○ 68 wt%

Reaction Time, 15 min

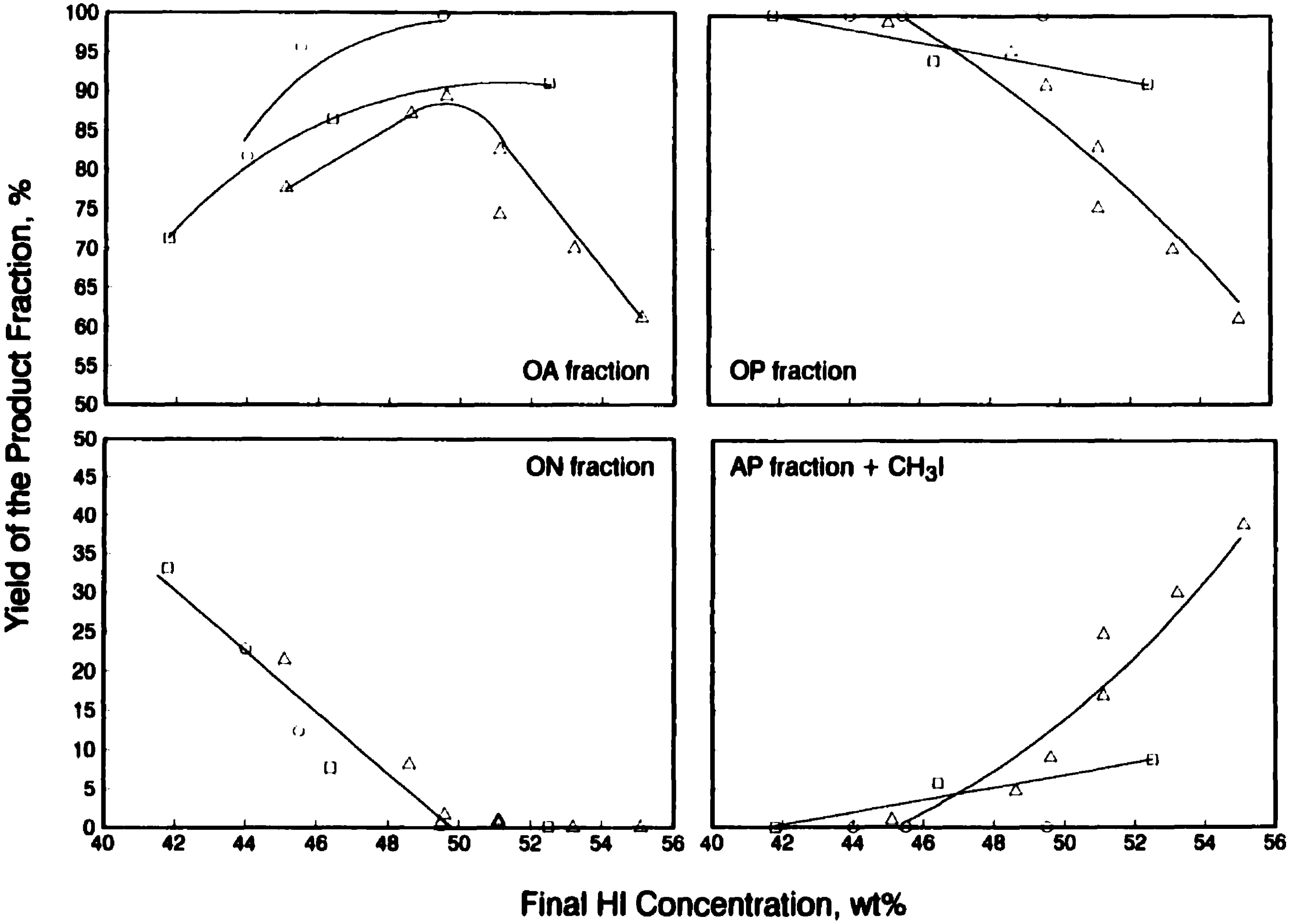


Figure 5.19 Effect of Final HI Concentration on Yield of Product Fractions

Initial [HI] : △ 57 wt%
□ 61 wt%
○ 68 wt%

Reaction Time, 15 min

increased by about 10 percentage points, i.e. in about direct proportion to initial HI concentration, Figure 5.20. The reason for this effect could be that the higher HI concentration solution acting as a better H^{-} donor reduces hydrogen loss from the organic product, as reviewed in Section 2.2.6. Above about R = 3 gmol HI/gmol C, the percent oxygen removal appears independent of stoichiometric ratio, Figure 5.21, but for R in the more important range 1 – 2 gmol HI/gmol C, a higher [HI] produces a more deoxygenated wood oil. When hydrogen retention and oxygen removal for the OP product is examined in Figures 5.22 and 5.23 relative to final HI concentration, the variability with the other parameter, initial HI concentration, is still present. Considering the four relations, Figures 5.20 – 5.23, hydrogen retention clearly shows more variability over this range of reaction conditions than does the level of deoxygenation of the OP product.

The I/C ratio of the OP product fraction appears related directly to the final I_2 concentration in the aqueous phase, Figure 5.24, in the same way as recorded on Figure 5.12 for experiments over the wider range of 15 – 68 wt% initial HI concentration. The relationship between final I_2 concentration, initial HI concentration and HI/wood stoichiometric ratio R is shown in Figure 5.25. The complete product composition data from which Figures 5.20 – 5.25 derive are given in Table 5.2.

The data of Section 5.5 are detailed in Appendices I and J.

5.6 Liquefaction of components of wood

Five substrates, hybrid poplar, microcrystalline cellulose, xylan, alkali lignin and Alcell lignin, were subjected to batch reactor liquefaction for 15 min using 57 wt% HI solution over the range of R from 2 to 8 gmol HI/gmol C in substrate. The corresponding elemental formulae of these substrates are, respectively, $CH_{1.59}O_{0.70}$, $CH_{1.67}O_{0.83}$, $CH_{1.61}O_{0.79}$, $CH_{1.15}O_{0.33}$ and $CH_{1.15}O_{0.31}$, as detailed in Section 5.1.3.

When the results are expressed as the stoichiometric Equations 5.10 and 5.11,

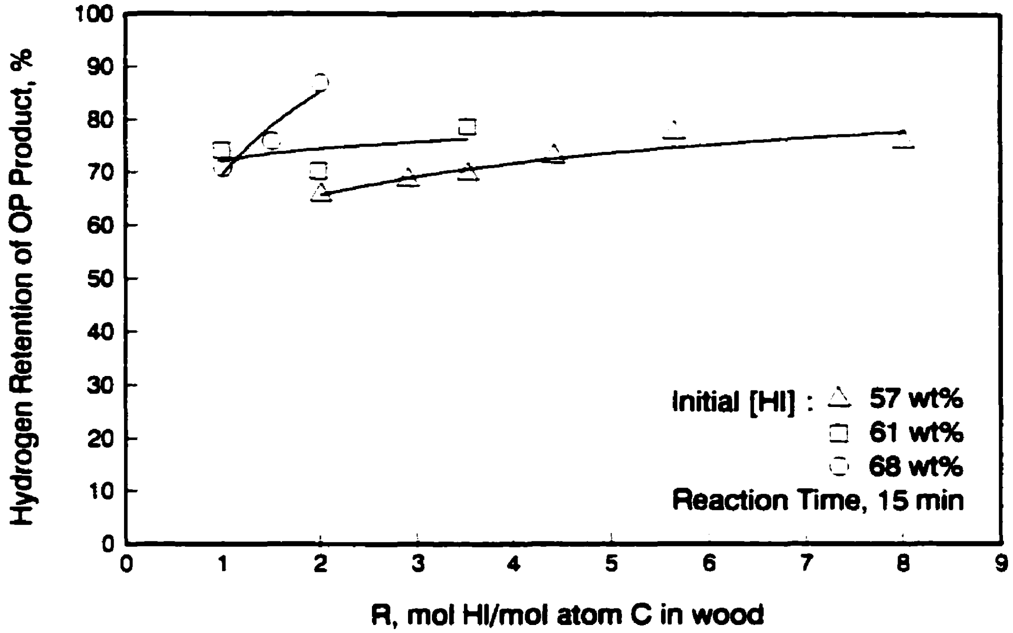


Figure 5.20 Effect of HI/Wood Stoichiometric Ratio on Hydrogen Retention of OP Product

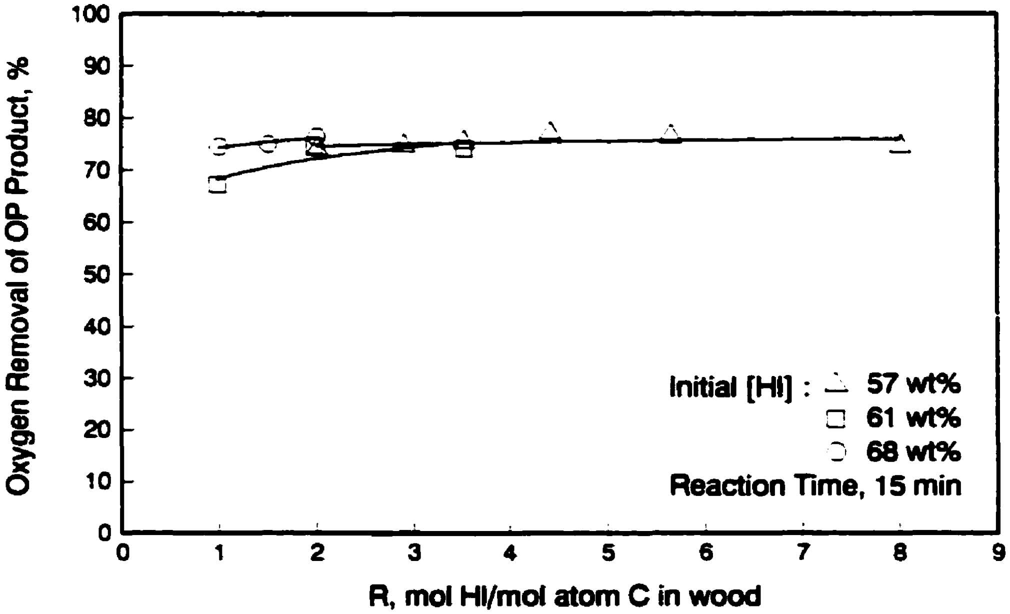


Figure 5.21 Effect of HI/Wood Stoichiometric Ratio on Oxygen Removal of OP Product

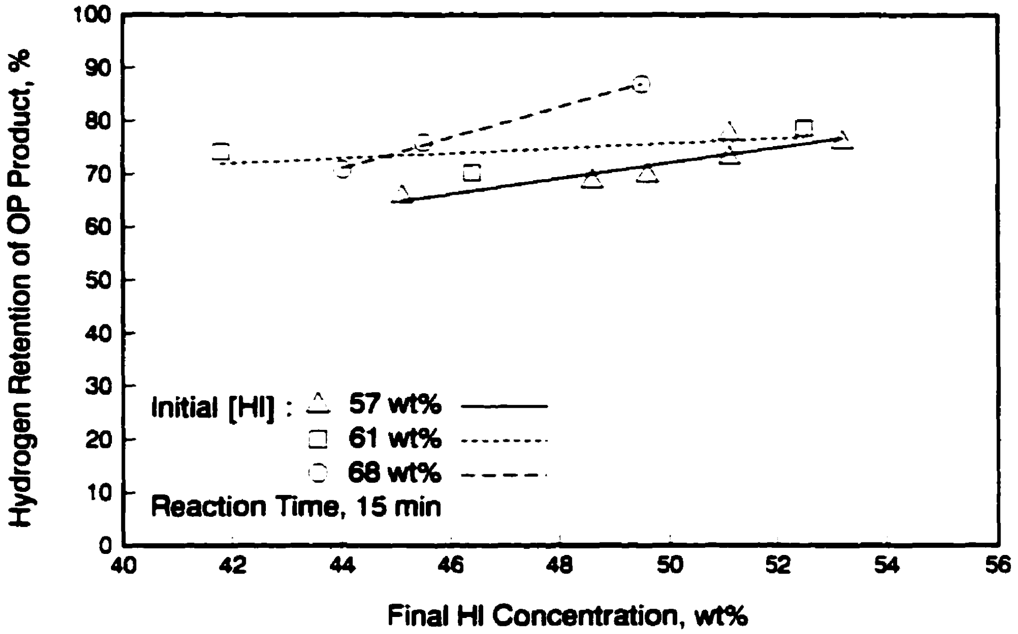


Figure 5.22 Effect of Final HI Concentration on Hydrogen Retention of OP Product

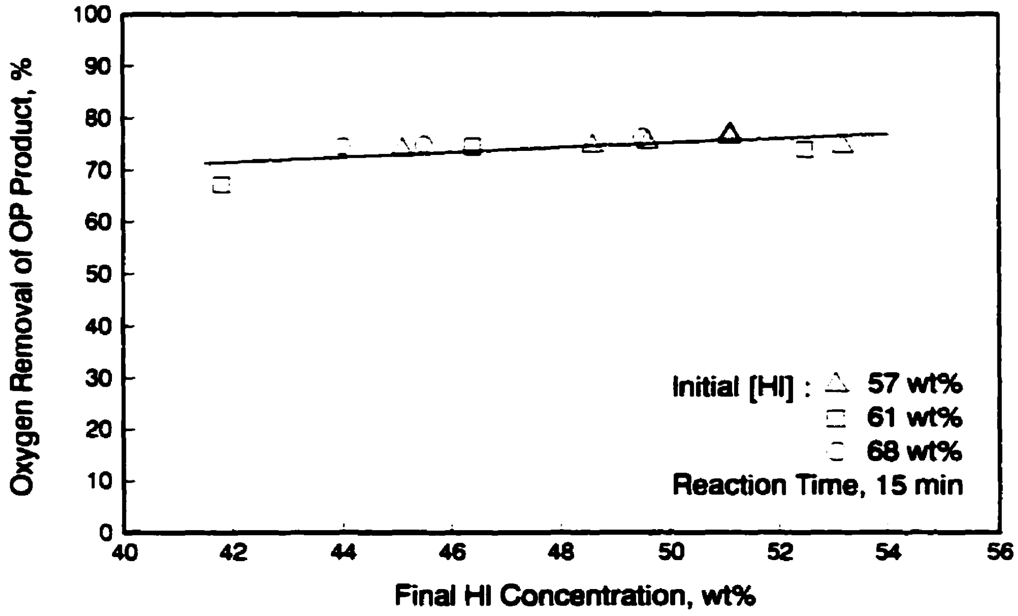


Figure 5.23 Effect of Final HI Concentration on Oxygen Removal of OP Product

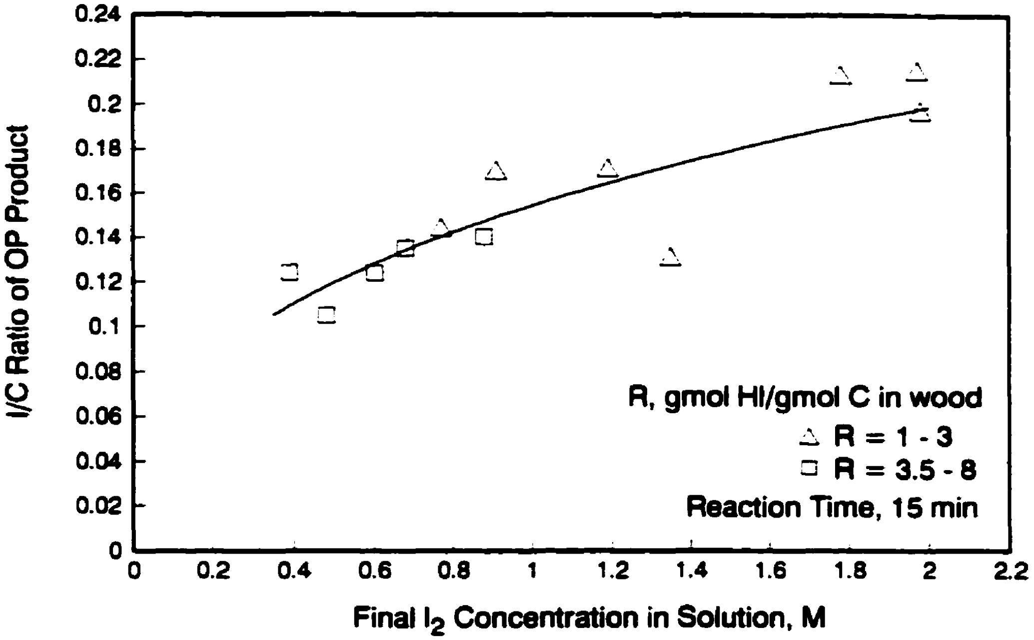


Figure 5.24 Effect of Final I_2 Concentration on I/C Ratio of OP Product

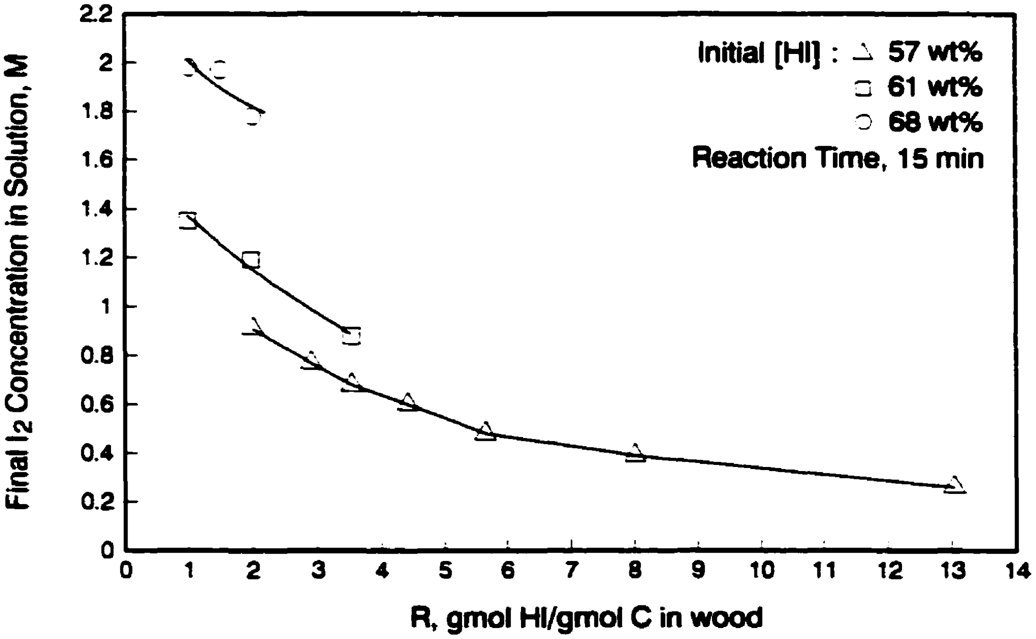


Figure 5.25 Effect of HI/Wood Stoichiometric Ratio on Final I_2 Concentration in Solution

Table 5.2 Effect on Product Composition of Initial HI Concentration: 57 to 68 wt%

	HI concentration		
	57 wt%	61 wt%	68 wt%
	OA Fraction		
R, gmol HI/gmol C			
1		$CH_{1.36}O_{0.160}I_{0.105}$	$CH_{1.39}O_{0.115}I_{0.090}$
1.5			$CH_{1.31}O_{0.122}I_{0.105}$
2	$CH_{1.45}O_{0.129}I_{0.103}$	$CH_{1.28}O_{0.153}I_{0.095}$	$CH_{1.35}O_{0.122}I_{0.101}$
2.9	$CH_{1.38}O_{0.164}I_{0.111}$		
3.5	$CH_{1.31}O_{0.164}I_{0.084}$	$CH_{1.37}O_{0.100}I_{0.075}$	
4.4	$CH_{1.31}O_{0.146}I_{0.076}$		
5.6	$CH_{1.32}O_{0.140}I_{0.071}$		
8.0	$CH_{1.32}O_{0.143}I_{0.071}$		
	ON Fraction		
R, gmol HI/gmol C			
1		$CH_{1.17}O_{0.214}I_{0.031}$	$CH_{1.21}O_{0.244}I_{0.039}$
1.5			$CH_{0.99}O_{0.143}I_{0.045}$
2	$CH_{1.01}O_{0.197}I_{0.032}$		$CH_{1.35}O_{0.122}I_{0.101}$
2.9	$CH_{1.08}O_{0.192}I_{0.019}$		
3.5	$CH_{1.07}O_{0.196}I_{0.020}$		
4.4			
5.6			
8.0			
	OP Fraction		
R, gmol HI/gmol C			
1		$CH_{1.18}O_{0.230}I_{0.130}$	$CH_{1.13}O_{0.178}I_{0.196}$
1.5			$CH_{1.21}O_{0.175}I_{0.214}$
2	$CH_{1.04}O_{0.182}I_{0.169}$	$CH_{1.12}O_{0.178}I_{0.170}$	$CH_{1.38}O_{0.165}I_{0.212}$
2.9	$CH_{1.09}O_{0.177}I_{0.143}$		
3.5	$CH_{1.11}O_{0.172}I_{0.135}$	$CH_{1.25}O_{0.181}I_{0.140}$	
4.4	$CH_{1.16}O_{0.161}I_{0.124}$		
5.6	$CH_{1.23}O_{0.165}I_{0.105}$		
8.0	$CH_{1.21}O_{0.178}I_{0.124}$		

the low values of the stoichiometric coefficients a and c with lignin as the substrate, Figure 5.26, indicate the significantly lower reactivity of lignin with HI relative to that of the cellulose and hemicellulose components of wood. As the stoichiometric coefficients are controlled by the oxygen content of the substrate, with substrates of considerably different O:C ratio it would be logical to base coefficients relative to oxygen, not carbon. When the reaction stoichiometric coefficients are reexpressed on the basis of oxygen instead of carbon the trend of reactivity of various substrates for liquefaction with aqueous HI remains the same, as shown in Figure 5.27. The relation between the HI/substrate stoichiometric ratio on the carbon basis, R, and on the oxygen basis, R_O, is simply:

$$R_O = R\ [(Z_{C,s}/A_C)\ /\ (Z_{H,s}/A_H)] \tag{5.22}$$

or

$$R_O = R\ /\ (O/C)_s \tag{5.23}$$

This lower reactivity of lignin appears also as a lower HI conversion, Figure 5.28, and a lower drop in the aqueous HI concentration after the batch reaction, Figure 5.29. Based on the criteria of stoichiometric coefficients a and c, HI conversion and drop in HI concentration, it is seen in Figures 5.26 – 5.29 that cellulose and xylan have a somewhat greater reactivity with HI than does hybrid poplar, corresponding to that for lignin being much lower. The trend of reactivity to liquefaction in aqueous HI for all these substrates is in the order:

Cellulose > Xylan > Hybrid Poplar > Lignin

In Figure 5.30 the yields of the product fractions ON and OP are shown going to 100% with the yields of OA and AP fractions going to zero for the limiting case of the substrate in water (R = 0). As reviewed in Section 2.2.1 and to be confirmed experimentally in Section 7.3, CH_3I is produced from lignin by reaction with HI at

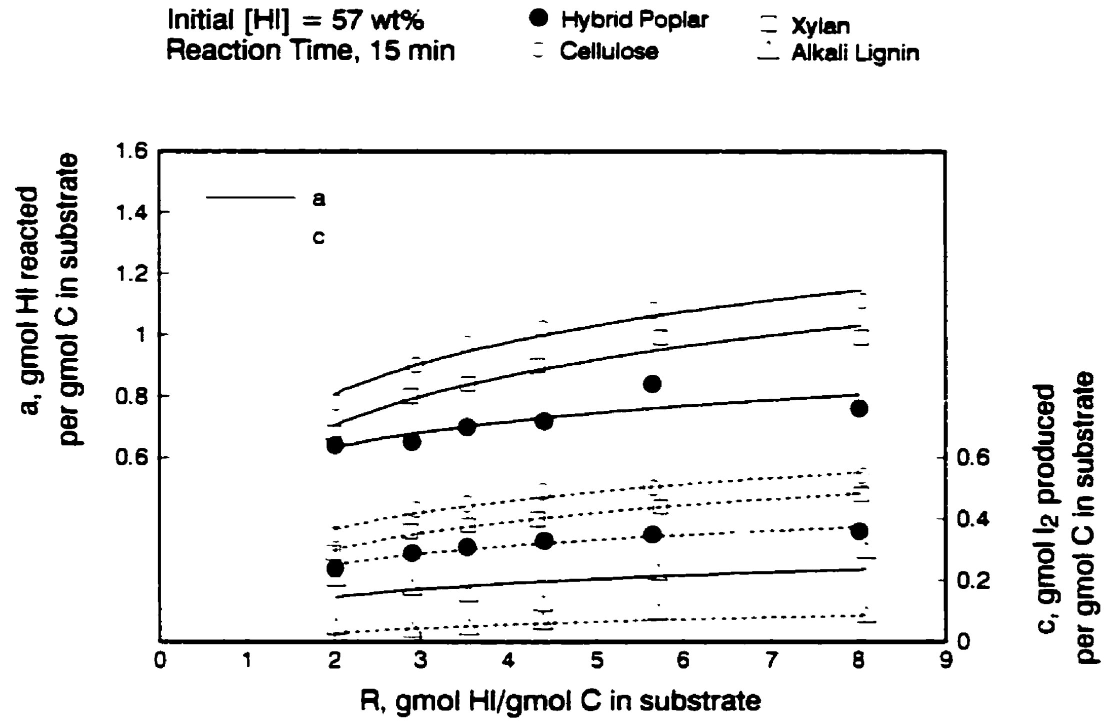


Figure 5.26 Effect of HI/Substrate Stoichiometric Ratio on Stoichiometric Coefficients (on Carbon Basis)

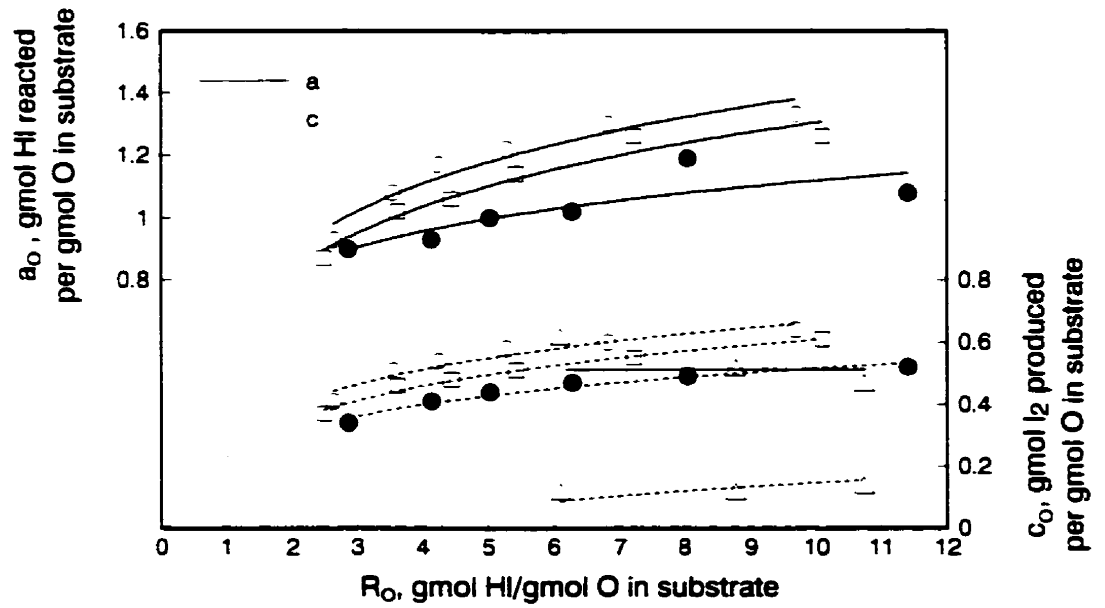


Figure 5.27 Effect of HI/Substrate Stoichiometric Ratio on Stoichiometric Coefficients (on Oxygen Basis)

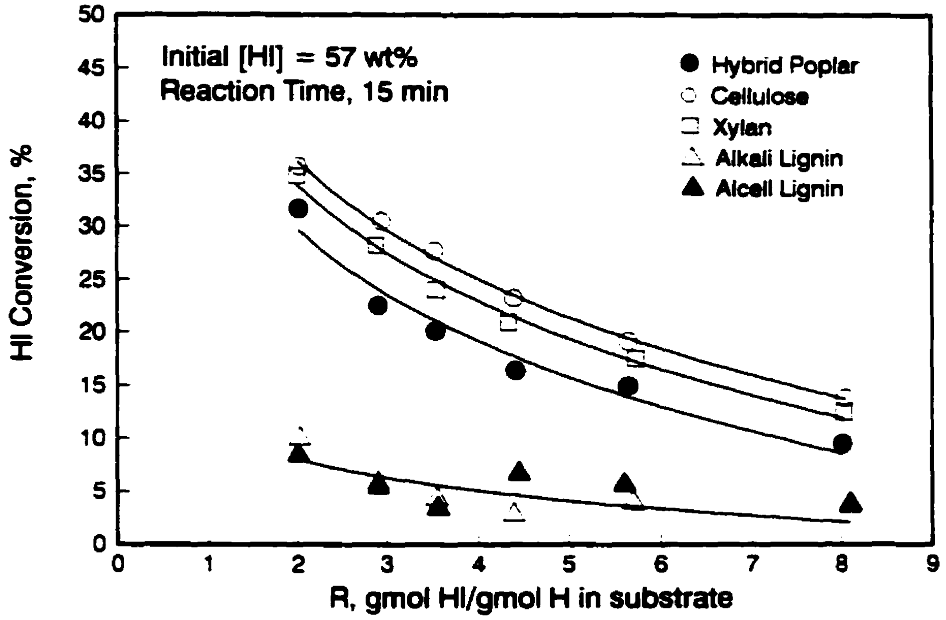


Figure 5.28 Effect of HI/Substrate Stoichiometric Ratio on HI Conversion

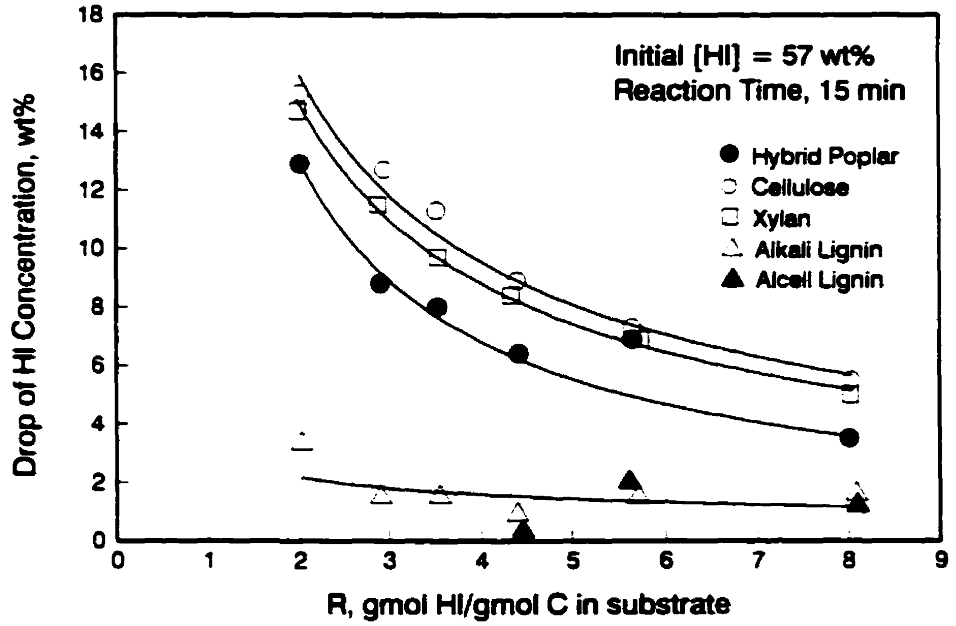


Figure 5.29 Effect of HI/Substrate Stoichiometric Ratio on HI Concentration Drop after Reaction

conditions used here. The yields of CH_3I and AP product fraction determined as described in Section 5.2.2 are again combined in Figure 5.30. Figure 5.30 shows that over the important range of R around 2 – 3 gmol HI/gmol C, cellulose is better than poplar, i.e. for the same value of stoichiometric ratio cellulose gives a lower yield of the undesired ON product fraction and a higher yield of the high value product, OA. Poplar is marginally better than pure xylan on this basis of comparison. At the same value of R, cellulose liquefaction gives a higher yield of the aqueous phase product fraction AP than other substrates, probably because of the ease of hydrolysis of cellulose.

The results confirm the expectation that lignin would give a high yield of the ON fraction, the insoluble residue. With alkali lignin as the substrate the yield of the ON insoluble residue is above 25%, even with $R > 3.5$ gmol HI/gmol C for which the ON product yield from poplar is completely suppressed. Results with Alcell lignin are difficult to interpret. For batch reactor experiments acetone is used to extract the OA product fraction from the total organic phase product fraction OP. However as Alcell lignin is itself 98% soluble in acetone, the OP product fraction from Alcell lignin was not fractionated with acetone. Therefore the yield of the ON product from Alcell lignin could not be determined. The yield of the OP product fraction from Alcell and alkali lignins was obtained directly from the weight and elemental analysis of this product, instead of by Equation 5.3. The solubility of alkali lignin in acetone is negligible, which underlines again the fact that the properties of lignin are generally altered by the method used to extract it from biomass. For alkali lignin the yield of the OA product fraction is the difference between the yield of the OP and ON product fractions. For cellulose and xylan the yield of the OP product was obtained as the sum of the yields of OA and ON fractions, i.e. by Equation 5.3.

The hybrid poplar used is 43.3% cellulose, 32.7% hemicellulose and 24.2% lignin according to Appendix G. When these proportions are applied to the yields of Figure 5.30, using alkali lignin to represent lignin, a theoretical yield for each product fraction can be calculated. This calculated yield is compared on Figure 5.31 with the

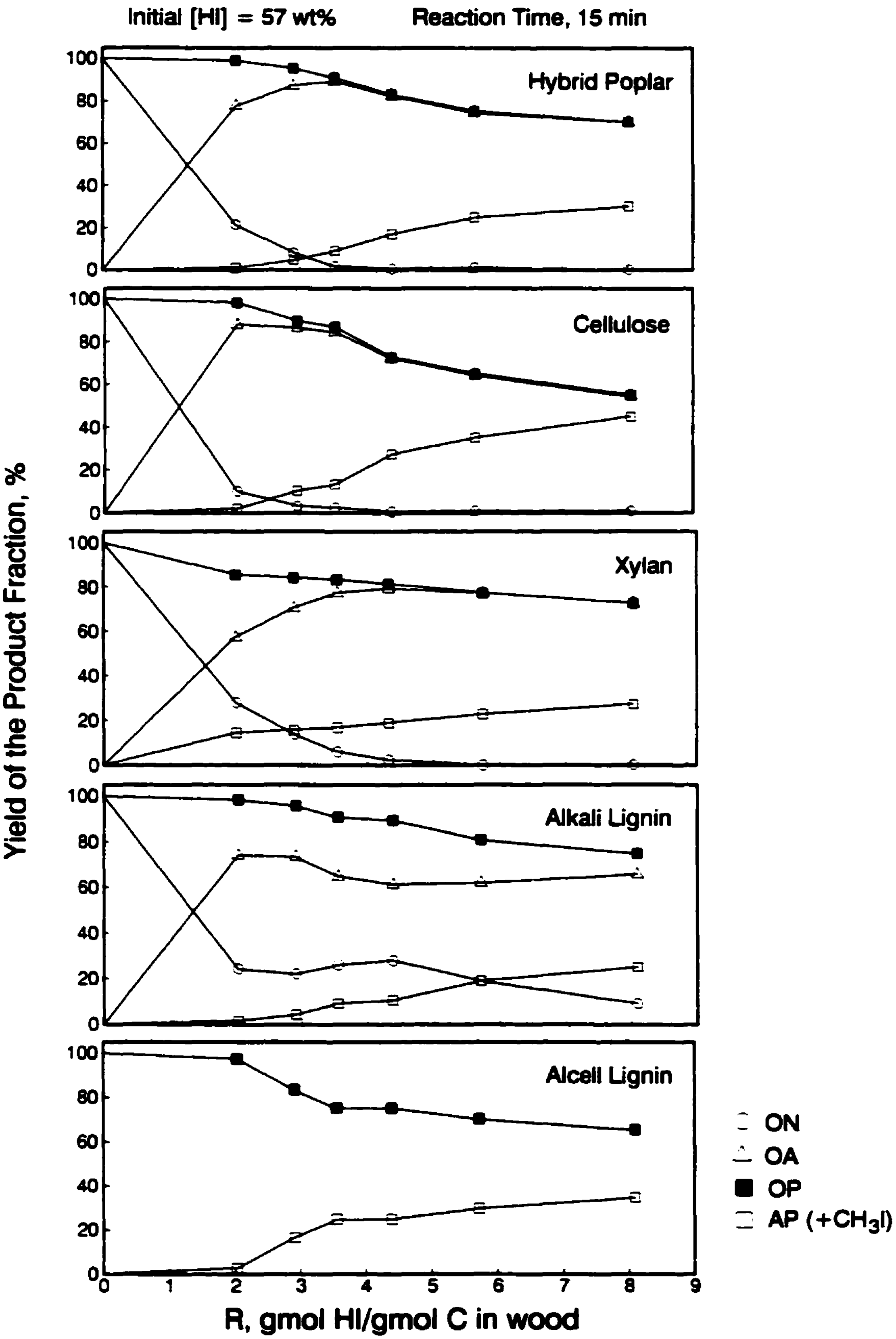


Figure 5.30 Effect of HI/Wood Stoichiometric Ratio on Yields from Various Substrates

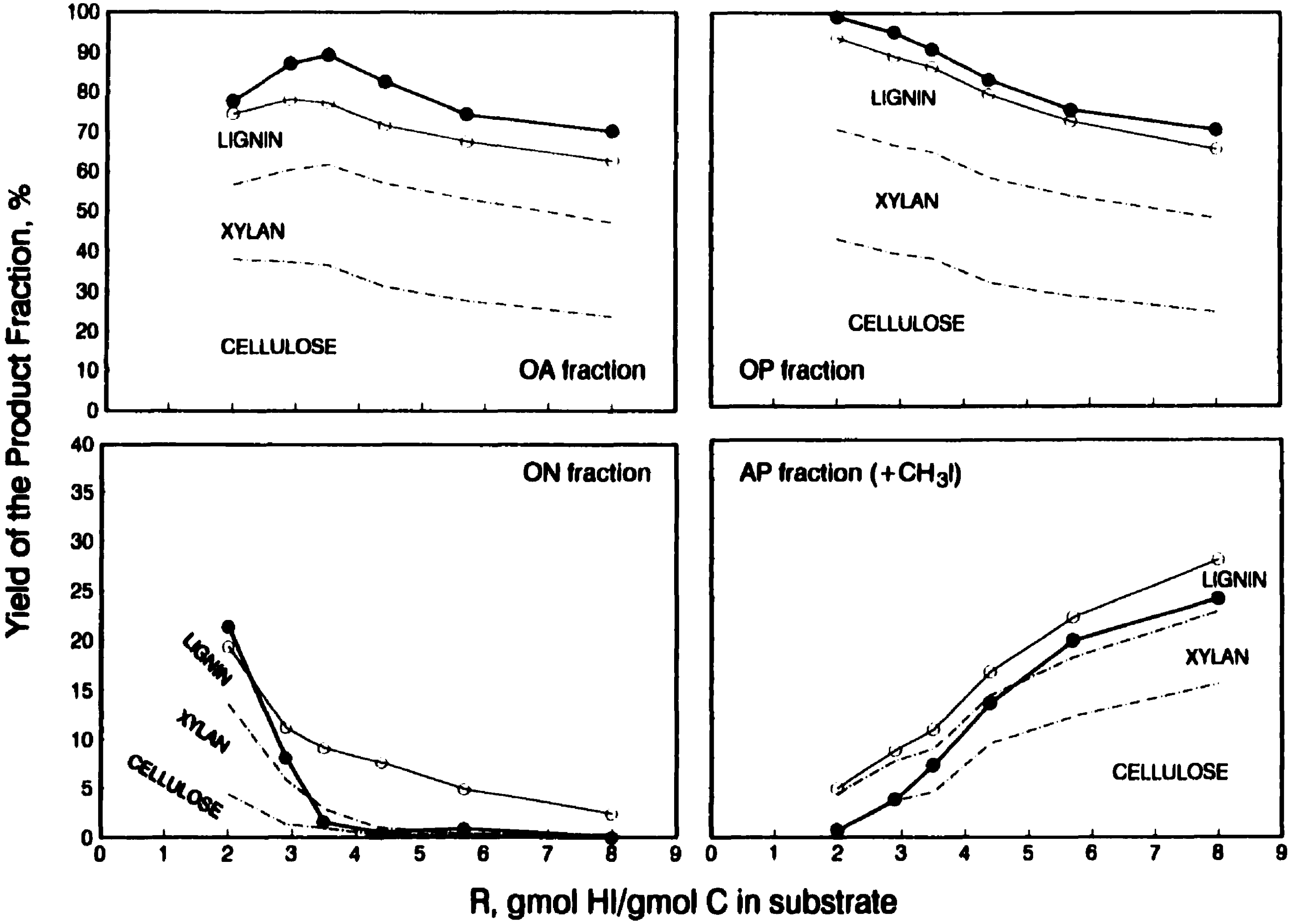


Figure 5.31 Total Yields from Poplar: Experimental and Calculated from Component Contributions

Initial [HI] = 57 wt%
Reaction Time, 15 min

—●— Hybrid Poplar

- - ○ Cellulose (43.3%)
Xylan (32.7%)
Alkali Lignin (24%)

product fraction yields as determined from experiments with poplar. Although the yields of the OA and OP fractions from wood predicted in this way are quite close to those obtained experimentally, the calculated yield of ON product at R of 3.5 gmol HI/gmol C and higher, essentially all from the lignin, is much too high. With as complex a reactant as wood and with the further complexity of the wood liquefaction reactions, one should expect there to be interactions which would make invalid the simple addition of yields from each component of the wood alone. Also, it is well known to be impossible to avoid altering lignin when extracting it from wood. It is apparent from the calculation of yield for the insoluble residue ON fraction that, in reaction with aqueous HI, the behaviour of alkali lignin is substantially different from "in situ" lignin. In this case the performance with wood is better than that which would be predicted based on the performance of its separate components, in that the actual yield of the most desired product fraction, OA, is higher and the yield of the least desired product, ON, is much lower than that calculated from the components of wood.

The elemental formulae of product fractions are given in Table 5.3.

The OP product fraction from cellulose corresponds to about 85 – 90% retention of the hydrogen, Figure 5.32, and to 80 – 90% removal of oxygen, Figure 5.33, relative to the substrate. The OP product fraction from xylan has the same level of deoxygenation but the hydrogen retention is 5 – 10% less than from cellulose. As compared to the OP product from xylan, that from wood liquefaction has about 10% lower hydrogen retention and 5 – 10% lower deoxygenation, with the somewhat lower performance for wood attributed to its lignin content. It should be noted that although hybrid poplar is 24% lignin, these performance indicators for poplar are only about 5 – 15% less than for pure cellulose. Thus although "in situ" lignin contributes the least to the desirable performance characteristics for this wood liquefaction process, these characteristics are reduced less than proportional to this substantial lignin content.

The final I_2 concentration for these substrates is given as a function of reaction conditions in Figure 5.34. As noted on Figures 5.12 and 5.24, the I/C ratio of the OP product for wood is independent of reaction conditions such as stoichiometric ratio and

Table 5.3 Product Composition for Liquefaction of Various Substrates

Substrate	Hybrid Poplar	Cellulose	Xylan	Alkali Lignin	Alcell Lignin
R			OA Fraction		
gmol HI/gmol C					
2	$CH_{1.45}O_{0.129}I_{0.103}$	$CH_{1.49}O_{0.133}I_{0.099}$	$CH_{1.44}O_{0.128}I_{0.138}$		
2.9	$CH_{1.38}O_{0.164}I_{0.111}$	$CH_{1.45}O_{0.133}I_{0.114}$	$CH_{1.35}O_{0.120}I_{0.121}$		
3.5	$CH_{1.31}O_{0.164}I_{0.084}$	$CH_{1.44}O_{0.114}I_{0.110}$	$CH_{1.35}O_{0.149}I_{0.095}$		
4.4	$CH_{1.31}O_{0.146}I_{0.075}$	$CH_{1.39}O_{0.100}I_{0.092}$	$CH_{1.31}O_{0.090}I_{0.092}$		
5.6	$CH_{1.32}O_{0.140}I_{0.071}$	$CH_{1.36}O_{0.089}I_{0.087}$	$CH_{1.36}O_{0.095}I_{0.086}$		
8.0	$CH_{1.32}O_{0.143}I_{0.072}$	$CH_{1.39}O_{0.082}I_{0.084}$	$CH_{1.36}O_{0.081}I_{0.083}$		
R			ON Fraction		
gmol HI/gmol C					
2	$CH_{1.01}O_{0.197}I_{0.032}$	$CH_{1.25}O_{0.206}I_{0.045}$	$CH_{1.07}O_{0.156}I_{0.027}$	$CH_{1.00}O_{0.236}I_{0.014}$	
2.9	$CH_{1.08}O_{0.192}I_{0.019}$	$CH_{1.14}O_{0.095}I_{0.043}$	$CH_{1.13}O_{0.137}I_{0.028}$	$CH_{1.13}O_{0.258}I_{0.015}$	
3.5	$CH_{1.07}O_{0.196}I_{0.020}$	$CH_{1.13}O_{0.094}I_{0.038}$	$CH_{1.13}O_{0.124}I_{0.031}$	$CH_{1.13}O_{0.263}I_{0.011}$	
4.4			$CH_{1.12}O_{0.107}I_{0.027}$	$CH_{1.13}O_{0.259}I_{0.018}$	
5.6					
8.0				$CH_{1.07}O_{0.261}I_{0.017}$	
R			OP Fraction		
gmol HI/gmol C					
2	$CH_{1.04}O_{0.182}I_{0.169}$	$CH_{1.44}O_{0.181}I_{0.223}$	$CH_{1.25}O_{0.181}I_{0.159}$	$CH_{1.13}O_{0.259}I_{0.088}$	$CH_{1.08}O_{0.296}I_{0.045}$
2.9	$CH_{1.09}O_{0.177}I_{0.143}$	$CH_{1.43}O_{0.164}I_{0.212}$	$CH_{1.31}O_{0.138}I_{0.156}$	$CH_{1.20}O_{0.267}I_{0.131}$	$CH_{1.04}O_{0.231}I_{0.040}$
3.5	$CH_{1.11}O_{0.172}I_{0.135}$			$CH_{1.19}O_{0.269}I_{0.115}$	$CH_{1.04}O_{0.264}I_{0.037}$
4.4	$CH_{1.16}O_{0.161}I_{0.124}$	$CH_{1.49}O_{0.142}I_{0.191}$	$CH_{1.35}O_{0.137}I_{0.157}$	$CH_{1.09}O_{0.268}I_{0.089}$	$CH_{1.17}O_{0.244}I_{0.066}$
5.6	$CH_{1.23}O_{0.165}I_{0.105}$		$CH_{1.41}O_{0.108}I_{0.155}$	$CH_{1.11}O_{0.245}I_{0.054}$	$CH_{1.13}O_{0.245}I_{0.061}$
8.0	$CH_{1.21}O_{0.178}I_{0.124}$		$CH_{1.48}O_{0.097}I_{0.155}$	$CH_{1.10}O_{0.247}I_{0.058}$	$CH_{1.13}O_{0.238}I_{0.048}$

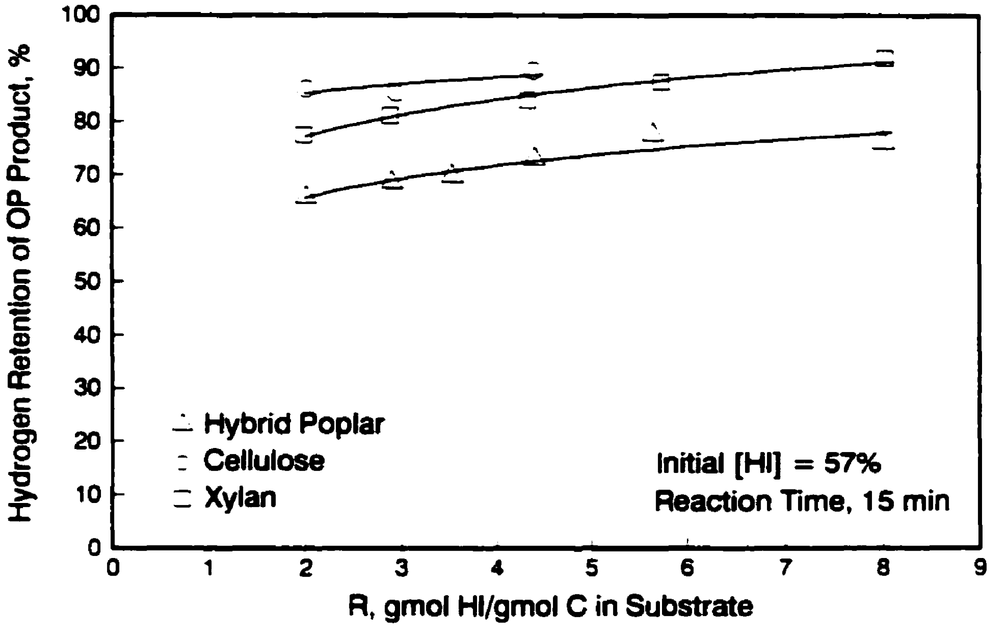


Figure 5.32 Effect of HI/Substrate Stoichiometric ratio on Hydrogen Retention of OP Product

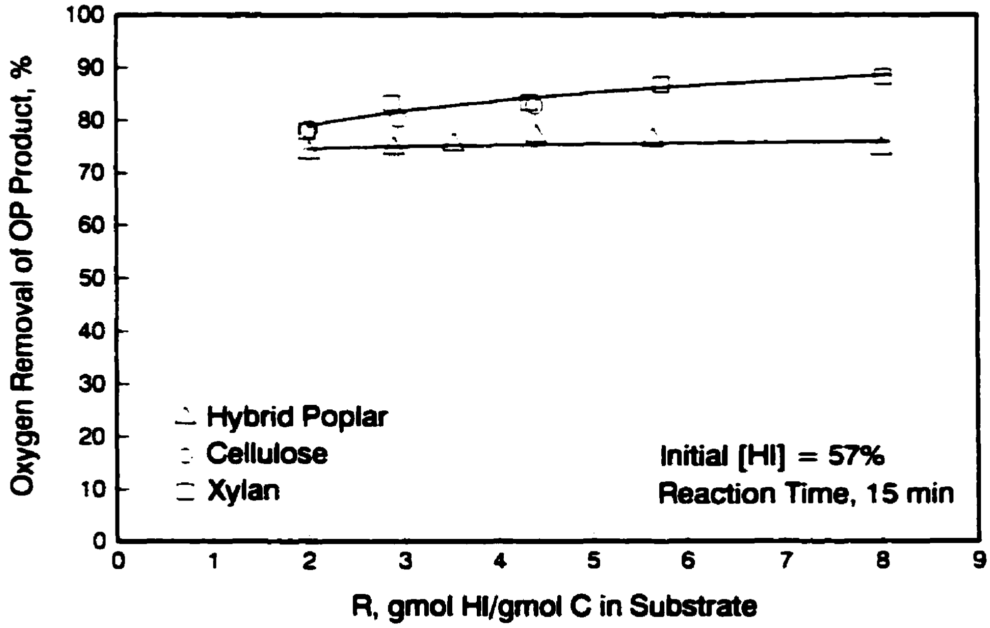


Figure 5.33 Effect of HI/Substrate Stoichiometric Ratio on Oxygen Removal of OP Product

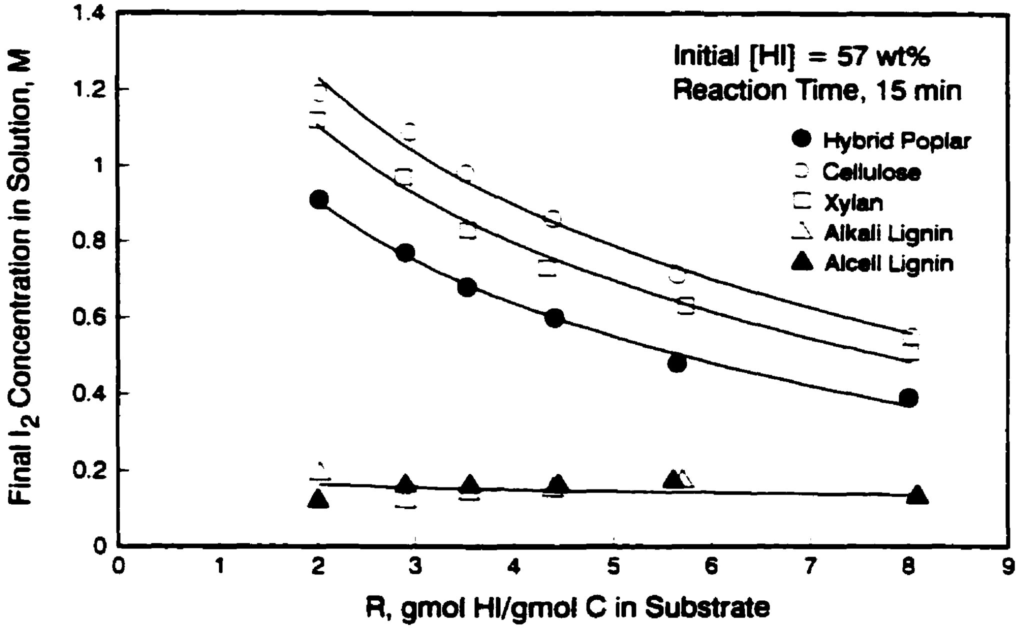


Figure 5.34 Effect of HI/Substrate Stoichiometric Ratio on Final I_2 Concentration

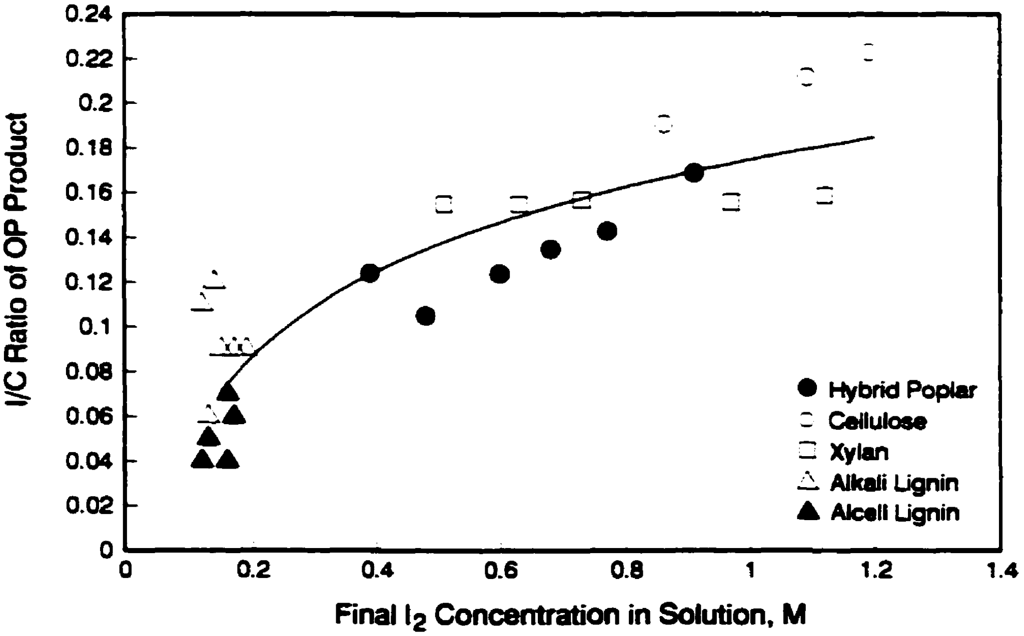


Figure 5.35 Effect of Final I_2 Concentration on I/C Ratio of OP Product

HI concentration and appears to be uniquely a function of the final I_2 concentration. To illustrate the conclusion that the iodine content of the OP organic product expressed as I/C ratio is unrelated to the type of substrate or to the liquefaction reaction conditions, Figure 5.35 consolidates the results for liquefaction of wood, which appeared earlier on Figures 5.12 and 5.24, with the results now for a variety of substrates, in all cases for a wide range of liquefaction conditions. The source of the degree of experimental scatter in the data will be discussed when the results for electrochemical liquefaction are integrated in Chapter 6.

The data of Section 5.6 are detailed in Appendices I and J.

5.7 Summary

(1) Stoichiometric equations for liquefaction reaction

At the conditions of 57 wt% initial HI concentration, HI to substrate stoichiometric ratio R = 4.4 gmol HI/gmol C, and reaction time t = 15 min, the reaction stoichiometric equation for hybrid poplar liquefaction is

$$\begin{aligned} CH_{1.59}O_{0.70} + 0.79\ HI = {} & 0.833\ CH_{1.16}O_{0.16}I_{0.12} + 0.118\ CH_{1.57}O_{0.20}I_{0.04} \\ & + 0.049\ CH_3I + 0.54\ H_2O + 0.32\ I_2 \end{aligned}$$

where the carbon-base yields of the OP and AP product fractions are respectively 83.3% and 11.8%. For these conditions there is no yield whatever of the char-like insoluble residue product from this biomass liquefaction process applied to wood. For cellulose liquefaction under the same batch reactor conditions the stoichiometric equation is

$$\begin{aligned} CH_{1.67}O_{0.83} + 1.18\ HI = {} & 0.727\ CH_{1.49}O_{0.14}I_{0.19} + 0.273\ CH_{1.63}O_{0.24}I_{0.03} \\ & + 0.66\ H_2O + 0.52\ I_2 \end{aligned}$$

where the yields of the OP and AP fractions are respectively 72.7% and 27.3%. The greater reactivity of HI in solution with cellulose than with wood is indicated by the higher stoichiometric coefficients for HI, 1.18 compared to 0.79. As HI reduces the substrate with the production of H_2O while the I^- is oxidized to I_2, part of this higher HI reactivity corresponds to the O/C ratio of cellulose being 19% higher than for hybrid poplar.

(2) Evolution of wood liquefaction over short reaction times

As HI is consumed and H_2O produced by the liquefaction reaction, during batch reaction the HI concentration drops from its initial value. When, as in the present work, an atmospheric pressure reactor is operated at the bubble point of the aqueous HI solution for which the maximum boiling azeotrope is 127°C at 56.5 wt% HI, the progress of the liquefaction reaction can be followed by monitoring the reactor temperature, a precise indicator of the HI concentration as it decreases during batch reaction. In this way it was determined that for some operating conditions the liquefaction reactions between substrate and HI are nearly complete in as little as 20s.

(3) Effect of HI concentration and HI/wood stoichiometric ratio

Of the three reaction conditions in batch reactor liquefaction, initial and final HI concentration in the aqueous phase and HI/wood stoichiometric ratio, two of these conditions are independent while the third is determined by the other two. A series of experiments were made to determine which of these parameters exerts the most direct effects on the various yield and product composition characteristics of wood liquefaction.

The reaction activity of aqueous HI with wood increases very strongly with HI concentration, a variable never investigated in the previous studies. For initial HI concentration lower than 45 wt% the reaction activity of HI acting as a reducing agent is very weak, becoming negligible at [HI] of 30 wt%. Even so, the effect of H^+ as catalyst hydrolyzes the polymers of wood to the extent of a 40% yield of aqueous HI phase soluble product for [HI] in the range 14 – 45 wt% HI. The evidence demonstrates that the hydrolysis step of wood liquefaction is fast and occurs even at weak conditions for liquefaction. The dehydration step of wood liquefaction may be slower and certainly requires stronger reaction conditions, i.e. initial concentrations in the range 55 – 65 wt% HI.

In batch liquefaction of hybrid poplar the yield of the undesired acetone-insoluble residue fraction, ON, can be totally eliminated by any combination of HI to wood stoichiometric ratio R, gmol HI/gmol C, and wt% initial HI concentration which gives a final HI concentration of 50 wt% HI or higher. Thus of the three inter-related parameters, final HI concentration alone controls the yield of this unwanted product.

In the stoichiometric equation for hybrid poplar liquefaction given in item (1) above, the stoichiometric coefficients for consumption of HI and production of I_2 were found to increase sensitively and linearly with final HI concentration over the wide range of 42 – 55 wt% HI regardless of the combinations of values of the two parameters, initial HI concentration and HI/wood reaction stoichiometric ratio, which determine final HI concentration.

The hydrogen retention of the OP product appears to be sensitive to both initial and final HI concentration. Hydrogen retention can be maintained at 70% or better for a variety of batch reaction conditions, but can be improved to about 85% by increasing initial HI concentration to 68 wt% HI. The extent of deoxygenation of the OP product fraction is about 75% and is relatively insensitive to HI concentration and to stoichiometric ratio R except that deoxygenation drops off sharply at some value of initial HI concentration not much lower than 57 wt% or for conditions giving final [HI] below 45 – 50 wt% HI in batch liquefaction of wood.

The iodine content of the OP product fraction, expressed as the atomic ratio I/C, is a unique function of the I_2 concentration at the end of batch liquefaction and appears unrelated to reaction conditions or to the type of substrate used.

(4) Liquefaction of individual components of wood

The trend of reaction activity to liquefaction in aqueous HI solution is in the order

Cellulose > Xylan > Hybrid Poplar > Lignin.

Relative to other lignocellulosic substrates, lignin liquefaction gives a significantly higher yield of the undesirable acetone-insoluble residue fraction, ON. Cellulose contributes more yield of the aqueous phase soluble product fraction, AP, apparently from the ease of cellulose hydrolysis in HI solution. The extent of deoxygenation and hydrogen retention for the liquefaction of cellulose and xylan is about 5 – 15% greater than for hybrid poplar because of the lignin content of the wood. The experimentally determined performance characteristics for the liquefaction of wood in aqueous HI solution is better than that which would be predicted from the characteristics of the components of wood determined separately. Thus for liquefaction in aqueous HI solution, the presence of 24% lignin in hybrid poplar lowers the important characteristics of wood liquefaction by only 5 – 15%.

CHAPTER 6

BATCHWISE ELECTROCHEMICAL WOOD LIQUEFACTION

6.1 Introduction

Preliminary batch and batchwise-continuous wood electrochemical liquefaction experiments were carried out with the initial concentration of aqueous HI to the ECLR fixed at 55 – 61 wt% HI. These batch reactor and then batchwise-continuous reactor runs were all carried out during the process of developing the design and the operating capability to achieve the fully continuous ECLR operation reported in Chapter 7. Although the experiments reported in Chapter 6 were in part a means to an end, much unique information concerning electrochemical wood liquefaction was determined in this way.

A run referred to here as "continuous" means a wood liquefaction experiment with rates of wood feed, rates of generation of I_2 from the liquefaction reactions and rates of electrochemical reduction of I_2 back to HI all partially or approximately continuous, but without continuous withdrawal of product from the reactor and without control of the HI concentration in the aqueous phase to a steady-state value. Thus although reactor operation was approximately continuous in some respects, with respect to the HI solution concentration, a variable of considerable importance as established in Chapter 5, this was not steady-state operation. The wood feed was either batchwise-continuous as described subsequently for runs *8, *9, *11, *12, *16 – *19ECLR, or fully continuous with the wood feeder for runs *14, *15 and *20ECLR. The cathode was changed for run *11ECLR from the original cylinder of platinum mesh, found to be rather fragile, to a larger cathode for which the cylinder was made from a solid sheet of platinum. Further modifications were implemented subsequently for the more controlled ECLR operation reported in Chapter 7.

The hybrid poplar wood used, from FORINTEK Canada Corp., has elemental composition $CH_{1.59}O_{0.70}$, as recorded in Appendix G. The 57 wt% aqueous HI and 38 wt% H_2SO_4 solutions used as catholyte and anolyte were supplied by ACP Chemical Inc.

6.2 Batch electrochemical wood liquefaction

6.2.1 Experimental procedure

Four batch wood electrochemical liquefaction experiments, #2, #5, #6 and #10ECLR, were carried out during the period when the capability of making long duration continuous runs was under development. The principal operating conditions were: approximately 55 wt% HI solution in the cathode compartment, 38 wt% H_2SO_4 solution in the anode compartment, HI to wood stoichiometric ratio R = 4.5 or 10 gmol HI/gmol C in wood, cell voltage of 4.5 or 6 V and cathode rotational speed 600 – 2000 rpm. Reaction time ranged from 15 to 140 min. The cylindrical cathode was 13 mm diameter x 50 mm long, of 0.15 mm thick platinum mesh with 0.36 mm square openings, the mesh being formed of 0.15 mm diameter wire. The anode was a lead plate, 50 mm square x 4 mm thick. The detailed experimental conditions are displayed in Table 6.1.

Before starting a batch liquefaction experiment the aqueous HI solution was brought to reaction temperature, about 125°C, with cathode rotation at the desired speed. The required amount of wood flour (oven dried for 2h at 80°C) satisfying the desired HI/wood ratio, R, was introduced quickly into the aqueous HI solution at reaction temperature in the ECLR. For runs #2, #5 and #6ECLR the cell voltage was established

Table 6.1 Experimental Conditions for Batch ECLR Wood Liquefaction

Experiment No.	#2ECLR	#5ECLR	#6ECLR	#10ECLR
Cathode Cell (HI solution)	250 ml	240 ml	240 ml	210 ml
Anode Cell (H_2SO_4 solution)	1330 ml	1300 ml	1300 ml	1300 ml
Cathode Dimensions, diam. x length, mm	13 x 50	13 x 50	13 x 50	13 x 50
Anode Dimensions, mm	50 x 50	50 x 50	50 x 50	50 x 50
Spacing: Cathode-Membrane-Anode, mm	25/20	25/20	25/20	25/20
Voltage, V	4.5	4.5	6	6
Cathode Rotation Speed, rpm	2000	1000	1000	600
R, gmol HI/gmol C in wood	4.5	4.5	10	10
Reaction Time, min	15	140	30	(+5)120
Current, A	~5	~4.5	~9	6 − 9
Current density, A/cm^2	0.5	0.5	0.9	0.6 −0.9
Cathode Cell Temperature, °C	120	124	121	122

at the desired level from the moment of introduction of the wood. For the #10ECLR test the power was supplied at 6 volts starting 5 minutes after wood liquefaction started.

After the desired reaction time the reactor contents were emptied into a flask and the part of the OP product fraction which was dispersed in the aqueous phase was separated by filtration. The yield of the OP product fraction was obtained by combining the weight of the OP product separated from the aqueous phase with the OP product that remained adhering to the reactor surfaces, determined gravimetrically. Prior to elemental analysis of the OP product from these 4 runs, this fraction was oven dried at 80°C for 2h in order to obtain it in the desired H_2O-free, HI-free state. The methods of elemental analysis are recorded in Appendix H.2. After each run the cathode was cleaned in the concentrated HNO_3 solution to remove all organic product.

The results of analysis of the aqueous HI solution for I_2 and HI concentrations, before, during and after reaction, as determined by the methods recorded in Appendix H.1, are shown in Table 6.2.

6.2.2 Electrochemical I_2 reduction with batch liquefaction

These batch reactor experiments provide the crucial first indication that it is in fact possible to reduce I_2 electrochemically in the presence of wood liquefaction, with the cathode exposed to the viscous wood oil product, and without generation at the cathode of H_2 by the competitive electrochemical reaction. The current was about 5 A at 4.5 V and 9 A at 6 V, respectively 0.5 A/cm^2 and 0.9 A/cm^2 cathode current density. With electrochemical batch wood liquefaction the cell current and cathode current density were decreased by about 20 – 30% compared to I_2 electrochemical reduction in the pure aqueous HI solution for which, with $[I_2] \approx 0.05$ M, 6 A cell current and 0.6 A/cm^2 cathode current density were obtained at 4 V, and 12 A or 1.2 A/cm^2 at 6 V.

For the batch reactor mode operation of the ECLR the I_2 concentration in solution passes through a sharp maximum because at short times the rate of generation of I_2 exceeds the rate of electrochemical reduction of I_2 whereas later on the opposite

Table 6.2 Analysis of Aqueous HI Solution for Batch ECLR Wood Liquefaction

Experiment No.		*2ECLR			*5ECLR			*6ECLR			*10ECLR		
		R = 4.5 gmol HI/gmol C						R = 10 gmol HI/gmol C					
		Concentration											
Time (min)	Cell Voltage	$[I_2]$ (M)	[HI] (M)	[HI] (wt%)	$[I_2]$ (M)	[HI] (M)	[HI] (wt%)	$[I_2]$ (M)	[HI] (M)	[HI] (wt%)	$[I_2]$ (M)	[HI] (M)	[HI] (wt%)
0	without										0.003	7.02	54.5
5	without										0.14	6.54	52.2
0	with	0.004	7.27	55.6	0.007	7.17	55.2	0.007	7.17	55.2	0.14	6.54	52.2
15	with	0.31	6.23	50.6									
30	with				0.32	6.23	50.6	0.018	6.66	52.8			
60	with				0.19	6.35	51.2				0.008	6.53	52.1
90	with										0.003	6.49	51.9
120	with				0.11	6.37	51.3				0.002	6.49	51.9
140	with				0.086	6.35	51.2						

is the case. As discussed in Section 5.3, with initial 57 wt% HI solution the wood reaction with HI could be complete in as little as 20s, which would correspond to generating about 40 g I_2 over the first 20s. By contrast, at 8 V and I_2 concentration around 0.02 – 0.45 M with the mesh cathode, the I_2 reduction rate as recorded in Section 4.3 is at around 1.2 – 1.6 g/min.

For run *10ECLR at a high HI:wood ratio, R = 10 gmol HI/gmol C in wood, the $[I_2]$ was 0.14 M after 5 min batch reaction without electrochemical current which, as discussed in Section 5.3, would correspond to completion of the reaction with HI and hence the generation of I_2. By the end of 1h, I_2 concentration was reduced from 0.14 M to 0.008 M, a very low level, i.e. 94% of the I_2 converted back to HI. At the end of 2h when the experiment was stopped the I_2 concentration was only 0.002 M, essentially I_2-free. Thus even the early operation of the ECLR in batch reactor mode provided evidence that one basic objective of the present study was achieved, i.e. that electrochemical reduction of I_2 back to I^- can be obtained in the presence of wood liquefaction and of the viscous crude wood oil product around the cathode.

The competitive cathodic reaction of H_2 generation occurred only when the I_2 concentration became low, around 0.1 M, with this mesh cathode. This condition existed after about 60 min for run *5ECLR, and after about 15 min electrochemical reduction time for the lower HI/wood stoichiometric ratio of runs *6 and *10ECLR.

The HI concentration decreases initially because the rate of consumption of HI by the wood-HI reaction is greater than the rate of electrochemical reduction of I_2 to HI, as well as because the HI solution is diluted by H_2O produced from wood-HI reaction, Equation 5.10.

6.2.3 Composition and yield of crude product

With initial aqueous solution about 55 wt% HI but without make-up HI to maintain the HI concentration constant, the composition of the crude product from batch electrochemical wood liquefaction typically has 65 – 82% hydrogen retention and 70

– 78% oxygen removal relative to the wood, Table 6.3. As the composition of the crude product would be determined by the HI-wood reactions which, according to Section 5.3, may be nearly completed as little as 20s, it is as expected that the levels of hydrogen retention and deoxygenation of the product with batch liquefaction are essentially independent of whether or not the I_2 produced is subsequently reduced electrochemically.

The iodine content of the crude product, represented as the I:C atomic ratio, decreases with decreasing I_2 concentration in the aqueous phase, as demonstrated in Table 6.3. Thus this early data indicates that the I:C ratio in the OP product from run #10ECLR is 0.04 at an I_2 concentration of 0.002 M. These values are significantly less than the typical level of 0.12 – 0.16 I/C ratio in the OP product from nonelectrochemical batch liquefaction with initial 57 wt% HI solution and final $[I_2]$ of 0.6 – 1.4 M at realistic values of HI to wood stoichiometric ratio and initial HI concentration. Although this iodine content of the crude product is still much higher than the ultimate objective, the fact that it is lower with electrochemical than nonelectrochemical wood liquefaction is encouraging.

The carbon-base yield of the OP product fraction, determined only for two runs, was 81.4% for run #2ECLR and 39.0% for run #10ECLR. These yields were somewhat higher than for nonelectrochemical batch wood liquefaction at the same conditions of HI/wood stoichiometric ratio and initial HI concentration from Figure 5.18. Except for run #2ECLR the OP product was not extracted with acetone as was usually done for the nonelectrochemical batch liquefaction experiments reported in Chapter 5. When the OP product fraction from run #2ECLR was subjected to acetone extraction to determine the yield of the acetone-insoluble fraction, ON, it was found that for these conditions, giving final [HI] = 50.6 wt%, the yield of this undesired product fraction was totally suppressed. This finding is consistent with the results of Chapter 5 which showed that the ON product fraction is eliminated when the final HI concentration is above about 48 – 49 wt%.

Table 6.3 Elemental Analysis of OP Product Fraction for Batch ECLR Wood Liquefaction

Experiment No.	$[HI]_{final}$ (wt%)	$[I_2]_{final}$ (M)	Elemental Analysis								Hydrogen retention %	Oxygen removal %
			Elemental content, wt%					Atomic ratio				
			C	H	O	I	Total	H/C	O/C	I/C		
#2ECLR	50.6	0.31	49.76	5.41	11.78	35.16	102.11	1.31	0.199	0.075	82.4	71.4
#5ECLR	51.2	0.086	54.27	5.05	12.75	31.03	103.10	1.12	0.176	0.055	70.4	74.9
#6ECLR	52.8	0.018	59.40	5.08	13.16	24.26	101.90	1.03	0.166	0.039	64.8	76.3
#10ECLR	51.9	0.002	54.13	5.61	11.48	25.86	97.08	1.24	0.159	0.045	78.3	77.3

6.3 Batchwise-continuous electrochemical wood liquefaction

6.3.1 Experimental procedure

This type of operation involved runs generally of 5h with batchwise-continuous wood feed and corresponding generation of I_2 and electrochemical reduction of I_2 back to HI, but no flow of the product or aqueous HI solution from the reactor and no make-up HI to maintain HI concentration at a steady-state value in the liquefaction reactor. Without the control provided subsequently (Chapter 7) the HI concentration decreased during these runs by from 5 to 13 wt% HI. Although this type of operation does not include all aspects of a steady-state flow reactor, it represents some key characteristics of a continuous ECLR system.

For all 11 runs of this series the anode compartment was charged with 1300 ml of 38 wt% H_2SO_4 solution for the production of O_2 at the anode. The anode was lead plate of same dimensions as for the batch electrochemical reactor experiments. For runs #8 and #9ECLR the cathode was the original platinum mesh cylinder, 13 mm diameter x 50 mm long x 0.15 mm wall thickness mesh made from 0.15 mm diameter wire with 0.36 mm square openings in the mesh. The membrane-to-cathode closest point distance was 25 mm, as for the batch experiments. A basic difference for runs #11 – #20ECLR was the change to the platinum sheet cathode, 25 mm diameter x 50 mm long x 1 mm wall thickness, with the membrane-to-cathode closest point distance 20 mm but the membrane-to-anode distance unchanged at 20 mm. The initial volume of aqueous HI solution was 350 ml for runs #8 and #9ECLR, 195 – 220 ml thereafter.

The batchwise-continuous wood feed was by addition of a small batch, every 5 minutes, at the rate 0.05 – 0.15 g/min (oven dried wood for 2h at 80°C) directly into the top of the cathode cell compartment, except for runs #14, #15 and #20ECLR for which wood was fed automatically by the continuous feeder. However without the addition of HI make-up to control HI concentration in the ECLR the latter cases still lacked that essential feature of steady-state flow reactor operation. The cathode rotational speed was varied during the first four runs of this series, then in runs #14 –

"20ECLR was maintained constant at 1200 rpm, a speed determined to be adequate to minimize mass transfer resistance. The electrochemical circuit was operated at 6 volts, except for run "16ECLR at 7 volts. The temperature of the cathode cell was maintained at about 120°C, just slightly lower than the bubble point in order to minimize vapour loss from the wood feeder connection when it was opened for batchwise wood feeding and to avoid sticking of the wood flour to the wall by wet vapour when wood flour was fed from the top. The temperature of the anode cell was about 70°C. The complete operating conditions are displayed in Table 6.4.

Small samples of aqueous solution, about 3 − 5 ml, were withdrawn from the cathode cell every 30 min for determination of I_2 and HI concentrations by the methods recorded in Appendix H.1. With no HI make-up, the HI concentration decreases continuously, Appendix K, by an amount depending on the wood feed rate, the area of the cathode and the initial HI concentration of the aqueous solution. Although HI was regenerated from I_2 by electrochemical reduction, some iodine becomes tied up with the product and some in the aqueous HI inventory in the ECLR, the volume of which increases by water of reaction from wood liquefaction, Equation 5.10, and by water transport from the anode to the cathode compartment as discussed in Section 4.4.5. With runs 5h long starting from about 55 wt% HI solution, the HI concentration decreased to 50 − 52 wt% with the mesh cathode, to 44 − 48 wt% with the subsequent larger cathode. Runs "19 and "20ECLR were started with the initial aqueous HI concentration enhanced to 60 − 61 wt% by adding I_2 to the standard strength HI in the ECLR solution and electrochemically reducing this I_2 to HI directly in the ECLR prior starting wood feed. To limit the drop in HI concentration, these particular runs were planned for 3h instead of the customary 5h and the HI concentration dropped over a 3h run from about 60 − 61 wt% to about 51 − 52 wt%. The average HI concentration recorded in Table 6.5 is the average value of HI concentration during the run from Appendix K. These HI concentration drops are only a characteristic of the incomplete laboratory version of continuous ECLR operation and are not relevant to a fully continuous, steady-state operation with a totally controlled ECLR system. Run "18ECLR

Table 6.4 Experimental Conditions for Batchwise-Continuous ECLR Wood Liquefaction

Run No.	Voltage (V)	Cathode (rpm)	Run Time (min)	ELECTRODES				Anode Compartment***		Cathode Compartment***	
				Anode	Cathode		Spacing ** (mm)	Initial Volume (ml)	Average Temp. (°C)	Initial Volume (ml)	Average Temp. (°C)
				Dimensions (mm)	Dimensions (mm)	Area* (cm^2)					
#8ECLR	6	560	300	50x50	13diam.x50	10.4	25/20	1300	~70	350	122
#9ECLR	6	610	300	50x50	13diam.x50	10.4	25/20	1300	~70	350	123
#11ECLR	6	1500	280	50x50	25diam.x50	14.7	20/20	1300	~70	220	115
#12ECLR	6	1000	300	50x50	25diam.x50	14.7	20/20	1300	~70	195	115
#14ECLR	6	1200	345	50x50	25diam.x50	14.7	20/20	1300	~70	215	115
#15ECLR	6	1200	300	50x50	25diam.x50	14.7	20/20	1300	~70	220	115
#16ECLR	7	1200	300	50x50	25diam.x50	14.7	20/20	1300	~70	220	115
#17ECLR	6	1200	300	50x50	25diam.x50	14.7	20/20	1300	~70	220	120
#18ECLR	6	1200	180	50x50	25diam.x50	14.7	20/20	1300	~70	220	120
#19ECLR	6	1200	180	50x50	25diam.x50	14.7	20/20	1300	~70	220	123
#20ECLR	6	1200	180	50x50	25diam.x50	14.7	20/20	1300	~70	220	120

* Effective area: 1/4 x 3/4 x (total surface area)
Total surface area of 13 mm diam. x 50 mm cathode: 55.9 cm^2
Total surface area of 25 mm diam. x 50 mm cathode: 78.5 cm^2

** Electrode spacing : 25/20 indicates 25 mm cathode to membrane, 20 mm anode to membrane for 13 mm diam. x 50 mm cathode
20/20 indicates 20 mm cathode to membrane, 20 mm anode to membrane for 25 mm diam. x 50 mm cathode

*** Anode compartment solution : 38 wt% H_2SO_4 solution
Cathode compartment solution : see Table 6.5

Table 6.5 Experimental Results for Batchwise-Continuous ECLR Wood Liquefaction

Run No.	CURRENT		WOOD FEED		HI SOLUTION								
					Initial				Final				average
	Average current (A)	Average Cathode Current Density (A/cm^2)	Average Feed Rate (g/min)	Total Weight (g)	[I_2] (M)	[HI] (M)	[HI] (wt%)	Volume (ml)	[I_2] (M)	[HI] (M)	[HI] (wt%)	Volume (ml)	[HI] (wt%)
#8ECLR	7.5	0.72	0.050	14.972	0.006	7.24	55.5	350	0.047	6.11	50.0	372	52.5
#9ECLR	7.8	0.75	0.047	14.149	0.002	7.09	54.8	350	0.033	7.41	52.0	366	52.8
#11ECLR	12	0.82	0.096	26.933	0.007	7.40	56.2	220	0.063	5.91	49.0	235	53.4
#12ECLR	11.6	0.80	0.091	27.316	0.009	7.47	56.4	195	0.045	5.14	44.6	237	50.0
#14ECLR	11.5	0.78	0.095	28.5	0.004	6.42	51.6	215	0.048	5.11	44.5	250	47.6
#15ECLR	11.5	0.78	0.100	30.0	0.003	7.28	55.7	220	0.074	5.01	43.9	291	50.0
#16ECLR	15	1.02	0.101	30.071	0.005	7.56	56.9	220	0.063	5.20	44.0	289	50.1
#17ECLR	8.8	0.60	0.050	15.008	0.0004	7.49	56.6	220	0.026	5.81	48.4	263	51.9
#18ECLR	9.4	0.64	0.150	26.99	0.0016	7.37	56.1	220	0.092	5.87	48.7	236	52.1
#19ECLR	10.4	0.71	0.100	18.041	0.001	8.22	59.7	220	0.098	6.39	51.4	260	55.2
#20ECLR	12.5	0.85	0.086	15.607	0.0064	8.58	61.1	220	0.048	6.61	52.5	191	56.4

was for 3h using initial HI solution containing 0.14 M KI to investigate product solubility effects.

At the end of a run the reactor contents were emptied into a flask and the part of the OP product fraction which was dispersed in the aqueous phase was separated by filtration. The yield of the OP product fraction was obtained by combining the weight of the OP separated from the aqueous phase as noted above, with the OP product that remained adhering to the reactor surfaces, determined gravimetrically. For none of these batchwise-continuous runs was the OP product fraction subjected to acetone extraction as was usually done for the nonelectrochemical batch liquefaction in Chapter 5. The yield of the aqueous phase soluble product AP was obtained by difference because this fraction was difficult to determine directly, as noted in Chapter 5. The methods of elemental analysis of the product fractions are recorded in Appendix H.2. The cathode was cleaned as described for the batch experiments.

6.3.2 Electrochemical I_2 reduction with batchwise-continuous liquefaction

The major issues concerning the possibility of carrying out electrochemical reduction of I_2 simultaneous with wood liquefaction in the same reactor have been identified as: (1) the extent of decrease in the electrochemical reduction rate because of the presence of the viscous crude oil product, (2) the effect of simultaneous liquefaction on the small range over which, in the absence of liquefaction, I_2 reduction may be obtained to the exclusion of the competitive electrochemical reaction of hydrogen generation, and (3) the level of I_2 concentration that can be maintained in the presence of liquefaction. These issues are now examined through the results of the batchwise continuous runs *8 – *20ECLR, summarized in Table 6.5 and Appendix K.

Considering first the effect of wood liquefaction on the electrochemical reduction rate, the electrochemical cell current, stable over that extended time, was in the range 7.5 – 7.8 A or a cathode current density i of 0.72 – 0.75 A/cm^2 (runs *8 and *9ECLR) with the smaller cathode of platinum mesh, while for about the same operating conditions these values were 11.5 − 12 A or i of 0.78 − 0.82 A/cm^2 (runs #11, #12, #14 and #15ECLR) with the larger cathode constructed from continuous sheet metal. These runs establish for the first time that stable operation is obtainable over a significant period while feeding wood to the ECLR system.

The uncertainty in estimating the effective area of the cylindrical cathode, described in Section 4.1, and the further uncertainty between effective area for a cathode constructed from mesh (#8 and #9ECLR) or from continuous sheet metal (#11ECLR and all subsequent runs) makes it impossible to make precise comparisons between the current densities obtained for the two cathodes tested. With these reservations, however, it is not surprising to find current densities with liquefaction about 10% lower for the mesh cathode because the approximately 0.36 mm square openings in this mesh could more easily be blocked by the viscous crude wood oil than the smooth surface of the continuous sheet metal cathode. Partial blockage of the cathode surface would reduce the current, giving an apparent lower current density. The lower cathode rotation speed for the #8 and #9ECLR runs with the mesh cathode (510 −610 rpm) than with the subsequent cathode could also be a factor lowering the current density. With the continuous sheet cathode, runs #11, #12 and #14ECLR at the same operating conditions except for variable cathode rotation speed established that electrochemical current was not very sensitive to cathode speed over the range 1000 − 1500 rpm for the sheet metal cathode. Thus from #14ECLR the cathode rotation speed was fixed 1200 rpm.

With the continuous platinum sheet cathode at the same cell voltage and with similar I_2 concentration, the electrochemical current and cathode current density are significantly lower in the presence of wood liquefaction than with the same apparatus used for I_2 reduction in pure aqueous HI without wood liquefaction. For I_2 electrochemical reduction in pure aqueous HI solution with the mesh cathode at 6 V and $[I_2] \approx 0.05$ M, the current is about 12.5 A, corresponding to 1.2 A/cm^2 cathode current density, Figure 4.1, while for the larger sheet cathode the corresponding values at 6 V and $[I_2] \approx 0.05$ M are 15 A and 1 A/cm^2 for the continuous sheet cathode, Figure 4.5. These measurements from Chapter 4 and those obtained here with liquefaction indicate that for the same cell voltage and HI concentration and for comparable I_2 concentrations, the decrease in cell current and cathode current density with wood liquefaction relative to that without liquefaction was by about 25% with the electrode fabricated of continuous sheet, by about 40% with the mesh electrode which facilitates blockage of surface area by the viscous product as already noted. Thus in the first attempt to obtain I_2 reduction simultaneously with wood liquefaction, the better of the two designs of cathode shows only a 25% decrease in current density because of the presence of the viscous crude wood oil product.

The second major issue examined is the problem of obtaining I_2 reduction to the exclusion of the competitive cathode reaction of H_2 generation. The generation of H_2 was observed for runs #8 and #9ECLR with the mesh cathode at 6 V and with $[I_2]$ in the range 0.02 – 0.04 M. With the switch from the mesh to the continuous sheet cathode, at the same cell voltage and similar other conditions the cathode current density increased by about 10%, as noted earlier, and H_2 generation disappeared for runs #11, #12 and #14ECLR. The only exception was that when run #14ECLR was continued after 5h for another 3/4h but with no wood feed, the $[I_2]$ dropped and H_2 generation recurred. No conditions for runs #15 – #20ECLR, all with the continuous surface cathode, gave H_2 generation at the cathode. The sharply curved surfaces of the mesh cathode may produce local current density conditions more conducive to H_2 production. Run #17ECLR was operated at a wood feed rate only 1/3 – 1/2 that of all other runs with the sheet cathode, yet even then H_2 was not generated. This finding further indicates that the small scale geometry of the cathode surface can play an important role in controlling H_2 evolution. As discussed in Section 3.2 and Appendix C.6, the voltage range of 0.66 V over which it should be possible to obtain I_2 reduction but without H_2 generation is the same for both the mesh and sheet cathodes. Although the few experiments made with the mesh cathode did not succeed in identifying conditions for good current density but without H_2 generation, with the cathode surface of continuous sheet metal all the conditions tested with any wood feed rate gave I_2 reduction to the exclusion of H_2 generation.

The third major question to be explored with these batchwise-continuous runs concerns the level of $[I_2]$ that can be maintained in a continuous wood liquefaction reactor with simultaneous electrochemical reduction of I_2 to HI. The I_2 generation rate is controlled by the wood feed rate, while the I_2 reduction rate is affected by I_2 concentration, cathode geometry, cell voltage and cathode rotation speed as discussed in Chapter 4. The batchwise-continuous runs were started with HI solution that was nearly I_2-free, i.e. $[I_2]$ about 0.001 – 0.006 M. The evolution during these runs of I_2 concentration in the ECLR aqueous HI solution that is illustrated in Figure 6.1 should be viewed in the context of nonelectrochemical liquefaction. With the later, Figure 5.13 shows that for a realistic range of reaction conditions, i.e. stoichiometric ratio R of 2 – 3.5 gmol/gmol and initial [HI] of 56 – 64 wt%, the I_2 concentration at the end of batch reactor liquefaction reaches 0.6 M – 1.4 M. For all of the Figure 6.1 data except for runs #18 and #19ECLR, I_2 concentration after 5h operation is in the range 0.025 – 0.05 M and is either slowly increasing or decreasing, indicating that the ECLR runs operated with conditions of approximate balance between I_2 generated from wood liquefaction and I_2 reduced electrochemically to I^-. For the special cases of #18 and #19ECLR, it is believed that the higher I_2 concentration derived from the corrosion that was subsequently detected on the connection between the platinum cathode shaft and the stainless steel support shaft because the current, 9.4 – 10.5 A, was lower than the normal value of 11.5 – 12 A obtained for runs #11, #12, #14 and #15ECLR at the same voltage of 6 V. A new stainless steel shaft was installed for run #20ECLR, and the I_2 concentrations were substantially lower than in #19ECLR. Considering all the runs of the #8 – #20ECLR series, exclusive of runs #18 and #19ECLR for the above reason, Figure 6.1 illustrates the effectiveness of electrochemical reduction of I_2 during wood liquefaction in maintaining $[I_2]$ at about 5% of the value reached in nonelectrochemical batch reactor liquefaction.

	Run No.	Cathode area cm^2	Run time h	Wood feed rate g/min	Cell voltage V	Cell current A	Initial [HI] wt%	Final [HI] wt%
✱	#8ECLR	10.4	5	0.05	6	7.6	55	50
▬	#9ECLR	10.4	5	0.05	6	7.6	55	52
●	#12ECLR	14.7	5	0.09	6	11.6	56	45
■	#14ECLR	14.7	5+0.75*	0.1	6	11.5	52	45
○	#15ECLR	14.7	5	0.1	6	11.5	56	44
☐	#16ECLR	14.7	5	0.1	7	15	57	44
▲	#17ECLR	14.7	5	0.05	6	8.8	57	48
○	#18ECLR	14.7	3	0.15	6	9.4	56	49
☐	#19ECLR	14.7	3	0.1	6	10.5	60	51
△	#20ECLR	14.7	3	0.09	6	12.5	61	53

* 0.75h without wood feed

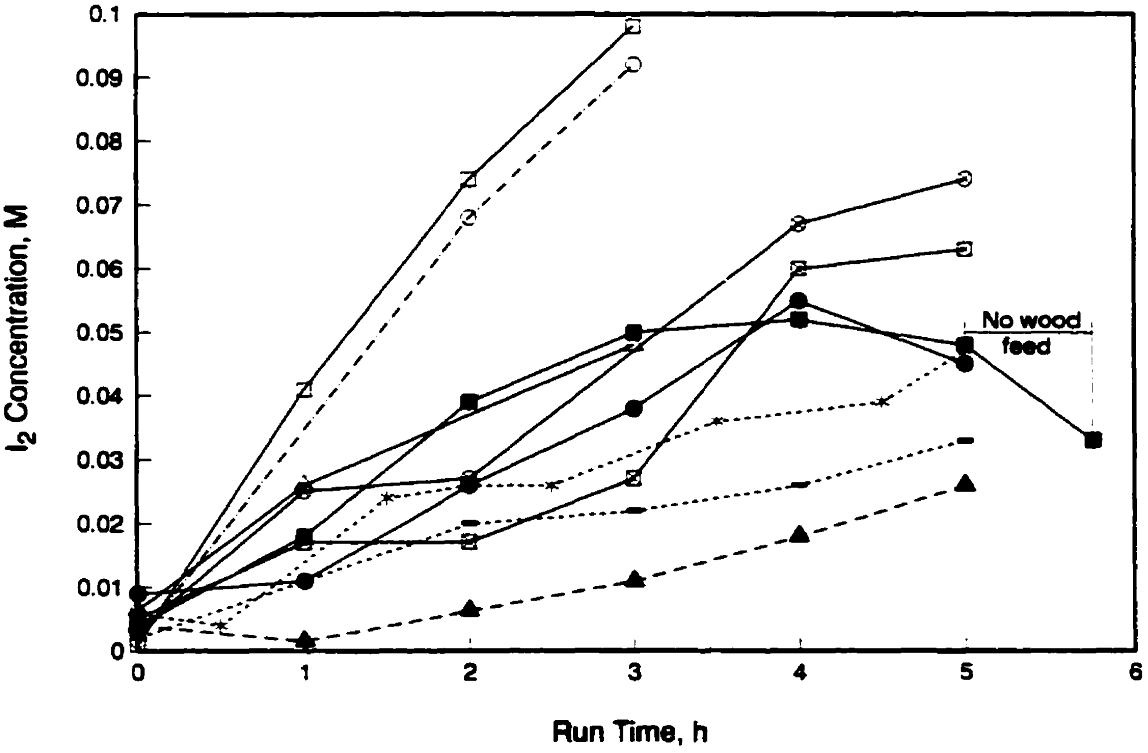


Figure 6.1 Evolution of Aqueous Phase I_2 Concentration during Electrochemical Liquefaction

6.3.3 Iodine content of crude product

The above experiments, batch or batchwise-continuous, establish that this ECLR design is quite effective at reducing I_2 in solution back to HI, even in the presence of the wood feed and of the liquefaction reaction and organic reaction products. Table 6.6 lists as $(I/C)_{OP}$ the iodine content of the OP product fraction from electrochemical wood liquefaction runs #2 – #20ECLR together with those for some reference nonelectrochemical wood liquefaction batch reactor experiments.

Normally the OP fraction analyzed was a sample of all the OP product produced during an ECLR run. For run #15ECLR however, samples of the OP product were withdrawn for analysis each hour during the run, while at the end of the run samples of OP product were taken from several locations in the cathode compartment. The resulting I:C ratios show a tendency to increase with time during the run, as did I_2 concentration also. From Table 6.6 it is seen that the I/C ratio of the OP fraction at the end of #15ECLR varied randomly with position in the reactor. Most significantly, even the OP product that adhered directly to the surface of the cathode where the reduction of I_2 to HI occurs had an I/C content no different from that for product adhering to the reactor wall, far from the cathode. This finding confirmed that the viscous OP product, which has I_2 associated physically with it as is established in section 6.3.4, does not participate in the electrochemical reduction of I_2 reaction occurring at the cathode surface.

The objective for run #14ECLR was to continue the electrochemical operation for 0.75h after the end of the 5h of wood feeding, thereby decreasing the level of $[I_2]$ in the reactor aqueous phase at the end of 5.75h, to determine whether this lowered the I/C ratio of the crude organic product fraction OP. During this 0.75h with no wood feed the $[I_2]$ decreased from 0.048 M to 0.033M but H_2 bubble generation at the cathode was observed. H_2 production occurs when there is insufficient I_2 at the cathode surface to satisfy the electrochemical current with I_2 reduction to HI. Elemental analysis established that the I/C ratio of the crude OP product taken from the reactor at the end of run #14ECLR was not lower than normal.

Table 6.6 Iodine Content of Crude Product

Run No	Conditions	$[I_2]_{final}$ (M)	$[HI]_{initial}$ (wt%)	$[HI]_{final}$ (wt%)	$(I/C)_{OP}$	Comments
	R, gmol/gmol					
*2ECLR	4.5	0.31	55.6	50.6	0.075	Batch ECLR
*5ECLR	4.5	0.086	55.2	51.2	0.055	without make-up HI
*6ECLR	10	0.018	55.2	52.8	0.039	10.4 cm^2 cathode
*10ECLR	10	0.002	54.5	51.9	0.045	
	F_{wood}, g/min					Batchwise-Continuous ECLR
*8ECLR	0.050	0.047	55.5	50.0	0.063	without make-up HI
*9ECLR	0.047	0.033	54.8	52.0	0.058	10.4 cm^2 cathode
*15ECLR	t, h		55.7			
	1	0.025		53.2	0.069	Batchwise-Continuous ECLR
	3	0.027		48.4	0.060	without make-up HI
	4	0.067		46.8	0.078	14.7 cm^2 cathode
	5	0.074		43.9	0.092	F_{wood} = 0.10 g/min
	Product from					
	Cathode				0.061	
	ECLR wall				0.063	
	ECLR bottom				0.090	
	Composite				0.10	
*14ECLR	5	0.048	51.6	44.5	0.061	F_{wood} = 0.095 g/min
	5.75	0.033		44.3	0.070	F_{wood} = 0 after 5h
*17ECLR	t, h		56.6			
	1	0.0015		54.0	0.052	Batchwise-Continuous ECLR
	2	0.0063		52.3	0.046	without make-up HI
	3	0.011		50.9	0.048	14.7 cm^2 cathode
	4	0.018		49.3	0.046	F_{wood} = 0.050 g/min
	5	0.026		48.4	0.045	
	F_{wood}, g/min					
*12ECLR	0.091	0.045	56.4	44.6	0.063	Batchwise-Continuous ECLR
*14ECLR	0.095	0.048	51.6	44.5	0.061	without make-up HI
*15ECLR	0.100	0.074	55.7	43.9	0.087	14.7 cm^2 cathode
*16ECLR	0.101	0.063	56.9	44.0	0.074	$[HI]_{initial}$ = 56 − 57 wt%
*17ECLR	0.050	0.026	56.6	48.4	0.045	t = 5h
*18ECLR	0.150	0.092	56.1	48.7	0.083	KI added; t = 3h
	F_{wood}, g/min					Batchwise-Continuous ECLR
*19ECLR	0.100	0.098	59.7	51.4	0.10	without make-up HI
*20ECLR	0.086	0.048	61.1	52.5	0.11	14.7 cm^2 cathode
						t=3h, $[HI]_{initial}$ = 60−61 wt%
	R, gmol/gmol					
78	4.4	0.60	57.4	51.1	0.12	Nonelectrochemical
79	3.5	0.68	57.6	49.6	0.14	batch wood liquefaction
80	2.9	0.77	57.4	48.6	0.14	$[HI]_{initial}$ = 57 wt%
81	2.0	0.91	58.0	45.1	0.17	
72	3.5	0.88	61.9	56.4	0.14	$[HI]_{initial}$ = 61 wt%
77	2.0	1.19	61.0	58.6	0.17	
73	1.0	1.35	61.3	52.9	0.13	
75	2.0	1.78	68.6	49.5	0.21	$[HI]_{initial}$ = 68 wt%
76	1.5	1.97	68.5	45.5	0.21	
74	1.0	1.98	68.3	44.0	0.20	

For run *17ECLR the wood feed rate was 1/2 the normal feed rate, which led to I_2 concentration in the aqueous solution about 1/2 the normal level, Figure 6.1. For this run samples of the OP product, withdrawn each hour, showed that the iodine content was moderately lower. Thus the I:C ratio in the product varies with ECLR conditions, but is not as sensitive as was hoped.

Run *18ECLR was a speculative run with the initial aqueous HI solution containing also KI at a concentration of 0.14 M. Moreover, the wood feed rate was 50% higher than for runs *11 – *16ECLR. In HI solution, KI may act as a hydrotropic solvent to increase the solubility of low solubility material such as the liquefaction product and thereby might change the I/C ratio of the crude wood oil product. With the much higher wood feed rate, the I_2 concentration at 3h was also much higher than all previous runs and the I/C ratio for the OP product was also high. Thus the use of the hydrotropic salt effect did not lead to a lower I/C ratio in the OP product.

From the perspective of all of the results of Chapter 5 for I/C ratio of organic products from nonelectrochemical batch reactor experiments and from the batch and batchwise-continuous ECLR runs of Chapter 6, it appears that the I/C ratio of the crude liquefaction product shows no significant dependence on reaction time or length of continuous run, reaction temperature, HI concentration, stoichiometric ratio R or type of lignocellulosic substrate, whether the liquefaction is nonelectrochemical or electrochemical, batch or continuous ECLR operation. To illustrate this conclusion Figure 6.2 shows all the I/C ratio results of OP product fraction for nonelectrochemical batch liquefaction with wood, Figures 5.12 and 5.24, results with wood, cellulose, the hemicellulose xylan and lignin as substrates, Figure 5.34, along with the Chapter 6 results for operation as a batch ECLR and as a batchwise-continuous ECLR. This collection of data provides a perspective with I_2 concentration varying by about a factor of 1000. From Figure 6.2 it may be concluded that over this very wide range of I_2 concentration in the aqueous HI solution, i.e. for $[I_2]$ from about 0.0015 to 2 M, the iodine content of crude organic product from biomass liquefaction is controlled by the I_2 concentration in the aqueous phase regardless of major changes in all other

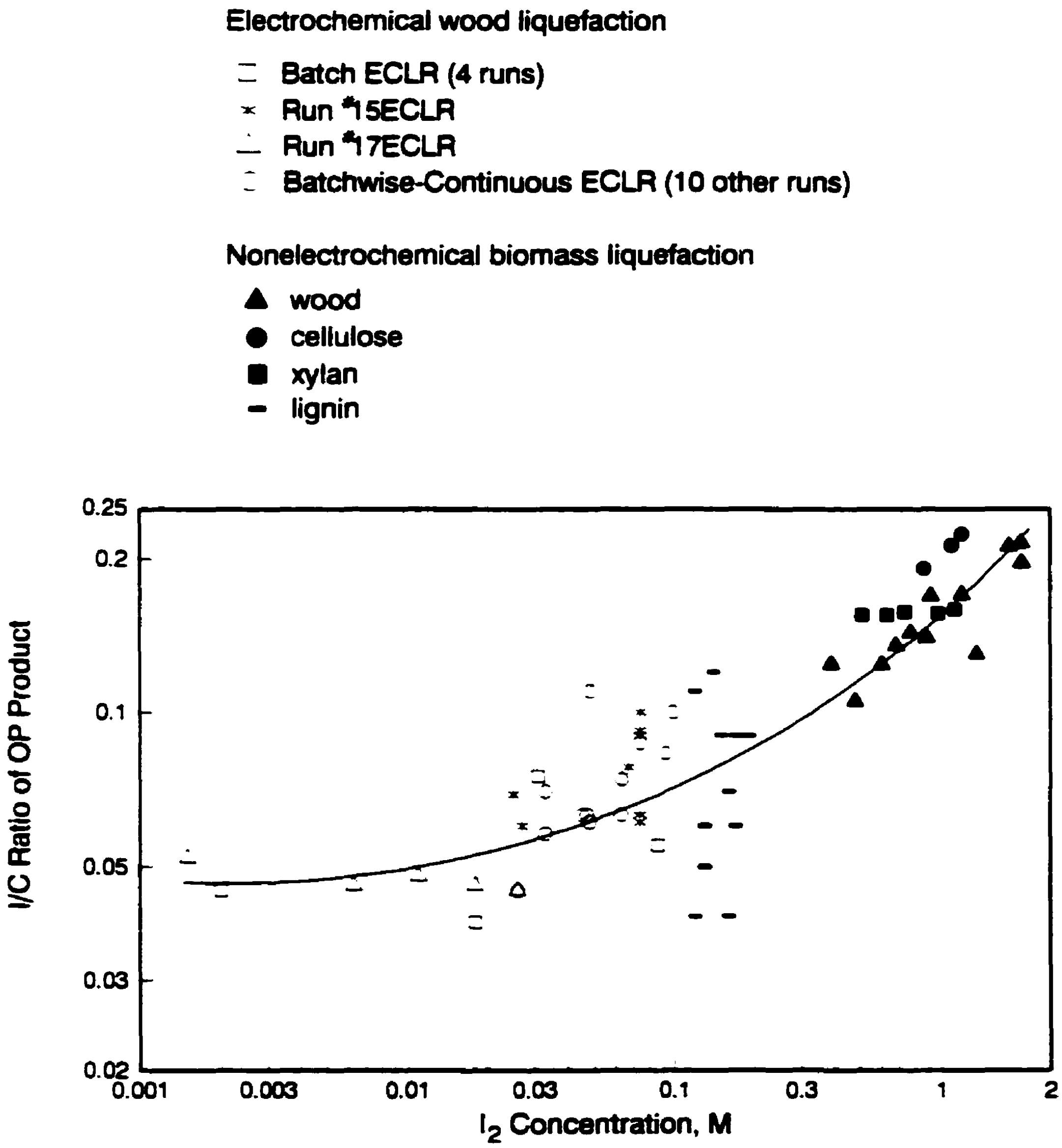


Figure 6.2 Relation of I_2 Concentration of Aqueous Phase and Iodine Content of OP Product

liquefaction reaction conditions. Because the method of analysis for iodine content of the crude product is quite precise, the substantial variability in I/C ratio on Figure 6.2 does not derive from the analysis. As a relationship between [I_2] and the I/C ratio in the product is apparent, and as the viscous product adheres to surfaces in the reactor in aggregations of greatly variable size, the scatter observed in Figure 6.2 probably derives from the quite variable degree of contact between of the viscous product and the aqueous phase.

As it is not possible at least in the present design of ECLR to maintain the [I_2] below about 0.03 M without loss of electrochemical efficiency from the onset at the cathode of H_2 generation, the competitive reaction to I_2 reduction, that level of [I_2] = 0.03 M appears to determine the lower limit of organic product I/C ratio for electrochemical liquefaction. As the preferred range of conditions for nonelectrochemical batch liquefaction ([HI] of 57 – 64 wt%, stoichiometric ratio R of 2 – 3 gmol HI/gmol C) produces levels of [I_2] in the range 0.7 – 1.4 M, Figure 6.2 shows that this range of [I_2] would about I/C = 0.15 in the crude product. For electrochemical liquefaction it is possible to maintain [I_2] at about 0.03 M, for which Figure 6.2 shows that the crude product iodine content could be maintained at about I/C = 0.06. Thus although electrochemical liquefaction reduced the I/C content less than had been hoped, the reduction is none the less significant - by about 60% from the level I/C content in the crude wood oil product for liquefaction without simultaneous reduction of I_2 back to HI.

6.3.4 I_2 physically associated on crude product

The work of Sneed, 1954, and Cotton and Wilkinson, 1988, shows that I_2 makes charge-transfer complexes with organic molecule structures such as a benzene ring, the oxygen atom of a carbonyl group or the iodine atom of an iodide. Some or all of these types of associations may co-exist, depending on conditions. These bonds are of widely variably strength but in general are stronger than typical physical adsorption but weaker than chemical bonds. To investigate this behaviour for the organic product from wood liquefaction, a Soxhlet extraction with CS_2 was performed on the OP product fraction from run #14ECLR, these results being detailed in Appendix L. The colourless CS_2 solvent became light yellow immediately, becoming gradually brown at longer extraction time. These colour phase phenomena are well known for the removal of charge-transfer complex I_2 into the solvent.

The results shown in Figure 6.3 indicate that the first 1/3 of the iodine content of the product was removed in about 8h extraction, then about 2.5 days to remove next 1/3 of the iodine, with further I_2 extraction occurring more slowly. The 6.4 wt% iodine remaining after 11 days extraction may be taken as the iodine content which is chemically bonded as organic iodide. The results of solvent extraction of the crude OP product therefore showed about 85% of the iodine to be physically associated with the product rather than as organic iodide. Thus the crude product in fact has a very much lower organic iodide content than had previously been supposed.

When the results of Figure 6.3 are re-expressed as only the I_2 content of the OP product, i.e. exclusive of the 6.4 wt% iodine believed to be as organic iodide, the extraction process is as shown by Figure 6.4. The I_2 content expressed as the I_{I_2}:C ratio is seen to drop in various stages, at successively decreasing rates. Of the various types of charge-transfer complex bonded I_2 molecules, the most weakly bonded is known to be I_2 on benzene rings of aromatic components, so this I_2 would be removed first. Next, the I_2 attached to carbonyl oxygen atoms would be removed as that bond is stronger than with benzene rings. As the I_2 associated with iodine atoms is the strongest charge-transfer complex bond, the I_2 complexed with the organic iodide in the crude organic product would be the last to be removed by solvent extraction. Thus the rate of extraction of I_2 is seen on Figure 6.4 to be highest at first when it may be assumed that the I_2 is being removed from benzene rings, is slower when I_2 is being removed from carbonyl oxygens, and is slowest for removal of I_2 from the iodide atom of the organic iodine content of the OP product.

The OP products from runs #15, #17 and #18ECLR and the AP product from run

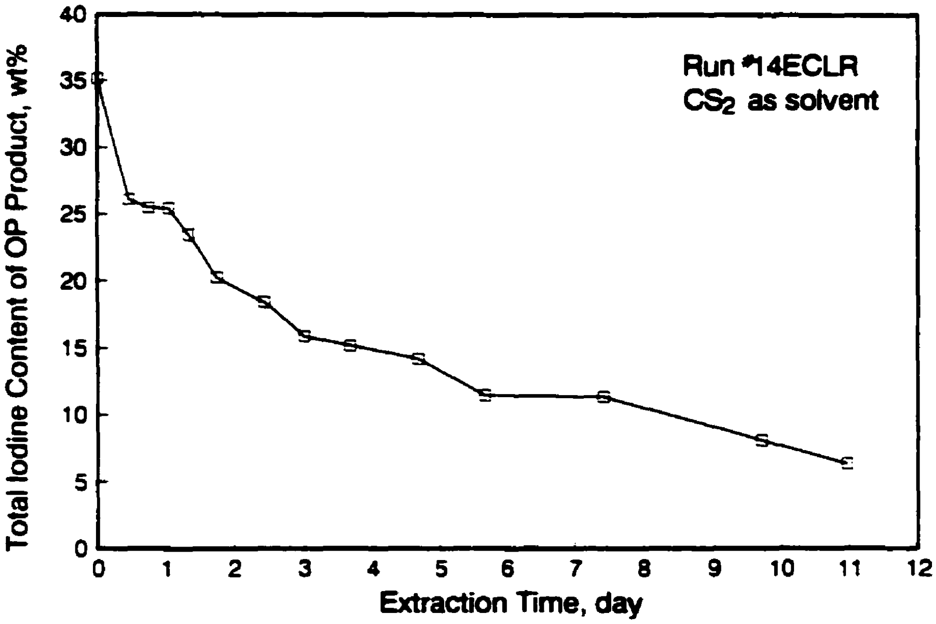


Figure 6.3 Effect of time of Solvent Extraction on Total Iodine Content of OP Product

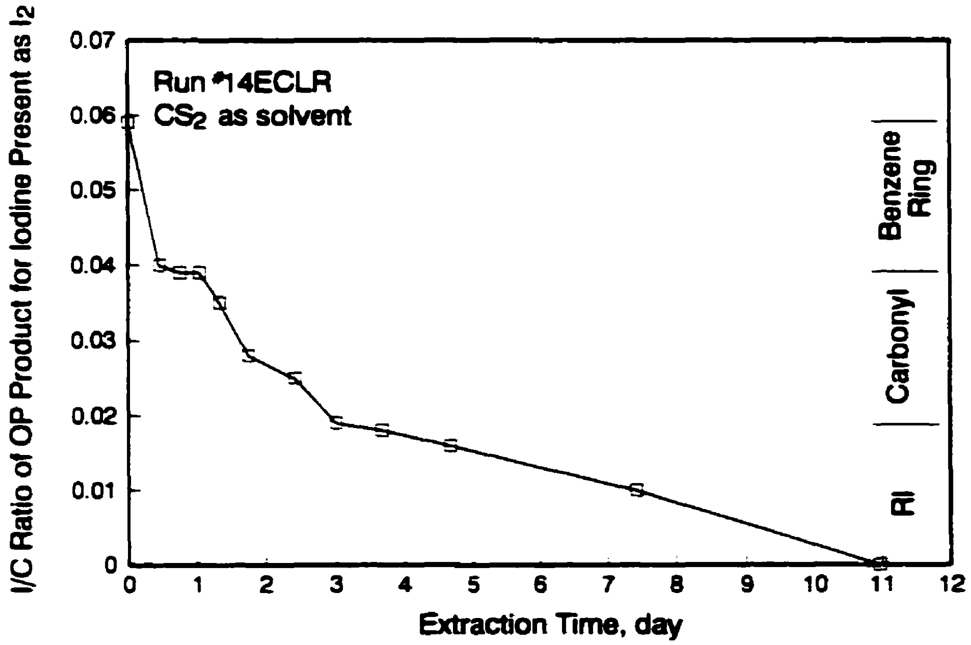


Figure 6.4 Effect of Time of Solvent Extraction on I_2 Content of OP Product

*12ECLR was treated with 0.3 M sodium thiosulphate solution, $Na_2S_2O_3$, to chemically reduce the I_2 that is physically associated on the crude product. From Table 6.7 it is seen that these product fractions after I_2 removal showed consistently that only 5 – 7% of the iodine content in the product is chemically bonded, i.e. that the atomic ratio I_{RI}/C is only 0.007 – 0.01 for the organic iodine content. The remaining iodine detected by elemental analysis is therefore I_2 associated physically with the crude product. The interpretation of these tests with solvent extraction and sodium thiosulphate treatment shows that the physical association between I_2 and the product is sufficiently strong that, as seen on Figure 6.2, it does not respond to reducing the I_2 concentration in the ECLR to very low levels in the aqueous solution.

6.3.5 Product composition and yield

The elemental composition of the OP product from batchwise-continuous electrochemical wood liquefaction with initial 55 – 57 wt% aqueous HI solution but without make-up HI typically gave values of H/C of 1.13 – 1.25 and O/C of 0.12 – 0.22 as shown in Table 6.7. Correspondingly, Table 6.8 shows that relative to the hybrid poplar feed the hydrogen retention and oxygen removal of the OP product fraction was, respectively, 71 – 78% and 69 – 82%.

With enhancing the initial HI concentration to 60 – 61 wt%, therefore having 51 – 52 wt% HI at the end of runs *19 and *20ECLR, as high as about 80 – 85% hydrogen retention is obtained and oxygen removal also reaches a higher level of about 81 – 83% for the OP product relative to the hybrid poplar feed. This observation of higher hydrogen retention and oxygen removal at higher levels of HI concentration suggests examining these characteristics as a function of HI concentration along with the corresponding results for nonelectrochemical liquefaction reproduced from Figures 5.22 and 5.23. This procedure leads to Figures 6.5 and 6.6, where the value of HI concentration for electrochemical wood liquefaction is the average of HI concentration during the run as recorded in Table 6.5. For comparison of hydrogen retention for

Table 6.7 Elemental Analysis of Crude Products for Batchwise-Continuous ECLR Wood Liquefaction

Run No.	Initial [HI] wt%	Final [HI] wt%	Average [HI] wt%	Final $[I_2]$ M	Product	As obtained from reactor								After treatment with sodium thiosulphate							
						Elemental Composition, wt%					Atomic ratio			Elemental Composition, wt%					Atomic Ratio		
						C	H	O	I	total	H/C	O/C	I/C	C	H	O	I	total	H/C	O/C	I/C
*8ECLR	55.5	50.0	52.5	0.047	OP	49.69	5.00	11.77	32.83	99.29	1.21	0.178	0.063								
*9ECLR	54.8	52.0	52.8	0.033	OP	52.55	5.38	11.12	32.24	101.29	1.23	0.158	0.058								
*11ECLR	56.2	49.0	53.4	0.063	OP	48.84	4.90	10.97	32.71	97.42	1.20	0.168	0.063								
*12ECLR	56.4	44.6	50.0	0.045	OP	52.09	5.05	8.62	34.53	100.29	1.16	0.124	0.063								
					AP									64.35	7.71	19.54	6.64	98.24	1.44	0.216	0.0098
*14ECLR	51.6	44.5	47.6	0.048	OP	49.69	4.68	13.10	32.03	99.50	1.13	0.198	0.061								
					AP	48.86	5.07	18.09	25.43	97.45	1.25	0.278	0.049								
*15ECLR	55.7	43.9	50.0	0.074	OP	41.57	4.12	12.01	38.07	95.77	1.19	0.217	0.087	63.55	5.99	17.39	4.83	91.76	1.13	0.205	0.0072
*16ECLR	56.9	44.0	50.1	0.063	OP	46.17	4.67	12.12	36.06	99.02	1.21	0.197	0.074								
*17ECLR	56.6	48.4	51.9	0.026	OP	55.10	5.66	14.05	26.30	101.11	1.23	0.191	0.045	66.05	6.40	14.17	6.62	93.24	1.16	0.161	0.0095
*18ECLR	56.1	48.7	52.1	0.092	OP	43.83	4.53	11.10	38.24	97.70	1.24	0.190	0.083	63.75	6.27	15.03	6.73	91.78	1.18	0.177	0.0100
*19ECLR	59.7	51.4	55.2	0.098	OP	42.02	4.48	7.48	45.76	99.74	1.28	0.134	0.103								
*20ECLR	61.1	52.5	56.4	0.048	OP	43.42	4.91	7.03	44.37	99.73	1.36	0.122	0.097								

Table 6.8 Hydrogen Retention and Oxygen Removal for Batchwise-Continuous ECLR Wood Liquefaction

Run No.	Average [HI] wt%	Product Fraction	Relative to Hybrid Poplar	
			Hydrogen Retention,%	Oxygen Removal,%
*8ECLR	52.5	OP	75.5	74.6
*9ECLR	52.8	OP	77.4	77.4
*11ECLR	53.4	OP	75.5	76.0
*12ECLR	50.0	OP	73.0	82.3
		AP*	90.6	69.1
*14ECLR	47.6	OP	71.1	71.7
		AP	78.6	60.3
*15ECLR	50.0	OP	74.8	69.0
*16ECLR	50.1	OP	76.1	71.9
*17ECLR	51.9	OP	77.4	72.7
*18ECLR	52.1	OP	78.0	72.9
*19ECLR	55.2	OP	80.5	80.9
*20ECLR	56.4	OP	85.5	82.6

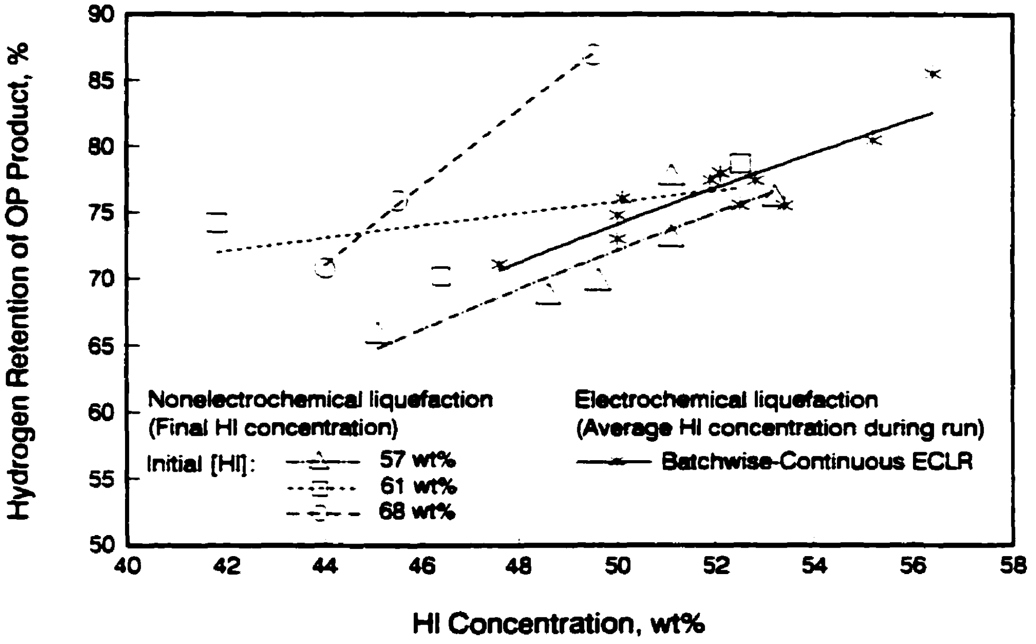


Figure 6.5 Effect of HI Concentration on Hydrogen Retention of OP Product

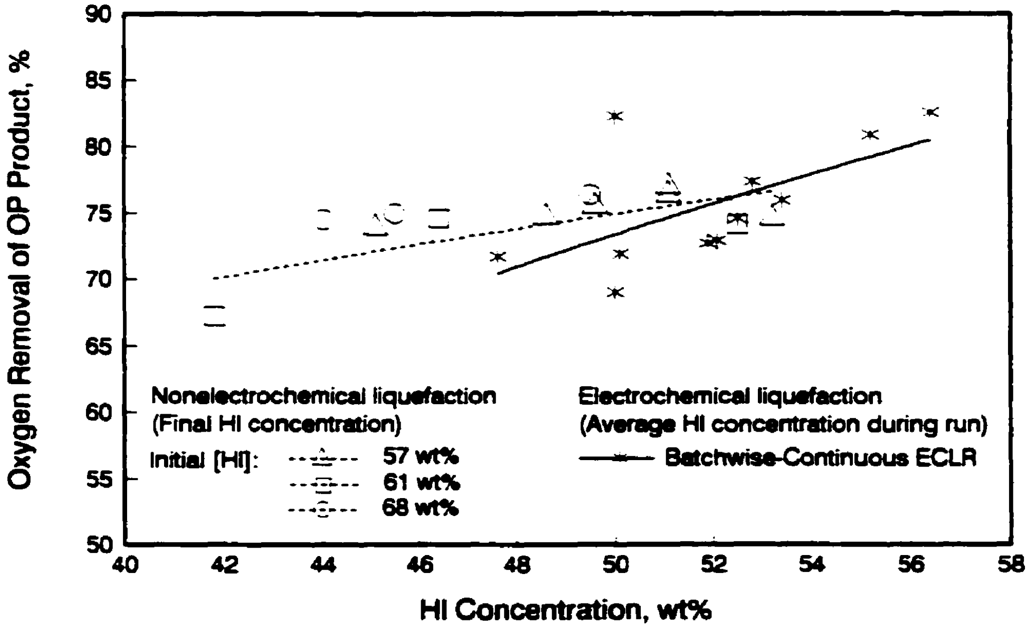


Figure 6.6 Effect of HI Concentration on Oxygen Removal of OP Product

batchwise electrochemical wood liquefaction operating at unsteady state HI concentration, the most comparable nonelectrochemical experiments on Figure 6.5 are the set for initial HI concentration of 57 wt%, which is very close to the initial value of [HI] for runs #8 – #18ECLR, Table 6.7. Comparison of these two correlation lines on Figure 6.5 indicates that batchwise-continuous electrochemical liquefaction gives about 5% higher hydrogen retention of OP product. This improvement in hydrogen retention in electrochemical liquefaction, although small, is an interesting aspect to be examined further with the data of Chapter 7. It is clear from Figure 6.5, however, that the hydrogen retention for ECLR wood oil product increases with the level of HI concentration in the aqueous phase, as was detected first in the nonelectrochemical batch reactor experiments. Likewise on Figure 6.6 the line from Figure 5.23 is also shown, thereby demonstrating that the deoxygenation for the OP products increases with HI concentration for both nonelectrochemical and electrochemical liquefaction, but in this case there is no significant difference apparent between the two types of operation.

A more detailed treatment of the composition of the product obtained from electrochemical liquefaction of wood in a continuous ECLR system is deferred to Chapter 7. The AP and OP product fractions after treatment with sodium thiosulphate to reduce physically associated I_2 show that when the iodine remaining is only that as organic iodide, then the I:C ratio is in the range 0.007 – 0.01, Table 6.7. Subtracting this amount of iodine present as organic iodide, I_{RI}:C of 0.007 to 0.01, from the total amount of iodine present, I:C of 0.05 to 0.10, indicates that the iodine present as I_2 physically associated with the product has a typical level of I_{I_2}:C in the range 0.05 – 0.09. That is, about 85 – 90% of the iodine content in the crude wood oil product is physically associated I_2.

The yield distribution for this series of batchwise-continuous runs is recorded in Table 6.9. The yield of the OP product fraction was obtained directly from the amount and composition of this product, as noted in Section 6.3.1. As discussed earlier, CH_3I is produced to the extent of 4.9% carbon-base yield. The yield of AP product is obtained difference. As shown in Figure 6.7 the yield of the OP product fraction

Table 6.9 Yield of Product Fractions for Batchwise-Continuous ECLR Wood Liquefaction

Run No.	Average [HI] (wt%)	Before Reaction		After Reaction				
		Wood		OP			AP	CH_3I
		Feed Wood (g)	Carbon Content (wt%)	Weight OP (g)	Carbon Content (wt%)	Yield $Y_{C/OP}$ (%)	Yield* $Y_{C/AP}$ (%)	Yield $Y_{MI/AP}$ (%)
*8ECLR	52.5	14.972	48.2	9.673	49.69	66.6	28.5	4.9
*9ECLR	52.8	14.149	48.2	5.702	52.55	43.9	51.2	4.9
*11ECLR	53.4	26.933	48.2	13.309	48.84	50.1	45.0	4.9
*12ECLR	50.0	27.316	48.2	16.781	52.09	66.4	28.7	4.9
*14ECLR	47.6	28.5	48.2	15.323	49.69	55.4	39.7	4.9
*15ECLR	50.0	30.0	48.2	21.410	41.57	61.5	33.6	4.9
*16ECLR	50.1	30.017	48.2	20.999	46.17	67.0	28.1	4.9
*17ECLR	51.9	15.008	48.2	6.371	55.10	48.5	46.6	4.9
*18ECLR	52.1	26.990	48.2	21.049	43.83	70.9	24.2	4.9
*19ECLR	55.2	18.041	48.2	14.973	42.02	72.3	22.8	4.9
*20ECLR	56.4	15.607	48.2	12.326	43.42	71.2	23.9	4.9

* Obtained by difference

increases and the AP product fraction necessarily decreases with increasing average HI concentration. As the yield of AP product represents the aqueous HI solution being saturated with product, the AP yield depends on the amount of aqueous HI solution used, which is different in the batchwise-continuous mode from the batch reactor operation of Chapter 5. Thus no general comparisons are made between yields here and those for the earlier nonelectrochemical batch reactor results. As earlier work, Douglas, 1986, and Ladanowski, 1986, established that in a fully continuous reactor system with recycle of the aqueous phase back to the liquefaction reactor the AP product is converted to the OP crude wood oil. As the yield of AP product thereby goes to zero for a fully continuous ECLR system at steady-state, the levels of OP and AP yield in the present experiments are not of particular importance. However as Figures 6.5 and 6.6 showed the improvement in product quality by operation at higher levels of HI concentration, the significance of Figure 6.7 is in showing that fortunately the yield of the OP product would increase along with product quality.

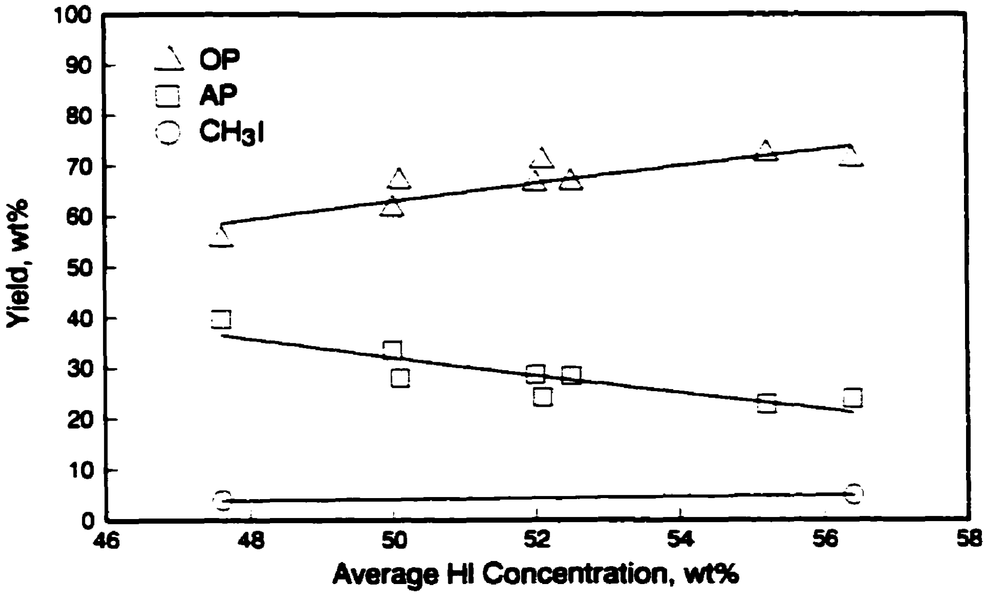


Figure 6.7 Effect of Average HI Concentration on Yield for Batchwise-Continuous Wood Liquefaction

6.3.6 Reaction stoichiometric equation and coefficients

Information is available for application of the reaction stoichiometric Equations 5.10 and 5.11 for two unsteady batchwise-continuous runs *12ECLR and *14ECLR, for which the yield and composition data are recorded in Tables 6.7 and 6.9. The aqueous phase product fraction AP was obtained for elemental analysis by methylene chloride extraction from the aqueous HI solution after that solution had been treated with $Na_2S_2O_3$ solution to reduce all the I_2 to I^-, as recorded in Section 5.2.2. For run *14ECLR the composition of the AP product by direct elemental analysis was determined to be $CH_{1.25}O_{0.278}I_{0.049}$. As the yield of CH_3I would be 4.9%, the yield of the AP product fraction is 39.7% by difference with Equation 5.4. Therefore the reaction stoichiometric Equation 5.11 can be written for batchwise-continuous run *14ECLR as:

$$\begin{aligned} CH_{1.59}O_{0.70} + a\ HI = 0.554\ CH_{1.13}O_{0.198}I_{0.061} + 0.397\ CH_{1.25}O_{0.278}I_{0.049} \\ + 0.049\ CH_3I + b\ H_2O + c\ I_2 \end{aligned} \tag{6.1}$$

By balancing Equation 6.1 for H, O and I the reaction stoichiometric coefficients are obtained as:

a = 0.64 gmol HI reacted/gmol C in wood
b = 0.48 gmol H_2O produced/gmol C in wood
c = 0.27 gmol I_2 produced/gmol C in wood

Relative to *14ECLR, run *12ECLR was with a somewhat higher initial [HI], 56.4 wt%, but the same final [HI], 44.6 wt%, therefore higher average [HI], 50.0%. The composition of the aqueous phase product fraction AP, obtained as discribed above and in Section 5.2.2, was determined to be $CH_{1.44}O_{0.216}I_{0.0098}$, free of any physically associated I_2. Allowing for the 4.9% CH_3I produced, the yield of the AP product fraction was 28.7% by difference from Equation 5.4. Thus the reaction stoichiometric equation is

$$CH_{1.59}O_{0.70} + a\ HI = 0.664\ CH_{1.16}O_{0.124}I_{0.063} + 0.287\ CH_{1.44}O_{0.216}I_{0.0098}$$
$$+ 0.049\ CH_3I + b\ H_2O + c\ I_2 \qquad (6.2)$$

Balancing Equation 6.2 for H, O and I as before yields the coefficients

a = 0.86 gmol HI reacted/gmol C in wood
b = 0.56 gmol H_2O produced/gmol C in wood
c = 0.38 gmol I_2 produced/gmol C in wood

As the I/C ratio of the crude product is not sensitive to the reaction conditions including the HI concentration, the iodine content of the crude AP product fraction including the physically associated I_2 may be taken as $(I/C)_{AP} = 0.05$ from run #14ECLR, which will subsequently be seen to be consistent with results from run #21ECLR, recorded in Sections 7.3 and 7.4. Therefore Equation 6.2 can be rewritten to compare with Equation 6.1 with the same types of the OP and AP product fraction as follows:

$$CH_{1.59}O_{0.70} + a\ HI = 0.664\ CH_{1.16}O_{0.124}I_{0.063} + 0.287\ CH_{1.44}O_{0.216}I_{0.05}$$
$$+ 0.049\ CH_3I + b\ H_2O + c\ I_2 \qquad (6.3)$$

Comparison with Equation 6.2 indicates that the only coefficient changed in Equation 6.3 will be the value of c, which is now 0.38 gmol I_2 produced/gmol C in wood.

Table 6.10 indicates that for run #14ECLR operated at 47.6 wt% average HI concentration the reaction stoichiometric coefficients, a and c, are close to those for nonelectrochemical wood liquefaction, Table 6.10, while for run #12ECLR at 50.0% average HI concentration these coefficients are about 20% higher than the values obtained from Figure 5.17 for nonelectrochemical wood liquefaction at the same HI concentration. In this comparison it is assumed that the extend of the HI-wood reaction would depend mostly on the final HI concentration in batch reaction, and mostly on the average HI concentration for batchwise-continuous reaction, although precise comparison are clearly not possible. For run #14ECLR the stoichiometric coefficients may be somewhat reduced by the relatively lower initial HI concentration of 51.6 wt%. Thus the comparison for run #12ECLR may be more valid, in which case the values of stoichiometric coefficients significantly higher for electrochemical than nonelectrochemical liquefaction are encouraging. The question of any differences between the chemistry of wood liquefaction with or without simultaneous electrochemical effects is deferred to Chapter 7 when more detailed results with a more controlled ECLR operation will be available.

Table 6.10 Reaction Stoichiometric Coefficients for Electrochemical and Nonelectrochemical Wood Liquefaction

Reactor	ECLR	Nonelectrochemical Reactor
Basis	#14ECLR	Figure 5.17
Initial [HI], wt%	51.6	57
Final [HI], wt%	44.5	47.6
Average [HI], wt%	47.6	
Reaction Stoichiometric Coefficients		
a. gmol HI reacted/gmol C in wood	0.64	0.66
b. gmol H_2O produced/gmol C in wood	0.48	
c. gmol I_2 produced/gmol C in wood	0.27	0.28
Basis	#12ECLR	Figure 5.17
Initial [HI], wt%	56.4	57
Final [HI], wt%	44.6	50.0
Average [HI], wt%	50.0	
Reaction Stoichiometric Coefficients		
a. gmol HI reacted/gmol C in wood	0.86	0.72
b. gmol H_2O produced/gmol C in wood	0.56	
c. gmol I_2 produced/gmol C in wood	0.38	0.32

6.4 Summary

The principal questions addressed in this chapter were whether electrochemical reduction of I_2 could be obtained simultaneously with wood liquefaction, whether the viscous wood oil product blankets the cathode surface and/or the semipermeable membrane, whether it is still possible to obtain I_2 reduction with exclusion of the competitive reaction of H_2 generation, and whether a reasonably low level of I_2 concentration can be maintained with simultaneous wood liquefaction and I_2 reduction in such a reactor.

The preliminary 4 runs with batch electrochemical wood liquefaction established that I_2 produced by the reaction of wood with HI can be reduced simultaneously with wood liquefaction. Moreover with batch electrochemical liquefaction the I_2 concentration could be maintained lower than 0.01 M even in the presence of the crude wood oil. However on the mesh cathode used, the competitive reduction of $H^+ \rightarrow H_2$ occurred when I_2 concentration became lower than 0.1 M. The crude wood oil product had no major change in organic composition but its iodine content was reduced by about 1/3 compared with that from nonelectrochemical wood liquefaction.

The series of 11 runs with batchwise-continuous electrochemical wood liquefaction with the HI concentration not controlled to a steady value gave encouraging results, with reduction of I_2 to HI that maintained a low level of I_2 concentration in the presence of the wood liquefaction reaction and the viscous wood oil. The specific findings were:

(1) The cell current and cathode current density with electrochemical wood liquefaction is reduced relative to the system of pure I_2-HI aqueous solution because of partial blockage of the cathode surface by the viscous organic product. At comparable operating conditions the cathode current density with the cathode of continuous sheet metal is about 25% less with wood liquefaction than without.

(2) With the mesh cathode, H_2 generation was obtained at I_2 concentrations lower than 0.05 M, probably because of local electrochemical conditions at the sharply curved

surfaces of this mesh. With the change from the mesh cathode to one fabricated from continuous sheet metal, I_2 reduction was obtained without the competitive reaction of H_2 generation at the cathode during electrochemical wood liquefaction for conditions with any wood feed rate to the reactor.

(3) Even with the somewhat reduced cathode current density, batchwise wood feeding and the presence of viscous wood oil, stable operation was demonstrated up to the maximum run length tested, 5h, while maintaining the I_2 concentration not in excess of 0.1 M, averaging 0.03 – 0.04 M. This finding established that electrochemical liquefaction was obtained with an approximate balance in reaction rates between I_2 production from the wood-HI reaction and the I_2 reduction by electrochemical reaction.

(4) While the I_2 concentration in the aqueous HI solution was maintained at 0.03 – 0.05 M, the iodine content of the OP product fraction from electrochemical wood liquefaction, as atomic ratio, was found to be I/C = 0.06. This iodine content of the OP product fraction is about 60% lower than that obtained for the nonelectrochemical batch wood liquefaction.

(5) By application to the crude organic product of two independent methods, CS_2 solvent extraction and reduction of I_2 with sodium thiosulphate, it was found that about 85 – 90% of total iodine content is as I_2 physically associated with the crude wood oil, while only 10 – 15% of the iodine content is chemically bonded as organic iodide. Because the physical association between I_2 and the organic product is relatively strong, the iodine content of the crude product becomes asymtotic to a value of about I/C = 0.045 for I_2 concentration in the aqueous HI solution decreased to the very low value of 0.002 M during electrochemical wood liquefaction.

(6) The percent hydrogen retention and oxygen removal of the OP product both increase with concentration of HI in the aqueous phase in the liquefaction reactor. As HI concentration in the reaction aqueous phase dropped during these runs because the ability to control HI concentration to a steady value was not yet implemented, this trend for improved product quality at higher HI concentration was an important finding for subsequent development. The percent hydrogen retention appears to be measurably

better in electrochemical than in nonelectrochemical liquefaction of wood.

(7) The reaction stoichiometric equation for unsteady batchwise-continuous electrochemical wood liquefaction at the conditions of 6 V cell voltage, 1000 rpm cathode rotation speed, 0.091 g/min wood feed rate and 56.4 wt% initial and 50.0 wt% average [HI], is

$$\begin{aligned} CH_{1.59}O_{0.70} + 0.86\ HI = {} & 0.664\ CH_{1.16}O_{0.124}I_{0.063} + 0.287\ CH_{1.44}O_{0.216}I_{0.05} \\ & + 0.049\ CH_3I + 0.56\ H_2O + 0.38\ I_2 \end{aligned}$$

where the stoichiometric coefficients indicate carbon-base yields of 66.4%, 28.7% and 4.9% for respectively, the OP, AP and CH_3I product fractions. The extent of the HI-wood reaction at comparable conditions appears greater in electrochemical than in nonelectrochemical liquefaction of wood.

CHAPTER 7

CONTINUOUS ELECTROCHEMICAL WOOD LIQUEFACTION

7.1 Experimental basis for continuous electrochemical wood liquefaction

The present study was concluded with the most complete documentation and analysis of an electrochemical liquefaction run carried out with a considerably more elaborate experimental design. Specifically, run "21ECLR of the present study incorporated the following elements:

- continuous, steady wood feed to the liquefaction reactor by a metering wood feeder, giving a continuous steady rate of production of I_2,
- continuous steady electrochemical reduction back to HI of the I_2 produced by liquefaction reactions,
- make-up HI added at a continuous steady rate in order to maintain the aqueous HI concentration in the liquefaction reactor steady at a target value,
- the reactor totally sealed so that all gas product is collected for determination of its yield and composition,
- no withdrawal of aqueous or organic phase product during the run,
- measurement of the anode cell O_2 production rate,
- a program of sampling during the run and lengthy procedures subsequently to determine yield and composition information for the various product fractions.

This continuous electrochemical liquefaction run was carried out using the equipment shown in Figure 7.1, with the reactor flowsheet shown in Figures 7.2. The operating conditions were selected based on the experience gained with the simpler ECLR system reported in Chapter 6.

Figure 7.1 Continuous Electrochemical Wood Liquefaction system

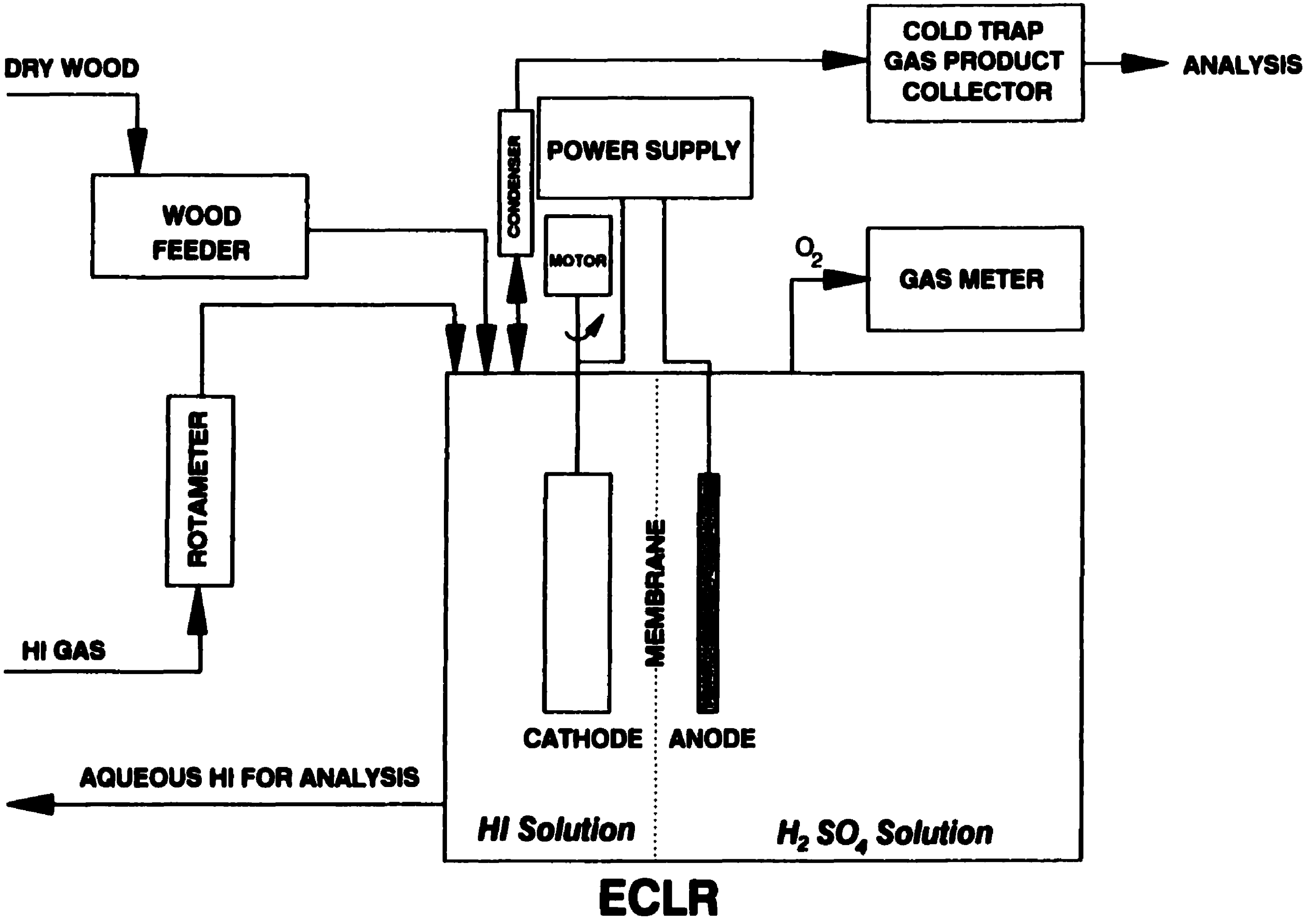


Figure 7.2 Schematic Diagram of Continuous Electrochemical Wood Liquefaction System

A steady controlled feed rate to the reactor of hybrid poplar flour, oven dried for 2h at 80°C, was started when the HI solution temperature became steady at the bubble point, about 125°C. Electrochemical reduction of I_2 at the rotating cylindrical platinum cathode was obtained at a steady cell voltage of 6 V. Continuous make-up HI gas to control aqueous phase concentration steady at about 55 wt% was fed into the ECLR through the head of the liquefaction reactor - cathode compartment. The gas product that was noncondensable in the water cooled condenser above the liquefaction reactor head was received in a cold-trap collector. The volume of O_2 produced by hydrolysis of water from H_2SO_4 solution at the lead anode was measured by a wet gas meter. The cell current and temperatures at key points were recorded. Samples of aqueous HI solution (2 ml) were withdrawn each half hour from the bottom of the liquefaction reactor for analysis.

The experiment was stopped after the planned run time of 5h. The organic phase, aqueous phase and gaseous phase product fractions were recovered to determine their yield and composition.

7.2 Operating conditions and characteristics

The ECLR operating conditions are displayed in Table 7.1.

The wood feed rate, determined by recalibration of the metering feeder immediately after the run, averaged 0.090 g/min over the 5h run length, fluctuating between 0.086 and 0.094 g/min at the set value of 20 rpm for the horizontal screw rotation speed. Thus the total weight of the wood fed in 5h was 27.0 g.

The cathode and anode cells were charged at the start of the run with 220 ml of 56.5 wt% aqueous HI and 1300 ml of 38 wt% H_2SO_4 solution. The cathode is a 25 mm diameter x 50 mm long cylinder, fabricated of 1 mm thick platinum sheet, placed with its axis vertical, with an effective area for electrochemical reaction of 14.7 cm^2 as noted

Table 7.1 Continuous ECLR Wood Liquefaction Conditions

Time (h)	Cathode Rotation (rpm)	Cell Voltage (V)	Cell Current (A)	Cathode Current Density (A/cm²)	HI Gas Feed Rate (g/min)	O_2 Produced		Cathode Cell Temp. (°C)
						Volume (ft^3)	Rate (g/min)	
0	1200	6	14.4	0.90				125
0.5	1200	6	12.7	0.86	0.20	0.051	0.064	124.5
1	1200	6	11.5	0.78	0.20	0.095	0.055	124.5
1.5	1200	6	11.5	0.78	0.22	0.142	0.059	124
2	1200	6	11.6	0.79	0.28	0.184	0.053	123.5
2.5	1200	6	11.7	0.80	0.40	0.228	0.055	123.8
3	1200	6	12.6	0.86	0.47	0.274	0.058	123.5
3.5	1200	6	12.5	0.85	0.60	0.315	0.052	124
4	1200	6	11.8	0.80	0.60	0.363	0.060	124
4.5	1200	6	11.5	0.78	0.58	0.410	0.059	125
5	1200	6	11.5	0.78	0.45	0.450	0.050	125
average			11.9	0.81	0.40		0.057	

Wood feed rate: 0.090 g/min (0.086 – 0.094 g/min)

Cathode: Platinum, 25 mm diam. × 50 mm
Anode: Lead, 50 mm square
Total cathode area: 75.8 cm²
Effective cathode area: 14.7 cm²
Spacing of cathode/membrane/anode: 20 mm/20 mm

Initial solution of cathode compartment: 220 ml of 56.5 wt% HI solution
Initial solution of anode compartment: 1300 ml of 38.6 wt% H_2SO_4 solution

Temperature of the anode cell: ~70°C
Temperature of the gas collector: −72°C

in Section 4.2. The anode is lead plate, 50 mm square x 4 mm thick, placed parallel to the cathode cylinder axis. The closest point distance between the semipermeable membrane and the cylindrical cathode is 20 mm. The distance between the membrane and the lead plate anode is 20 mm. The semipermeable membrane, Nafion 324, allows H^+ ions generated at the anode to pass to the cathode cell while preventing diffusion of I^- ions to the anode cell. The liquefaction reactor temperature was in the range 123.5 – 125°C. The anode cell temperature was about 70°C.

As one of the many changes from the operation described in Chapter 6, the liquefaction reactor was totally sealed throughout the run, with the gas product led off through a water cooled condenser and collected in a dry ice-ethanol cold trap at −72°C for subsequent determination of gas product yield and composition.

The electrochemical cell voltage was maintained at 6 V throughout the run. The cathode was rotated at 1200 rpm, a speed which the experiments reported in Chapter 6 indicated is sufficient to suppress mass transfer resistance for electrochemical reduction of I_2 at the cathode surface. At time zero the current was 14.4 A, the normal current at this voltage and low I_2 concentration without wood liquefaction, but the current dropped to about 12 A when wood was fed into the reactor. The average current during the 5h liquefaction run was 11.9 A, and was quite steady. The decrease in current by about 20% relative to that for reduction of I_2 from pure aqueous HI is attributed to some blockage of the cathode and membrane surface by the crude wood oil product. With 14.7 cm^2 cathode effective area as determined in Section 4.2, the 11.9 A cell current corresponds to a cathode current density of 0.81 A/cm^2.

This run with a more developed and controlled continuous ECLR system than that used for the results reported in Chapter 6 provides further confirmation that the electrochemical reduction of I_2 to HI still occurs with the addition of wood and with the presence of the viscous sticky crude wood oil product. During the 5h steady operation there was no observed evolution of H_2 at the cathode, indicating achievement of the objective of closing the HI $\rightarrow$ I_2 $\rightarrow$ HI loop yet without including the undesired competing electrochemical reduction of H^+ to H_2.

The I_2 and HI concentrations in the cathode compartment and the I_2 and H_2SO_4 concentrations in the anode compartment were determined by the methods recorded in Appendix H.1. The I_2 and HI concentrations in aqueous HI solution were analyzed each half hour during the run, as shown in Table 7.2. For the anode cell the concentrations of H_2SO_4 solution before and after reaction, and of I_2 after reaction were determined. The H_2SO_4 concentration increased slightly because of the water electrolyzed to form H^+ and O_2, and some water transferred to the cathodic cell as discussed in Section 4.4.5. The I_2 concentration in the anode cell after the run was determined to be zero, which confirms that no I_2 transferred through the membrane into the anode compartment.

The relation of I_2 concentration in the aqueous HI solution and run time is shown in Figure 7.3. The I_2 concentration remained at about 0.01 M – 0.02 M for 3.5h, then increased to about 0.09 M at the end of the 5h run. The higher I_2 concentration toward the end of the run may derive from more blockage of the cathode surface by the viscous organic product.

Some iodine is taken up by the wood liquefaction product and some I_2 remains unreduced in solution. Both the volume of this solution and its I_2 concentration increase during "21ECLR. Mass transfer effects establish a value of $[I_2]$ in the cathode cell solution, the volume of which increases by water of reaction, Equation 5.10, and by water transfer from the anode compartment, Section 4.4.5. This combination of effects, all of which tend to cause the concentration of HI to decrease with run time, were exactly compensated in this run by the make-up HI used to maintain the aqueous phase concentration constant at about 56 wt% HI. The HI gas feed rate was controlled according to HI concentration, with the bubble point temperature of the aqueous HI solution being used as the indicator of HI concentration according to the T-x diagram, Figure 5.1. The average HI gas feed rate was 0.40 g/min. Recalibration of the HI gas flowmeter after the run duplicated the earlier calibration, thereby confirming the accuracy of this flow rate. The procedure was successful, as during the run the bubble point temperature was steady at 123.5 – 125°C, which means that the HI concentration was steady between 54 – 56 wt%, averaging 54.8 wt%. This steady state condition for

Table 7.2 Analysis of Cathode and Anode Compartment Solution for Continuous ECLR Wood Liquefaction

Time (h)	ANALYSIS OF CATHODIC SOLUTION					ANALYSIS OF ANODIC SOLUTION				
	Volume (ml)	Density (g/ml)	$[I_2]$ (M)	$[H^+]$ (M)	[HI]* (wt%)	Volume (ml)	Density (g/ml)	$[I_2]$ (M)	$[H_2SO_4]$ (M)	$[H_2SO_4]$ (wt%)
0	220	1.69	0.0037	7.46	56.5	1300	1.292	0	5.09	38.6
0.5			0.0078	7.35	56.0					
1			0.0052	7.12	54.9					
1.5			0.0078	6.98	54.3					
2			0.012	6.90	53.9					
2.5			0.015	6.97	54.2					
3			0.015	6.96	54.2					
3.5			0.018	7.10	54.8					
4			0.044	7.21	55.3					
4.5			0.061	7.23	53.4					
5	318	1.67	0.094	7.20	55.3	1230	1.310	0	5.53	41.4

* average 54.8 wt%

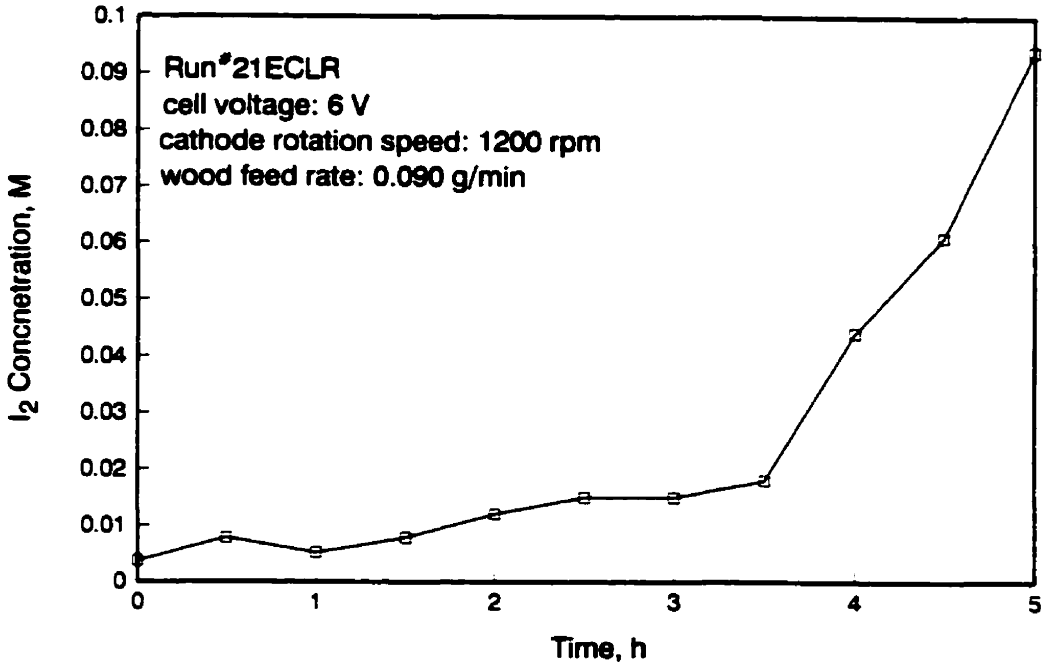


Figure 7.3 Relation of I_2 Concentration and Run Time

HI concentration contrasts with that for the Chapter 6 experiments where, with the same cathode, same cell voltage and same 5h run time, the HI concentration dropped by an average of about 10% HI for runs *11 – *15ECLR, Table 6.5.

The total volume of the aqueous solution in the cathode compartment at end of reaction was 318 ml, 98 ml more than the initial volume because of the production of water of reaction and transfer of water from the anode compartment. The volume of solution in the anode compartment was 1230 ml at the end of the run, which was a 70 ml volume decrease relative to the initial volume because of electrolysis of water to H^+ and O_2, plus water transfer to the cathode compartment. These aspects are treated quantitatively in Sections 7.9 and 7.10.

The O_2 production rate in the anodic cell, measured by the wet test gas meter, varied in the range of 0.050 – 0.064 g/min. The average of O_2 production rate over the 5h run was 0.057 g/min.

7.3 Product fraction treatment and yield

After the run the reactor contents were emptied into a flask for filtration to separate the part of the OP product fraction dispersed in the aqueous HI phase. The total amount of the OP product fraction was obtained by combining the weight of the OP separated from the aqueous phase with the OP product that remained adhering to the reactor surface, determined gravimetrically. The organic phase product fraction, OP, oven dried 2h at 80°C, was determined to be 23.80 g in the HI-free, H_2O-free state. After elemental analysis by the methods appearing in Appendix H.2, the carbon base yield of OP product was found to be 84.2%.

For removal of I_2 associated on the crude OP product fraction, demonstrated in Section 6.3.4 to be about 85 – 90% of the total iodine content of the crude product from the reactor, a sample of about 2 g of the HI- and H_2O-free OP product was treated with about 200 ml of 0.03 M $Na_2S_2O_3$ solution for 1 day in a flask with agitation by a magnetic bar. The OP product was separated from the aqueous solution by filtration, then washed with distilled water about 20 times until free of $Na_2S_2O_3$. To obtain H_2O-free OP product it was oven dried for 2h at 80°C. The iodine content of the OP product after treatment by $Na_2S_2O_3$ solution was determined by the method recorded in Appendix H.2.

Another sample of the OP product fraction was treated with acetone to determine the yield of the acetone-insoluble residue fraction, ON. In this way the ON product fraction was shown to be eliminated by the conditions of electrochemical liquefaction at a steady HI concentration of 54 – 56 wt% and a reactor temperature in the range 123.5 – 125°C. For the nonelectrochemical batch wood liquefaction operated at the bubble point temperature of the aqueous HI solution, the results of Chapter 5 showed that the yield of the undesirable acetone-insoluble residue fraction, ON, was totally eliminated at combinations of HI to wood stoichiometric ratio and initial HI concentration which gave a final HI concentration of 48 – 49 wt% HI or higher. As the *21ECLR run was carried out at a steady HI concentration of 54 – 56 wt% and at its bubble point temperature of 123.5 − 125°C, the finding of no acetone-insoluble residue product, ON, is as would be predicted based on the nonelectrochemical batch reactor results of Chapter 5.

The determination of the yield of the aqueous phase product fraction AP was complicated and difficult. The aqueous HI solution, removed hot from the reactor, is saturated with product at the reaction temperature of about 125°C. When cooled to room temperature some of the aqueous phase product AP dissolved at 125°C precipitates from solution. This fraction, denoted AP_1, was determined after oven drying for 2h at 80°C to be 0.652 g on an HI and H_2O-free base. To recover the AP product that remained dissolved in the room temperature aqueous HI solution, a sample of 25 ml of this solution was treated with 0.03 M $Na_2S_2O_3$ solution to reduce the I_2 in solution. This solution was extracted several times with CH_2Cl_2 until all the product had been extracted, indicated by the CH_2Cl_2 phase remaining colourless. This CH_2Cl_2 extract was very slowly separated from the aqueous phase by a separatory funnel, which required one repetition of the separation step. The CH_2Cl_2 solvent was removed in a distillation column. After distillation, this sample of AP, denoted AP_2, was dried under room conditions to constant weight. The amount of AP_2, expressed relative to the total 318 ml of reactor aqueous HI solution, was 1.890 g. The total amount of AP (AP_1 + AP_2) product fraction was then 2.542 g. After the elemental analysis of this AP fraction was determined by the methods appearing in Appendix H.2, its carbon-base yield could be determined as 10.8%.

The gaseous product, GP, was collected in the cold trap gas collector. The gas collector, removed from the ECLR system after the run, was placed in a freezer at −23°C. By weighting the gas collector before and after reaction, the gaseous product was determined to be 7.56 g. The GC-Mass spectra analyses showed that the gaseous product was pure CH_3I (b.p. 42.4°C, m.p. −64.4°C). Therefore the GP product yield is 4.9% on the carbon base. Thus it is confirmed that methoxy groups in the wood, determined in Appendix H.2 to be 4.7% on the carbon base, were completely converted to methyl iodide.

The complete set of mass balances for components of the wood liquefaction reaction system and the elemental balances for C, H, O and I are tabulated in Appendix M. The mass balances are in general surprisingly good considering the complexity of the system and of the number of basic measurements required in order to establish these mass balances. Summarized below are the principal results of material balances in the liquefaction reactor:

total mass	98.0 %
carbon	99.8 %
hydrogen	103.9 %
oxygen	100.0 %
total iodine	96.5 %
iodine as I_2	99.5 %

As detailed in Table 7.3, the carbon base yields are 84.2% OP product fraction, 10.8% AP product fraction and 4.9% GP product fraction, which is methyl iodide. For unsteady batchwise-continuous liquefaction at an average HI concentration of 54.8 wt%, the same concentration as for the *21ECLR run, Figure 6.7 indicates a yield distribution of about 72% OP – 23% AP product fraction. The *21ECLR split of 84% OP – 11% AP product fraction is then significantly better. The probable reason for the difference is that an average HI concentration of 55 wt% in the unsteady batchwise-continuous operation would correspond to the HI concentration dropping by about 10% from start to final of a 5h run, whereas for run *21ECLE the HI concentration was steady at 55 ± 1 wt% over the entire 5h of the run. For liquefaction reactor operation with significant change in HI concentration, the results of Chapters 5 and 6 provide examples of reaction characteristics depending on both initial and final HI concentration, so that the use of average HI concentration, such as Figure 6.7, is only an approximation.

Table 7.3 Product Elemental Analysis for Continuous ECLR Wood Liquefaction

		Elemental Content										C-Base yield
	Weight (g)	Elemental Analysis, (wt%)					Elemental ratio			Hydrogen retention (%)	Oxygen removal (%)	$Y_{C/j}$ (%)
		C	H	O	I	Total	H/C	O/C	I/C			
Wood	27.0	48.2	6.4	45.3	0	99.9	1.59	0.70	0			
OP	23.798	46.03	5.26	6.81	43.28	101.38	1.37	0.111	0.089	86.2	84.1	84.2
AP	2.542	54.96	6.60	7.77	31.04	100.37	1.44	0.106	0.053	90.6	84.9	10.8
GP	7.56	8.46	2.12	0	89.42	100	3	0	1	188.7	100	4.9
Total												99.9

7.4 Product composition

The product compositions are displayed in Table 7.3. The gaseous phase product, GP, is pure CH_3I. The H/C ratio of the AP product, 1.44, is slightly higher than that of the OP product, 1.37, giving a correspondingly slightly higher hydrogen retention for the AP product, 91% compared to 86%, while the I/C ratio in the AP product is substantially lower than in the OP product. Relative to the values typically found from nonelectrochemical batch liquefaction experiments, the compositions of the OP and AP fractions from the #21ECLR run are noteworthy by having an exceptionally high H/C ratio and exceptionally low O/C ratio. The dependence on HI concentration of the percent hydrogen retention and oxygen removal of the OP product fraction is examined by Figures 7.4 and 7.5, which reproduce Figures 6.5 and 6.6 with the addition of the results for the #21ECLR run. The latter result is located at the value of [HI] which is the average of HI concentration of #21ECLR in order to be consistent with the treatment of the Chapter 6 results for batchwise-continuous ECLR operation. It is significant that the hydrogen retention and oxygen removal values for the OP product from run #21ECLR are both significantly higher than would have been expected by the earlier results. The higher hydrogen retention and oxygen removal of the OP product from this electrochemical wood liquefaction run at steady HI concentration of 54 – 56 wt% may be caused by the action of H^+ which is continuously produced from the electrochemical reaction. This possibility is examined further in Section 7.7.

The path of the highly complex reactions of wood liquefaction may also be affected by the change from batchwise-continuous wood feeding in Chapter 6, to the steady-state operation of #21ECLR with continuous wood feeding and constant HI concentration. The batchwise-continuous wood feeding involved feeding a small batch of wood each 5 min. However the results of Section 5.3 show that the wood-HI reaction could be nearly complete in about 20s. Thus the steady conditions of run #21ECLR compared to the succession of short bursts of rapid reaction rate in the batchwise-continuous operation could lead to important changes in the reaction chemistry, with

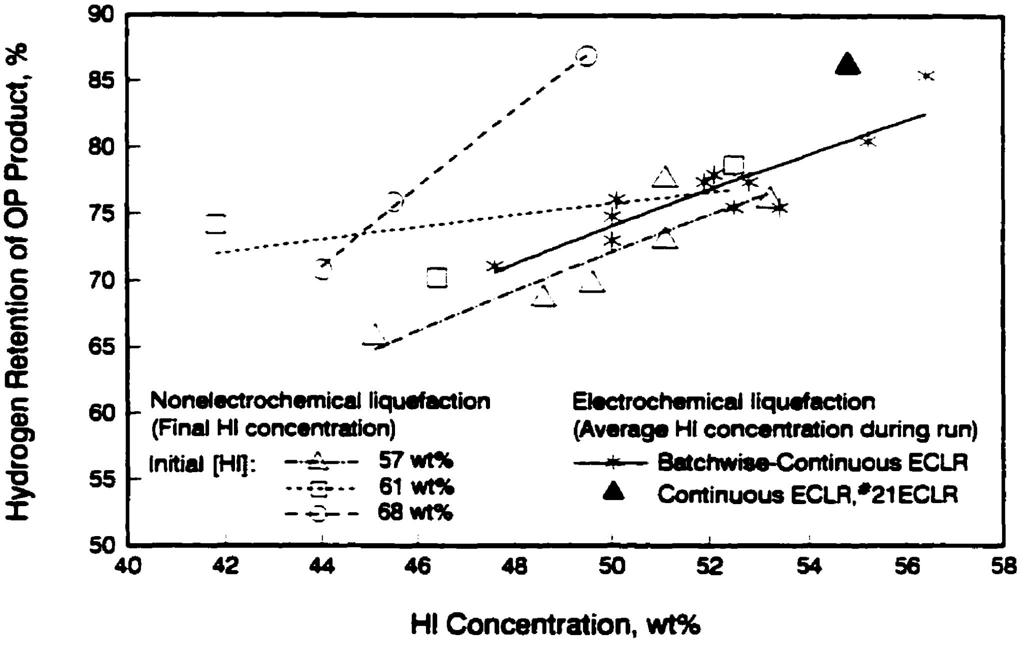


Figure 7.4 Effect of HI Concentration on Hydrogen Retention of OP Product

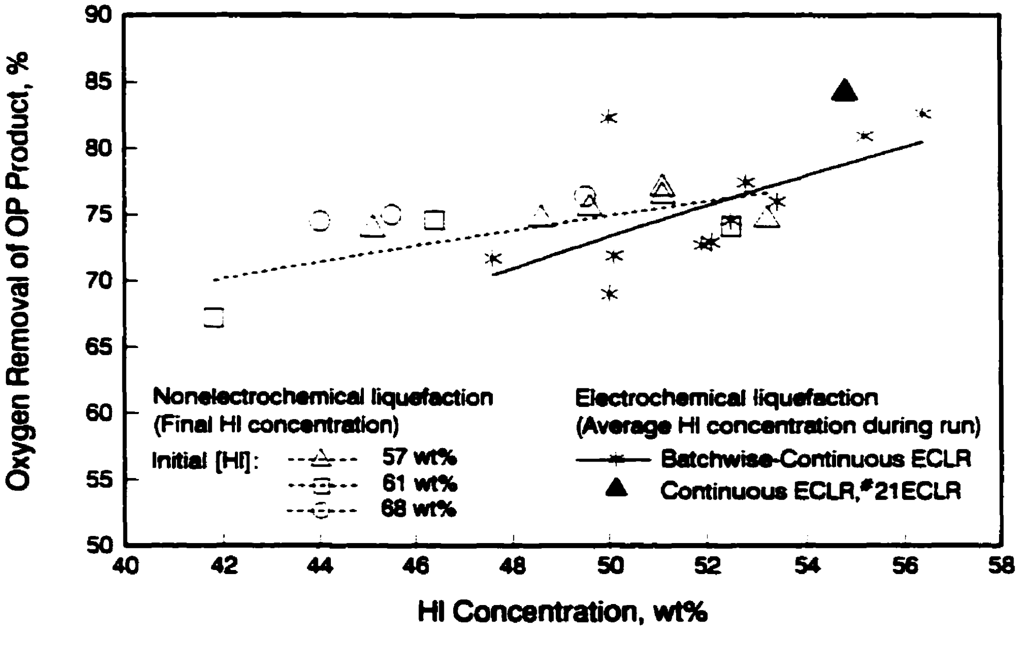


Figure 7.5 Effect of HI Concentration on Oxygen Removal of OP Product

corresponding significant changes in product composition of the type shown by Figures 7.4 and 7.5.

As discussed in Section 6.3.4, it has been established that about 85 – 90% of the iodine content of the product is associated with the product physically as I_2, rather than bound chemically as organic iodide. By concurrent work in this laboratory, not part of the present thesis, the OP product after treatment by $Na_2S_2O_3$ to reduce this physically associated I_2 was determined to contain 6.98 wt% of organic iodide. Douglas, 1993. Therefore the composition of the OP product on an I_2-free basis may be calculated from:

H/C = 1.37
O/C = 0.111
I = 6.98 wt%.

Thus the weight fraction carbon content is

$$(1 - 0.0698) / [1 + 1.37/12.01 + 0.111\ (16/12.01)] = 0.7371$$

The composition of the OP product on an I_2-free basis is then:

C : 73.71 wt%
H : 8.41 wt%
O : 10.90 wt%
I : 6.98 wt%

Thus in the OP product the atomic ratio of iodine as organic iodide, to carbon, was $I_{RI}/C = 0.0090$. As recorded in Table 7.3, the ratio of total iodine to carbon for OP was $I/C = 0.089$. Because the total iodine content is the sum of that present as organic iodide, I_{RI}, and that present as I_2, described as I_{I_2},

$$I/C = I_{RI}/C + I_{I_2}/C \tag{7.1}$$

it follows that in the OP product the atomic ratio to carbon of the iodine that is physically associated as I_2, is

$$I_{I_2}/C = I/C - I_{RI}/C = 0.080.$$

Thus 90% of the iodine present is as physically associated I_2, with only the remaining 10% of the iodine content of the product in the form of organic iodide. With I_{RI}/C = 0.0090, then the OP product formula can be written alternately as

$$CH_{1.37}O_{0.111}I_{0.089} = CH_{1.37}O_{0.111}I_{0.0090} \cdot 4.5\ (0.0090)\ I_2$$

The study of Powell and Campbell, 1947, of the solubility of I_2 in aqueous HI solution indicates that there may be two I_2 molecules associated with each iodine atom, Section 2.3.1. The above analysis with $I_{I_2}/C = 0.080$ would correspond to 4.5 molecules of I_2 associated with each iodine atom as organic iodide in the OP product. Section 6.3.4 discusses the various sites for I_2 molecules to become physically associated with a product molecule in addition to the iodine atoms of the organic iodide content.

After $Na_2S_2O_3$ treatment the iodine content of the AP product, determined as for the OP product, is 6.6 wt%, as appears in Table 6.7. Therefore the composition of AP product without associated I_2 is

H/C = 1.44
O/C = 0.106
I = 6.6 wt%.

The corresponding weight fraction carbon content is

$$(1 - 0.066) / [(1 + 1.44/12.01 + 0.106\ (16/12.01)] = 0.7406$$

The composition of the AP product fraction on an I_2-free basis is then

C : 74.06 wt%
H : 8.88 wt%
O : 10.46 wt%
I : 6.6 wt%

Thus for the AP product the ratio of iodine as organic iodide to carbon is I_{RI}/C = 0.0085. As the ratio of total iodine to carbon, Table 7.3, is $I/C = 0.053$, therefore the ratio of iodine as physically associated I_2, to carbon is

$$I_L/C = I/C - I_{RI}/C = 0.045.$$

Then the formula of the AP product can be written alternately as

$$CH_{1.44}O_{0.106}I_{0.053} = CH_{1.44}O_{0.106}I_{0.0085} \cdot 2.5\ (0.0085)\ I_2$$

indicating 2.5 molecules of physically associated I_2 for each atom of iodine as organic iodide. As noted in connection with the OP product fraction, there are sites for physical association of I_2 molecules in addition to the iodine atoms of the organic iodide content.

7.5 Reaction stoichiometric equation and coefficients

The reaction stoichiometric Equation 5.10, which can be written as

$$CH_{1.59}\, O_{0.70} + a\ HI = \Sigma\ Y_{C/j}\ (CH_k\, O_l\, I_m)_j + b\ H_2O + c\ I_2 \qquad (7.2)$$

can be determined from the product fraction yields and compositions. The stoichiometric coefficients can be obtained by balancing the equation, written below with the carbon-base yields and the elemental composition of the product fractions given in Table 7.3:

$$\begin{aligned} CH_{1.59}\, O_{0.70} + a\ HI = {} & 0.842\ CH_{1.37}\, O_{0.111}\, I_{0.089}\ (OP) + 0.108\ CH_{1.44}\, O_{0.106}\, I_{0.053}\ (AP) \\ & + 0.049\ CH_3I + b\ H_2O + c'\ I_2 \end{aligned} \qquad (7.3)$$

As it has been established that most of the iodine content with the product is physically associated I_2 rather than chemically bound iodine as organic iodide, and elemental formulae for the OP and AP product fractions were given in Section 7.4 showing the associated I_2. Equation 7.3 can be expressed alternately as:

$$\begin{aligned} CH_{1.59}O_{0.70} + a\,HI = {} & 0.842\,CH_{1.37}O_{0.111}I_{0.0090} \cdot 4.5\,(0.0090)\,I_2\ (OP) \\ & + 0.108\,CH_{1.44}O_{0.106}I_{0.0085} \cdot 2.5\,(0.0085)\,I_2\ (AP) \\ & + 0.049\,CH_3I + b\,H_2O + c'\,I_2 \end{aligned} \qquad (7.4)$$

From a reaction stoichiometry perspective there is no distinction between the I_2 which is dissolved in the aqueous HI solution and that which is associated physically with the product. The stoichiometric equation written without distinction as to the physical distribution of the I_2 then becomes:

$$\begin{aligned} CH_{1.59}O_{0.70} + a\,HI = {} & 0.842\,CH_{1.37}O_{0.111}I_{0.0090}\ (OP) \\ & + 0.108\,CH_{1.44}O_{0.106}I_{0.0085}\ (AP) \\ & + 0.049\,CH_3I + b\,H_2O + c\,I_2 \end{aligned} \qquad (7.5)$$

Solving for the stoichiometric coefficients yields a = 1.07, b = 0.60, c = 0.52. Written as Equation 7.4, a and b have the same values but c' would have the value of 0.47, which is meaningful in giving the distribution of I_2 between the product and the aqueous HI solution but is not meaningful from a strictly stoichiometric view.

The reaction stoichiometric coefficients, a and c, for run *21ECLR wood liquefaction should be considered relative to the coefficients for nonelectrochemical wood liquefaction as presented on Figure 5.17 and reproduced on Figure 7.6. For the same value of aqueous phase HI concentration, 54.8 wt%, Figure 7.6 indicates that the values for nonelectrochemical wood liquefaction would be a = 0.84, c = 0.41. As noted in earlier comparisons, it is believed that in batch reaction the extent of the HI-wood reaction would depend mostly on the final HI concentration, hence the use of that basis of comparison in Table 7.4. Thus at the same values of aqueous phase HI concentration, Table 7.4 shows that the values of both stoichiometric coefficients are about 27% higher for electrochemical liquefaction. These values of the stoichiometric coefficients for this electrochemical wood liquefaction run seem too much higher to be just the result of aqueous phase HI concentration effects, but may be attributed to key differences

Table 7.4 Reaction Stoichiometric Coefficients for Electrochemical and Nonelectrochemical Wood Liquefaction

Reactor	ECLR	Nonelectrochemical Reactor
Basis	*21ECLR	Figure 5.17
Initial [HI], wt%	56.5	57
Final [HI], wt%	55.3	54.8
Average [HI], wt%	54.8	
Reaction Stoichiometric Coefficients		
a. gmol HI reacted/gmol C in wood	1.07	0.84
b. gmol H_2O produced/gmol C in wood	0.60	
c. gmol I_2 produced/gmol C in wood	0.52	0.41

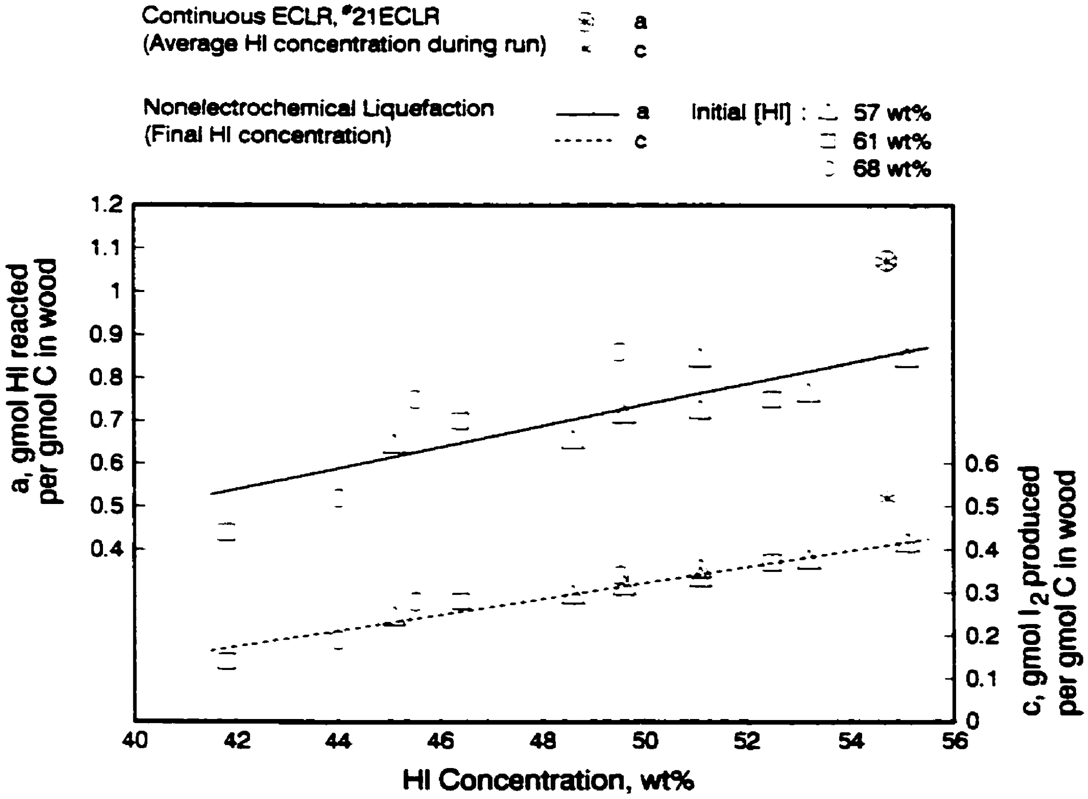


Figure 7.6 Effect of HI Concentration on Stoichiometric Coefficients

between electrochemical and nonelectrochemical wood liquefaction. As the above comparison of coefficient was for matched values of HI concentration, two remaining differences are:

(1) In the ECLR system, H^- passes through the liquefaction reactor from the membrane to the cathode.

(2) In ECLR operation, $[I_2]$ is in the range 0.01 M – 0.09 M, whereas in the non-electrochemical batch reactor, $[I_2]$ reaches about 0.7 M – 1.4 M.

Of these differences it is believed that (2) plays no significant role due to the relative chemical inertness of I_2 in the presence of its acid, HI. In the presence of HI, I_2 would not react further with the liquefaction product under the reaction conditions used, as discussed in Section 2.2.6. Thus it is believed that the characteristics of the product do not change whether I_2 concentration in the aqueous HI is high, as much as 1.4 M in nonelectrochemical liquefaction, or low, as little as 0.01 M in the ECLR system.

Thus the higher stoichiometric coefficients from electrochemical wood liquefaction compared to nonelectrochemical wood liquefaction at the same value of HI concentration may be attributed to item (1) above, the H^- generated during electrochemical reaction. The passage of H^- through the wood liquefaction reactor, from the membrane to the cathode, could affect the chemistry of wood liquefaction, increasing the HI-wood reactivity and hence increasing the hydrogen retention and the deoxygenation of the crude wood oil product, as apparent on Figures 7.4 and 7.5, and increasing the values of the stoichiometric coefficients, as seen on Figure 7.6.

7.6 I_2 reduction efficiency

The I_2 reduction efficiency is defined as the ratio of the rate at which I_2 is reduced electrochemically to HI, to the rate at which I_2 is produced by wood liquefaction. This ratio may be expressed as:

$$E_r = \frac{r_{I_2\ red.}}{r_{I_2\ pro.}} = \frac{r_{I_2\ pro.} - (W_{I_2\ solution} + W_{I_2\ product}) / t}{r_{I_2\ pro.}} \tag{7.6}$$

where

E_r : I_2 reduction efficiency, %
$r_{I_2\ pro}$: I_2 production rate, g/min
$r_{I_2\ red.}$: I_2 reduction rate, g/min
t : length of run, 300 min, Table 7.1
$W_{I_2\ product}$: amount I_2 associated on product, g
$W_{I_2\ solution}$: amount I_2 in the solution, g

At a wood flow rate of F_{wood} = 0.090 g/min and reaction stoichiometric coefficient c = 0.52 gmol I_2/gmol C in wood, the I_2 production rate, is

$$r_{I_2\ pro.} = c\,\frac{M_{I_2}}{M_{CH_{1.39}O_{0.70}}}\,F_{wood} = 0.48\ g/min \tag{7.7}$$

where

$M_{CH_{1.39}O_{0.70}}$: formula weight of wood, 24.92 g/gmol C in wood
M_{I_2} : molecular weight of I_2, 253.8

Thus the total amount of I_2 produced by the wood liquefaction reaction is

$$W_{I_2\ produced} = (r_{I_2\ pro.})\ t = (0.48)\ 300 = 144\ g\ I_2$$

The amount of I_2 which went in the aqueous HI solution is

$$W_{I_2\,solution} = M_{I_2}\,[\,([I_2]V)_{after\ reaction} - ([I_2]V)_{before\ reaction}] = 7.38\ g\ I_2 \qquad (7.8)$$

where

$[I_2]$: I_2 concentration in the aqueous HI solution, M,
0.0037 M at start of run, 0.094 M at end of run, Table 7.2
V : volume of aqueous HI solution, l
0.220 l at start of run, 0.318 l at end of run, Table 7.2

The amount of I_2 which became physically associated with the OP and AP products is

$$W_{I_2\,product} = W_{OP}\,\frac{I_{OP} - (I_{RI})_{OP}}{1 - (I_{RI})_{OP}} + W_{AP}\,\frac{I_{AP} - (I_{RI})_{AP}}{1 - (I_{RI})_{AP}} = 9.95\ g\ I_2 \qquad (7.9)$$

where

I_{AP} : I content of AP product fraction, 31.04 wt%, Table 7.3
I_{OP} : I content of OP product fraction, 43.28 wt%, Table 7.3
$(I_{RI})_{AP}$: organic iodide content of AP product fraction, 6.6 wt%, Section 7.4
$(I_{RI})_{OP}$: organic iodide content of OP product fraction, 6.98 wt%, Section 7.4
W_{AP} : amount of AP product fraction, 2.542 g, Table 7.3
W_{OP} : amount of OP product fraction, 23.798 g, Table 7.3

The I_2 reduction rate is

$$r_{I_2\,red.} = r_{I_2\,pro.} - (W_{I_2\,solution} + W_{I_2\,product})\,/\,t \qquad (7.10)$$
$$= 0.48 - (7.38 + 9.95)/300 = 0.42\ g/min$$

and the total amount of I_2 electrochemically reduced back to I^- is

$$W_{I_2\ \mathrm{reduced}} = (r_{I_2\ \mathrm{red.}})\ t = (0.42)\ 300 = 126\ \mathrm{g}\ I_2$$

Therefore the iodine reduction efficiency, by Equation 7.6, is

$$E_r = \frac{r_{I_2\ red.}}{r_{I_2\ pro.}} = \frac{126}{144} = 88\%$$

Thus 88% of the I_2 that was produced by the wood liquefaction reaction has been reduced back to I^- in the aqueous HI solution. Of the 12% of I_2 produced that was not reduced back to HI, there was (7.38/144 =) 5% of the I_2 produced which remained in the aqueous HI solution and (9.95/144 =) 7% of the I_2 produced which was physically associated on the product and therefore unavailable for reduction.

As only I_2 in solution can be reduced electrochemically, as discussed in Section 6.3.3, it is of interest to examine the ratio of amount of I_2 reduced to the amount of I_2 available for reduction, $W_{I_2\ \mathrm{reduced}}/W_{I_2\ \mathrm{available\ for\ reduction}}$. The amount of I_2 available for reduction is the difference of the I_2 total amount of produced by the wood liquefaction reaction and the amount of I_2 physically associated on the product, i.e.

$$W_{I_2\ \mathrm{available\ for\ reduction}} = W_{I_2\ \mathrm{produced}} - W_{I_2\ \mathrm{product}} \tag{7.11}$$

The iodine reduction efficiency for I_2 dissolved in the solution is

$$E'_r = W_{I_2\ \mathrm{reduced}}/W_{I_2\ \mathrm{available\ for\ reduction}} \tag{7.12}$$

where

$W_{I_2\ \mathrm{produced}}$ = 144 g
$W_{I_2\ \mathrm{product}}$ = 9.95 g
$W_{I_2\ \mathrm{reduced}}$ = 126 g

therefore $W_{I_2 \text{ available for reduction}} = 144 - 9.95 = 134.05$ g

and

$$E'_r = 126/134.05 = 94\%$$

Thus the iodine reduction efficiency for I_2 dissolved in the solution, E'_r, is 94%. As the other 6% is the I_2 dissolved in the aqueous HI solution in the liquefaction reactor, this I_2 in solution, as a percent of the I_2 produced, would decrease steadily with run length, i.e. from 6% for the 5h test run reported here, to 3% for a 10h run, to 0.6% for 50h operation, etc. In the context of long-term steady continuous operation of the ECLR system, 100% of the I_2 produced is reduced to HI, except for the I_2 associated with the product and thereby not available for reduction. In "21ECLR, 7% of the I_2 produced is associated with the product and thereby not available for reduction. On this basis the iodine reduction efficiency for long-term steady continuous operation of this system would be 93%. In this sense the present study has solved 93% of the problem of closing the HI → I_2 → HI loop of this wood liquefaction process, while the remaining 7% concerns removal of the I_2 associated physically with the product, a subject beyond the scope of the present study.

7.7 Current efficiency and H^+ generation

(a) Current efficiency

For the anode reaction

$$H_2O = 2\ H^+ + 1/2\ O_2 + 2e \tag{7.13}$$

the anode current efficiency for producing H^+ and O_2 can be calculated by the relation

$$E^{anode}_{c,\,H^+ - O_2} = \frac{\textit{Charge Used for Producing } H^+ - O_2}{\textit{Total Charge}} = \frac{4F}{60\ I_{ave}\ M_{O_2}}\ r_{O_2}$$

(7.14)

With the conditions recorded in Table 7.1 of average current, I_{ave} = 11.9 A, and an oxygen production rate of r_{O_2} = 0.057 g/min, the current efficiency for producing H^+ and O_2 at the anode is

$$E^{anode}_{c,\,H^+ - O_2} = 96\%$$

This high anode current efficiency, as expected, confirms the effectiveness of the anode cell design and operation. As the anode current efficiency is calculated based on the average cell current and the average oxygen production rate, as recorded in Table 7.1, the deviation of the anode current efficiency from 100% is easily within the accuracy of the measurements of cell current and O_2 production rate. During the ECLR run the colourless H_2SO_4 solution became orange colored and some precipitates formed in the anode cell. Such side reactions in the anode cell could also account for the 4% less reduction in anode current efficiency.

For the cathode reaction

$$I_2 + 2\ e = 2\ I^- \qquad (7.15)$$

the cathode current efficiency for reducing I_2 at an average current, I_{ave} = 11.9 A, and I_2 reduction rate, $r_{I_2\,red.}$ = 0.42 g/min, can be calculated by the relation

$$E^{cathode}_{c,\,I_2} = \frac{\textit{Charge Used For Reducing } I_2}{\textit{Total Charge}} = \frac{2F}{60\ I_{ave}\ M_{I_2}}\ r_{I_2,red.} \qquad (7.16)$$

i.e.

$$E_{c,\,I_2}^{cathode} = 45\ \%$$

where

$E_{c,\,H^+\text{-}O_2}^{anode}$: anode current efficiency for producing H^+ and O_2, %

$E_{c,\,I_2}^{cathode}$: cathode current efficiency for reducing I_2 to I^-, %

F : Faraday constant, 96487 C/mol

I_{ave} : average current, 11.9 A, Table 7.1

$M_{CH_{1.\text{[illegible]}}O_{0.\text{[illegible]}}}$: formula weight of wood, 24.92

M_{I_2} : molecular weight of I_2, 253.8

M_{O_2} : molecular weight of O_2, 32

r_{O_2} : O_2 generation rate, 0.057 g/min, Table 7.1

$r_{I_2\ red.}$: I_2 reduction rate, 0.42 g/min, Section 7.6

(b) H^+ generation

In the anode compartment H^+ is generated according to the reaction

$$H_2O = 2\ H^+ + 1/2\ O_2 + 2e \tag{7.13}$$

At the oxygen generation rate of 0.057 g/min the H^+ generation rate at the anode is

$$r_{H^+\ generation}^{anode} = 4\ \frac{1}{M_{O_2}}\ r_{O_2} = 0.0071\ gequiv\ H^+/\mathrm{min} \tag{7.17}$$

and the ratio of H^+ generation to C in wood, at the wood feed rate of 0.090 g/min, is

$$R^{anode}_{H^+\ generation} = \frac{r^{anode}_{H^+\ generation}}{F_{wood}\ /\ M_{CH_{1.59}O_{0.70}}} = 1.97\ gequiv\ H^+/gmol\ C\ of\ wood \quad (7.18)$$

In the cathode compartment, I^- is generated according to the reaction

$$I_2 + 2e = 2\ I^- \quad (7.15)$$

The I_2 reduction rate at the cathode, converted from the mass basis of Section 7.6, is

$$r^{cathode}_{I_2\ reduction} = \frac{1}{M_{I_2}}\ r_{I_2\ red.} = 0.0016\ gmol\ I_2/\mathrm{min} \quad (7.19)$$

The corresponding I^- generation rate at the cathode is

$$r^{cathode}_{I^-\ generation} = 2\ \frac{1}{M_{I_2}}\ r_{I_2\ red.} = 0.0032\ gequiv\ I^-/\mathrm{min} \quad (7.20)$$

Therefore the ratio of I_2 reduction at the cathode to C in wood is

$$R^{cathode}_{I_2\ reduction} = \frac{r^{cathode}_{I_2\ reduction}}{F_{wood}\ /\ M_{CH_{1.59}O_{0.70}}} = 0.45\ gmol\ I_2/gmol\ C\ of\ wood \quad (7.21)$$

and the ratio of I^- generation at the cathode to C in wood is

$$R^{cathode}_{I^-\ generation} = \frac{r^{cathode}_{I^-\ generation}}{F_{wood}\ /\ M_{CH_{1.59}O_{0.70}}} = 0.90\ gequiv\ I^-/gmol\ C\ of\ wood \quad (7.22)$$

This leads to the relation

$$R^{cathode}_{I_2\ reduction} = c\ E_r = 0.45\ gmol\ I_2/gmol\ C\ of\ wood \tag{7.23}$$

and

$$R^{cathode}_{I^-\ generation} = 2\ c\ E_r = 0.90\ gequiv\ I^-/gmol\ C\ of\ wood \tag{7.24}$$

The proportion of H^+ generation at the anode used to reduce I_2 at the cathode is

$$E^{I^-\ generation}_{H^+\ generation} = \frac{R^{cathode}_{I^-\ generation}}{R^{anode}_{H^+\ generation}} = \frac{0.90}{1.97} = 45\% \tag{7.25}$$

which may alternately be expressed as:

$$E^{I^-\ generation}_{H^-\ generation} = E^{cathode}_{c,\ I_2} = 45\% \tag{7.26}$$

because the current efficiency for I_2 reduction at the cathode is identical to the proportion of H^+ generation at the anode used to reduce I_2 at the cathode.

Where

c : reaction stoichiometric coefficient,
0.52 gmol I_2 produced/gmol C in wood, Equation 7.5
E_r : I_2 reduction efficiency, 88%, Section 7.6
F_{wood} : wood flow rate, 0.090 g/min, recorded in Table 7.1
$M_{CH_{[illegible]}O_{[illegible]}}$: formula weight of wood, 24.92
M_{I_2} : molecular weight of I_2, 253.8
M_{O_2} : molecular weight of oxygen, 32

$r_{I_2\ red.}$: I_2 reduction rate, 0.42 g/min, Section 7.6

r_{O_2} : O_2 generation rate, 0.057 g/min, recorded in Table 7.1

Thus according to Equation 7.26 only 45% of the H^+ generated at the anode combines with I^- for generation of HI at the cathode, far below the level of over 98% efficiency obtained with the same reactor under comparable conditions but without wood liquefaction, Chapter 4. This finding establishes that with liquefaction, about half the current is used for reactions other than I_2 reduction. As noted in Section 7.5, it appears that at the cathode surface the fraction of the H^+ which does not participate in I_2 reduction to HI in fact participates in wood liquefaction reactions, resulting in the higher level of hydrogen retention and deoxygenation of wood in the ECLR reactor, i.e. improved product composition, Section 7.4, and the higher values of the liquefaction reaction stoichiometric coefficients, Section 7.5. Thus in the ECLR process, although not all the H^+ produced participates in the reduction of I_2 to HI at the cathode, all the H^+ produced at the anode is usefully consumed.

7.8 Energy required

(1) Minimum theoretical energy required for I_2 reduction

For the electrode reactions

$$I_2 + 2\,e = 2\,I^- \qquad \text{(cathode)}$$

$$H_2O = 1/2\,O_2 + 2\,H^+ + 2\,e \qquad \text{(anode)}$$

and overall reaction

$$I_2 + H_2O = 1/2\,O_2 + 2\,HI$$

the Nernst voltage, V_{min}, is -0.83 V, Section 3.2.3, corresponding to the free energy of I_2 reduction as

$$\Delta G = -2\ F\ V_{min} = 160.2\ \text{kJ/mol}\ I_2$$

i.e. 38.3 kcal/mol I_2 (1 kcal = 4.1868 kJ).

With the reaction stoichiometric coefficient c = 0.52 gmol I_2/ gmol C in wood, the energy required for I_2 reduction is

$$\frac{38.3\ (kcal\ /\ mol\ I_2) \times 0.52\ (mol\ I_2\ /\ mol\ C\ of\ wood)}{24.92\times 10^{-3}\ (kg\ /\ mol\ C\ of\ wood)}$$

799 kcal/kg moisture-free wood, i.e. 0.929 kWh/kg moisture-free wood (1 kcal = 0.001163 kWh).

In fact the sum of the Nernst potentials for the cathode and anode reactions is not the minimum energy requirement. Before any current starts to flow, the overpotentials at the cathode and anode must also be satisfied. As there is no energy inefficiency until current starts, the condition which establishes the effective minimum energy is at the maximum voltage at which there is zero current:

$$V_T^{I\to 0} = V_{min} - |\eta_c^{I\to 0}| - |\eta_a^{I\to 0}| = -1.72\ \text{V}$$

where the Nernst potential is $V_{min} = -0.83$ V. From Section 3.2.3 at very low cell current, I = 0.1 A, the cathode overpotential $\eta_c^{I\to 0} = -0.002$ V and the anode overpotential $\eta_a^{I\to 0} = 0.89$ V. Thus the corresponding minimum energy requirement at the maximum voltage for zero current for I_2 reduction is

$$\begin{aligned} G_T = -2\ F\ V_T^{I\to 0} &= 331.9\ \text{kJ/mol}\ I_2 = 79.3\ \text{kcal/mol}\ I_2 \\ &= 1654\ \text{kcal/kg moisture-free wood} \end{aligned}$$

i.e. 1.92 kWh/kg moisture-free wood.

(2) Actual energy required for I_2 reduction

In an ECLR reactor, not only I_2 reduction but also some wood liquefaction electrochemical reactions occur at the cathode, as well as H^+ and O_2 generation and a very small amount of side reactions at the anode. For the system of run *21ECLR, the actual energy used for these several purposes was

$$\frac{V\, I_{ave}}{60\, F_{wood}} = \frac{6\ (11.9)}{60\ (0.09)} = 13.2\ \mathit{kWh/kg\ moisture\text{-}free\ wood}$$

The energy consumption for just the I_2 reduction occurring in the cathode cell is considered as

$$\frac{V\, I_{ave}\, E^{cathode}_{c,\,I_2}}{60\, F_{wood}} = \frac{6\ (11.9)\ 0.45}{60\ (0.09)} = 5.95\ \mathit{kWh/kg\ moisture\text{-}free\ wood}$$

where

I_{ave} : current, 11.9 A, Section 7.2

V : voltage, 6 V, Section 7.2

F_{wood} : wood flow rate, 0.09 g/min, Section 7.2

$E_{c,\,I_2}^{cathode}$: cathode current efficiency for reducing I_2, 45%, Section 7.7

Thus the energy efficiency required just for reducing I_2 with the electrochemical cell and operating conditions of *21ECLR is the ratio of the minimum energy required, 1.92 kWh/kg moisture-free wood, to the actual energy required for I_2 reduction, 5.95 kWh/kg moisture-free wood, i.e. (1.92/5.95 =) 32%.

It should be noted that the objective of the present study was to determine whether wood liquefaction and electrochemical reduction of I_2 to HI could be carried out in the same reactor without the undesired competitive electrochemical generation of H_2. Subsequent to achieving this objective many questions, including consideration of electrochemical efficiency, remain major topics requiring future intensive study.

7.9 Water transfer

The results recorded in Section 7.2 show that there is a 98 ml volume increase in the cathode compartment and a 100 ml volume decrease in the anode compartment, for the combination of reasons noted there.

For the cathodic cell,

initial amount of water: 161.73 g {= 220 ml (1.69 g/ml) (1 − 0.565)}
final amount of water: 237.38 g {= 318 ml (1.67 g/ml) (1 − 0.553)}
amount of water of reaction: {= b $M_{H_2O}/M_{CH_{[illegible]}O_{[illegible]}}$ 27.0 g}
11.70 g {= 0.60 (18/24.92) 27.0 g}

Therefore the net amount of water transferred into the cathode cell is:

63.95 g {= 237.38 g − 161.73 g − 11.70 g}

For the anodic cell,

initial amount of water: 1031.13 g {= 1300 ml (1.292g/ml) − 5.09 M (1.3 l)$M_{H_2SO_4}$}
final amount of water: 944.71 g {= 1230 ml (1.310g/ml) − 5.53 M (1.23 l)$M_{H_2SO_4}$}
amount of water hydrolyzed: 19.24 g {= 18/16 (0.057 g/min) 300 min}

Therefore the net amount of water transferred out of anode cell is:

67.18 g {= 1031.13 g − 944.71 g − 19.24 g}

Thus a very good water balance was obtained. The transfer of about 64 − 67 g H_2O over the 5h run into the cathode compartment from the anode compartment indicates a water transfer rate of about 13 ml/h. This transfer rate is comparable to the test without wood liquefaction but with electrochemical current, which gave a 12.3 g/h water transfer rate. If all of the H^+ generation rate of 0.0071 mol H^+/min (Section 7.7) in fact transferred as H_3O^+, which is the expected nature of the H^+ transport, this would account for $(0.0071 \cdot 18 \cdot 300 =)$ 38 g H_2O transferred into the cathode compartment. This amount indicates that about 60% of the water transfer was with the H^+ transfer as H_3O^+, leaving about 40% of the transfer H_2O alone.

7.10 Summary

Successful operation for steady continuous electrochemical wood liquefaction was obtained in a fully sealed reactor with continuous wood feeding, continuous I_2 generation, continuous I_2 reduction electrochemically, continuous make-up HI to maintain HI concentration at a steady-state value, continuous gas product collection and continuous O_2 production. The principal results and findings were:

(1) During a 5h run the continuous wood feed rate was maintained constant at 0.09 g/min. The aqueous phase HI concentration was maintained at a steady-state value of 54 – 56 wt% by the addition of 0.40 g/min of make-up HI. The liquefaction reactor was operated at the bubble point temperature of the aqueous HI solution, which thereby was used as sensitive indicator of HI concentration according to the T-x diagram for vapor-liquid equilibrium in the HI-H_2O system. Nearly 100% mass balances were obtained for carbon, hydrogen, oxygen, iodine, HI and H_2O.

(2) The I_2 concentration of the aqueous solution never exceeded 0.09 M over the 5h of the run, very much less than the typical levels of 0.7 – 1.4 M for nonelectrochemical batch liquefaction. These results further confirm that I_2 reduction can be obtained simultaneously with wood feeding and wood liquefaction and in the presence of the viscous crude wood oil product.

(3) No H_2 generation occurred at the cathode, thus establishing that for continuous ECLR operation at the conditions of this 5h run, reduction of I_2 is obtained without the

occurrence at the cathode of this competing electrochemical reaction.

(4) At a cell voltage of 6 V and 1200 rpm cathode rotation speed during a 5h run the current was steady, averaging 11.9 A, which corresponds to a cathode current density of 0.81 A/cm^2. Because of partial blockage of cathode surface by the viscous wood oil product the cell current and cathode current density are decreased by 20% relative to I_2 reduction in pure aqueous HI solution at comparable conditions.

(5) 100% of the carbon of wood is recovered, with the carbon base yields being 84.2% of organic phase product, 10.8% of aqueous phase organic product, 4.9% of CH_3I gaseous product, while at the conditions of this run the yield of the undesired, acetone-insoluble residue was totally suppressed. As the aqueous phase organic product is simply an inventory item, for long term operation the carbon base yields for the ECLR process would be 95.1% organic phase product, 4.9% CH_3I.

(6) When the product was treated with $Na_2S_2O_3$ solution to remove the physically associated I_2 on the product, it was determined that the organic iodide content of the organic product corresponds to only about 6 – 7 wt% iodine content, i.e. to an atomic ratio I/C = 0.0090. Thus the composition of the OP product can be expressed as:

$$CH_{1.37}O_{0.111}I_{0.089} = CH_{1.37}O_{0.111}I_{0.0090} \cdot 4.5\ (0.0090)\ I_2$$

with 4.5 I_2 molecules physically associated per carbon atom. On the same basis the composition of the AP product fraction that remained dissolved in the aqueous HI phase was

$$CH_{1.44}O_{0.106}I_{0.053} = CH_{1.44}O_{0.106}I_{0.0085} \cdot 2.5\ (0.0085)\ I_2$$

indicating 2.5 I_2 molecules physically associated per carbon atom. Such charge-transfer complex type physical association of I_2 molecules occurs with iodine atoms, carbonyl group oxygen atoms and benzene rings of the organic product.

(7) The reaction stoichiometric equation combining the results of the above items

(5) and (6) is

$$
\begin{aligned}
CH_{1.59}O_{0.70} + 1.07\ HI = {} & 0.842\ CH_{1.37}O_{0.111}I_{0.0090}\ (OP) \\
& + 0.108\ CH_{1.44}O_{0.106}I_{0.0085}\ (AP) \\
& + 0.049\ CH_3I + 0.60\ H_2O + 0.52\ I_2
\end{aligned}
$$

(8) The higher reactivity between wood and HI and the higher levels of hydrogen retention and oxygen removal of the crude wood oil product relative to that obtained in the earlier nonelectrochemical batch wood liquefaction appear attributable in part to changes in reaction chemistry that accompany fully continuous wood liquefaction, in part to the higher level of HI concentration maintained in the continuous reaction operation than that at the end of batch reaction and in part to some of the H^+ produced electrochemically participating in wood liquefaction reactions at the cathode.

(9) Of the total I_2 produced, 88% is reduced to HI. As only the I_2 in solution can be reduced electrochemically, the I_2 reduction efficiency of dissolved I_2 is even higher, 94%. The 6% of I_2 in solution that was not reduced during this run is simply an inventory of dissolved I_2 in the reactor aqueous phase. As the only I_2 unavailable for reduction is the 7% which is associated physically with the organic product, 93% of the I_2 produced would be reduced to HI in steady, continuous operation of an ECLR system.

(10) The current efficiency for H^+ generation is 96%. Of the H^+ generated, 45% is used for I_2 reduction and the remainder for electrochemical organic reactions with the wood oil product. For this organic product the high hydrogen retention and high oxygen removal, both above 85%, are in both cases significantly better than for the product from nonelectrochemical wood liquefaction.

CHAPTER 8

CONCLUSION

8.1 Summary

1. Electrochemical liquefaction reactor concept

A novel design of an electrochemical liquefaction reactor (ECLR) contained two electrolytic cells separated by a semipermeable membrane. The cathode cell is the reactor for direct liquefaction of biomass in concentrated aqueous HI solution and at the same time is the electrochemical reactor where I_2, which is produced by the oxidation of I^- that accompanies the reduction of wood, is reduced at a platinum cathode back to the HI reactant. With a lead electrode the anode cell produces H^+ ions and O_2 from hydrolysis of water in concentrated H_2SO_4 solution, the H^+ being transported through the semipermeable membrane to the cathode where HI is thereby regenerated.

2. Electrochemical characteristics of the ECLR reactor

For a purely inorganic HI-I_2-H_2O system, various electrochemical performance characteristics - current, current density, I_2 reduction rate, current efficiency - were determined as a function of cell voltage, I_2 concentration, cathode rotational speed and inter-electrode spacing. With the use of platinum as the cathode metal, the overvoltages for I_2 reduction and the competitive reaction of H_2 generation are such that for a significant range of conditions it is possible, fortunately, to obtain the former to the total exclusion of the latter.

Over a broad range of operating conditions the cathode current efficiency is high, in the range 90 - 100 %, and stable with respect to cell voltage, cathode rotational speed and I_2 concentration. The I_2 concentration at which cathode current efficiency starts to drop because of mass transfer control at the cathode was determined as a function of cell voltage, cathode rotational speed and inter-electrode spacing. This threshold I_2 concentration is in the range 0.04 – 0.08 M, concentrations which are very low relative to typical levels of about 0.7 – 1.4 M reached in nonelectrochemical batch wood liquefaction in aqueous HI solution.

3. Characteristics of nonelectrochemical liquefaction

For nonelectrochemical batch wood liquefaction at HI/wood stoichiometric ratio of 1.0 – 4.4 gmol HI/gmol C in wood, in 57 – 61 wt% aqueous HI solution, the crude wood oil product has about 70 – 80% hydrogen retention and 70 – 80% oxygen removal relative to the wood. The I_2 concentration in the aqueous solution after reaction is in the range of 0.7 – 1.4 M.

(a) Stoichiometric equations for liquefaction

At the conditions of 57 wt% initial HI concentration, HI to substrate stoichiometric ratio R = 4.4 gmol HI/gmol C in wood, the stoichiometric equation for liquefaction of hybrid poplar is

$$\begin{aligned} CH_{1.59}O_{0.70} + 0.79\ HI = {} & 0.833\ CH_{1.16}O_{0.16}I_{0.12}\ (OP) + 0.118\ CH_{1.57}O_{0.20}I_{0.04}\ (AP) \\ & + 0.049\ CH_3I + 0.54\ H_2O + 0.32\ I_2 \end{aligned}$$

and for liquefaction of cellulose is

$$\begin{aligned} CH_{1.67}O_{0.83} + 1.18\ HI = {} & 0.727\ CH_{1.49}O_{0.14}I_{0.19}\ (OP) + 0.273\ CH_{1.63}O_{0.24}I_{0.03}\ (AP) \\ & + 0.66\ H_2O + 0.52\ I_2 \end{aligned}$$

where the carbon base yields of the organic phase (wood oil) products are 83.3% and 72.7%, respectively, as indicated by the above stoichiometric coefficients for the product fraction designated as OP. The yields of the product remaining dissolved in the aqueous HI phase, designated as AP, is of secondary importance as earlier work showed that when recycled to the reactor it is converted to the OP, wood oil type product. Of basic importance is that with these conditions, and in contrast to other biomass liquefaction processes, no char-type residue is produced. For any lignin containing biomass these conditions convert the methoxy groups to methyl iodide, this yield from hybrid poplar being 4.9% as indicated by the above stoichiometric coefficient. The greater reactivity of HI with cellulose than with wood is indicated by the higher stoichiometric coefficients, 1.18 compared to 0.79. As HI reduces the substrate with the production of H_2O while I^- is oxidized to I_2, part of this higher HI reactivity corresponds to the O/C ratio of cellulose being 19% higher than for hybrid poplar.

(b) Evolution of wood liquefaction over short batch reaction times

The concentration and temperature of aqueous HI solutions which are effective for biomass liquefaction correspond coincidentally to those of the bubble point compositions for vapor-liquid equilibrium in the HI-H_2O system in the vicinity of the sharply defined maximum boiling azeotrope at 56.5 wt% HI and 127°C. As HI is consumed and H_2O produced by the liquefaction reaction, the HI concentration drops during batch reaction. By operating the liquefaction reactor at the bubble point of the aqueous HI solution the extent of the HI-wood reaction can be followed accurately by monitoring the reactor temperature. In this way it was determined that when the initial concentration in the aqueous phase is 57 wt% HI or slightly higher, the liquefaction reactions between substrate and HI are nearly complete in as little as 20s.

(c) Effect of HI concentration and HI/wood stoichiometric ratio

The reaction activity of aqueous HI with wood was found to increase very strongly with HI concentration. For initial aqueous phase concentration of 45 wt%, the activity of HI acting as a reducing agent is very weak, but the effect of the H^+ as a catalyst for hydrolysis of wood polymers provides a 40% yield of aqueous HI phase soluble product. This evidence demonstrates that the hydrolysis step of wood liquefaction occurs even at conditions too weak for removal of oxygen. The dehydration step of wood liquefaction requires stronger reaction conditions, i.e. initial concentrations of the aqueous phase in the range 55 – 65 wt% HI for batch reactor liquefaction of wood.

The yield of the residue fraction, ON, a char-type product, can be totally eliminated at strong reaction conditions such as any combination of HI to wood stoichiometric ratio R, gmol HI/gmol C, and wt% initial HI concentration which gives a final HI concentration of 50 wt% HI or above.

The values of the coefficients of the stoichiometric equations as indicated in (a) above increase sensitively and linearly with final HI concentration over the wide range of 42 – 55 wt% HI regardless of the combinations of values of the two parameters, initial HI concentration and HI/wood stoichiometric ratio, giving these values of final HI concentration.

(d) Liquefaction of individual components of wood

The trend of reaction activity to liquefaction in aqueous HI solution is in the order

Cellulose > Xylan > Hybrid Poplar > Lignin.

Relative to other lignocellulosic substrates, lignin liquefaction gives a significantly higher yield of the undesirable char-type residue fraction, ON.

(e) Characteristics of the OP product

The hydrogen retention of the OP product fraction can be maintained at 70% or better relative to hybrid poplar for a variety of reaction conditions, but can be improved to about 85% by increasing the initial HI concentration to 68 wt% HI. The extent of deoxygenation of the OP product fraction is about 75% relative to the poplar wood and is relatively insensitive to HI concentration and to stoichiometric ratio R except that deoxygenation drops off sharply at some value of initial HI concentration not much lower than 57 wt% HI or for conditions giving final aqueous phase concentration below 45 – 50 wt% HI. The extent of deoxygenation and hydrogen retention for the liquefaction of cellulose and xylan is about 5 – 15% greater than for hybrid poplar because of the lignin content of wood.

The iodine content of the OP product fraction, expressed as the atomic ratio I/C, is a unique function of the I_2 concentration at the end of batch liquefaction and appears unrelated to reaction conditions or to the type of substrate used.

4. Preliminary electrochemical liquefaction reactor testing

Batch and batchwise-continuous mode operation of the ECLR established that I_2 produced by the reaction of wood with HI can be reduced simultaneously with wood liquefaction in spite of the presence of the viscous crude wood oil product. At comparable operating conditions the cell current and cathode current density with electrochemical wood liquefaction is reduced by about 25% relative to the system of pure I_2-HI aqueous solution because of partial blockage of the cathode surface by the viscous product. With any wood feed rate to the reactor, reduction of I_2 was obtained without the unwanted competitive reaction of H_2 generation at the sheet metal cathode during electrochemical wood liquefaction. Stable batchwise-continuous operation of the ECLR was obtained while maintaining the I_2 concentration not in excess of 0.1 M. This finding established that electrochemical liquefaction was obtained with an approximate balance between the rate of I_2 produced from the wood-HI reaction and the rate of I_2 reduced by electrochemical reaction.

5. Characteristics of continuous electrochemical liquefaction reactor operation

(a) A successful 5h run with steady operation of a fully sealed liquefaction reactor was obtained with continuous wood feeding, continuous I_2 generation, continuous I_2 reduction electrochemically, continuous make-up HI to maintain HI concentration at a steady-state value, continuous liquefaction gas product collection and continuous O_2 production. The aqueous phase HI concentration was maintained at 54 – 56 wt% by the addition of make-up HI. The liquefaction reactor was operated at the bubble point temperature of the aqueous HI solution, about 125°C. At a cell voltage of 6 V and 1200 rpm cathode rotation speed the current was steady, averaging 11.9 A or a cathode current density of 0.81 A/cm^2. Electrochemical reduction of I_2 was obtained without the occurrence at the cathode of the competing reaction of H_2 generation. The I_2 concentration of the aqueous solution never exceeded 0.09 M over the 5h of the run, very much less than the typical levels of 0.7 – 1.4 M reached in nonelectrochemical batch liquefaction.

(b) Near 100% mass balances were obtained for carbon, hydrogen, oxygen, iodine, HI and H_2O. 100% of the carbon of wood is recovered, with the carbon base yields being 84.2% of crude wood oil product and 4.9% of CH_3I gaseous product while at the conditions of this run the yield of the undesired char type residue was totally suppressed. The yield of aqueous phase soluble organic product, 10.8%, is of lesser importance because this is simply a reactor inventory which in long term continuous ECLR operation would go to zero.

(c) The higher reactivity between wood and HI relative to that obtained in the earlier nonelectrochemical wood liquefaction appears attributable to the higher level of HI concentration maintained in the continuous reaction operation than that at the end of batch reaction.

(d) Of the total I_2 produced, 88% is reduced to HI. As only the I_2 in solution can be reduced electrochemically, the I_2 reduction efficiency of dissolved I_2 is even higher, 94%. The 6% of I_2 in solution that was not reduced during this run is simply the I_2 dissolved in the reactor aqueous phase and as such is another reactor inventory term which would go to zero in long term continuous ECLR operation.

(e) The current efficiency for H^+ generation is 96%. Of the H^+ generated, 45% is used for I_2 reduction and the remainder is for electrochemical organic reactions for the wood oil product.

6. Iodine behaviour with the product

With the I_2 concentration in the aqueous HI solution was maintained at 0.03 – 0.05 M by electrochemical wood liquefaction, the iodine content of the OP product fraction expressed as atomic ratio was found to be I/C = 0.06. By both CS_2 solvent extraction and sodium thiosulphate treatment of the crude organic product it was found that about 85 – 90% of this total iodine content is as I_2 physically associated with the crude wood oil, while only 10 – 15% of the iodine content is chemically bonded as organic iodide. A charge-transfer complex type of physical association of I_2 molecules occurs with iodine atoms, carbonyl group oxygen atoms and benzene rings of the organic product. Because the physical association between I_2 and the organic product is relatively strong, the iodine content of the crude product becomes asymtotic to a value of about I/C = 0.045 even when I_2 concentration in the aqueous HI solution phase is decreased to almost nil (0.002 M) during electrochemical wood liquefaction. Although the iodine content of the OP product fraction under practical ECLR operating conditions is limited to about I/C = 0.06, this level of iodine content is none the less substantially less than without simultaneous electrochemical reduction of I_2 to HI.

7. Characteristics wood oil product of continuous electrochemical liquefaction

By the methods noted in item 6, the iodine content present as organic iodide in the product was demonstrated to correspond to an I/C atomic ratio of only about 0.009, the remainder of the iodine content being the physically associated I_2. Thus the stoichiometric equation for the continuous wood liquefaction at steady 54 – 56 wt% HI concentration is

$$\begin{aligned} CH_{1.59}O_{0.70} + 1.07\ HI = {} & 0.842\ CH_{1.37}O_{0.111}I_{0.0090}\ (OP) \\ & + 0.108\ CH_{1.44}O_{0.106}I_{0.0085}\ (AP) \\ & + 0.049\ CH_3I + 0.60\ H_2O + 0.52\ I_2 \end{aligned}$$

where the I_2 produced (0.52 gmol HI/gmol C in wood) is distributed between the aqueous HI solution and that associated physically with the product. Liquefaction simultaneous with electrochemical reduction has improved the quality of the wood oil product through electrochemical organic reduction reactions simultaneous to I_2 reduction. This effect is evidenced by the higher reactivity of the wood-HI reaction, i.e. higher reaction stoichiometric coefficients, as well as by the higher levels of hydrogen retention and oxygen removal relative to wood, both above 85%, for this wood oil product as compared to the product from nonelectrochemical wood liquefaction. The higher reactivity between wood and HI and higher quality of the organic product is related to some of the H^- produced electrochemically having participated in wood liquefaction reactions at the cathode.

8.2 Contributions to knowledge

1. Basic characteristics of biomass liquefaction by HI in aqueous solution

Batch reactor studies revealed several new aspects concerning the direct liquefaction of wood with concentrated aqueous HI solution to a wood oil product under low severity conditions, atmospheric pressure and low temperature, around 125°C. It was found that the wood-HI reaction is fast, nearly complete as little as 20s when the initial aqueous phase concentration is 57 wt% HI or greater. The yield of the char-type residue can be completely eliminated by any conditions giving a final aqueous phase concentration of 50 wt% HI or greater.

2. Electrochemical wood liquefaction reactor design

A novel concept electrochemical liquefaction reactor (ECLR) was designed in which wood liquefaction occurs in the cathode cell simultaneously with electrochemical reduction back to HI of the I_2 produced by the wood liquefaction reaction, thereby closing the HI→I_2→HI loop. Electrolysis of water from H_2SO_4 solution in the anode cell generates O_2 and the H^+ required for HI regeneration at the cathode.

3. Basic characteristics of electrochemical liquefaction of wood in aqueous HI

Batch, batchwise-continuous and steady continuous operation of this ECLR established that wood liquefaction and electrochemical reduction of I_2 back to HI can be obtained simultaneously in spite of the presence of the viscous wood oil product, and without generation of H_2 by the competitive electrochemical reaction at the cathode. As operating conditions were demonstrated for which there is no production of the char-type product common to other liquefaction processes, long term steady ECLR operation would generate only three products, 95.1% yield of crude wood oil product, 4.9% yield of methyl iodide from the methoxy groups of the lignin and O_2 from the anode cell. Of the H^+ generated at the anode, about half is used for regeneration of the HI and half for electrochemical liquefaction reactions which are reflected in the exceptionally high levels of hydrogen retention and oxygen removal of the wood oil product relative to the wood, in both cases above 85%.

4. Iodine content of the crude wood oil product

Two independent methods established that about 85 – 90% of the iodine content of the crude wood oil product is as physically associated I_2 while only 10 – 15% of this iodine content is as organic iodide. This finding greatly simplifies the challenge for future work of producing an iodine-free wood oil product because the removal of I_2

physically associated with the product is intrinsically much easier than the removal of iodine present as organic iodide. The latter is shown to be very small, corresponding to an iodine to carbon atomic ratio of about 0.009, or one iodine atom for about every 110 carbons.

8.3 Recommendations for future studies

Further studies to elucidate and develop the process should include the following approaches to a number of questions that remain to be answered.

1. Investigation of practical methods for removal of the I_2 associated physically with the product, corresponding to an iodine to carbon atomic ratio of about 0.08, or one I_2 molecule for about every 25 carbon atoms.

2. Investigation of practical methods of removal of the iodine present in the product as organic iodide to the extent of an iodine to carbon atomic ratio of about 0.009, or one iodine atom for about every 110 carbon atoms.

3. A full characterisation of the nature and properties of the wood oil product should be made.

4. An ECLR system should be developed with recycle to the reactor of the aqueous phase reactor effluent which contains the dissolved aqueous phase product fraction.

5. It would be interesting to investigate the nature of the electrochemical organic

reactions that occur during the electrochemical wood liquefaction process.

6. Work should be done on design of an electrochemical wood liquefaction reactor of high electrochemical efficiency, including decreasing the IR drop, increasing the energy efficiency, and research for semipermeable membranes of greater effectiveness including reduction of water transfer from the anode to cathode cell.

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APPENDIX A

PHYSICAL PROPERTIES OF HI SOLUTION

A.1 Vapor-liquid equilibrium data for HI-H_2O system at atmospheric pressure

Liquid phase composition wt%	Bubble point temperature °C	Reference	Vapor phase composition wt%	Dew point temperature °C	Reference
0	100		0.03	100	(1)
15.1	102	(1)	0.1	100.1	(1)
27.3	105	(1)	0.2	100.25	(1)
33.6	107	(1)	0.3	101	(1)
39	109	(1)	0.5	101.5	(1)
42.7	111	(1)	1.5	105	(1)
48	116	(1)	5	120	(1)
50	118	(1)	15	122	(1)
52.5	123.2	(1)	23	123.2	(1)
52.75	124	(1)	51.7	125.5	(1)
54	125.2	(1)	55	126	(1)
54.9	125.8	(1)	56.7	126.5	(1)
55.5	126	(1)	69.8	122	(1)
56.7	126.5	(1)	70	121	(1)
56.8	127	(2)	90	95	(1)
58	123	(1)	93	84	(1)
59.4	118	(1)	96	75	(1)
60	112	(1)	98.5	62	(1)
61.1	108	(1)	98.8	60	(1)
64	100	(1)			
64.9	86	(1)			
69.1	20	(3)			
72.0	10	(3)			
73.4	0	(3)			
74.7	-10	(3)			
75.8	-20	(3)			
100	-35.3	(2)			

References :
(1) Carrière et Ducasse, 1926
(2) Kirk-Othmer, 1963
(3) Ahmed et al., 1970

A.2 Density of HI solution

Density at 20°C			Density at 25°C			Reference
HI Concentration		Density	HI Concentration		Density	
wt%	mol/l	g/ml	wt%	mol/l	g/ml	
				0.001009	0.9971	(1)
				0	0.99707	(2)
				0.002152	0.9972	(1)
				0.005144	0.9975	(1)
				0.01036	0.9980	(1)
				0.02507	0.9996	(1)
				0.05435	1.0025	(1)
1	0.0786	1.0054	1	0.0785	1.0042	(1)
				0.1124	1.0082	(1)
2	0.1583	1.0127	2	0.1581	1.0114	(1)
				0.2217	1.0181	(1)
4	0.3214	1.0277	4	0.3209	1.0262	(1)
6	0.4893	1.0431	6	0.4885	1.0415	(1)
8	0.6623	1.0589	8	0.6613	1.0573	(1)
10	0.8405	1.0751	10	0.8392	1.0573	(1)
11.64	1	1.0986				(1)
12	1.0243	1.0918	12	1.0228	1.0902	(1)
14	1.2139	1.1091	14	1.2120	1.1074	(1)
16	1.4097	1.1270	16	1.4075	1.1252	(1)
				1.3099	1.14084	(2)
18	1.6120	1.1456	18	1.6094	1.1437	(1)
20	1.8214	1.1649	20	1.8183	1.1629	(1)
20.77	1.9061	1.1739	20.77	1.9029	1.1719	(3)
21.65	2	1.1815				(1)
22	2.0381	1.1850	22	2.0345	1.1829	(1)
24	2.2626	1.2059	24	2.2585	1.2037	(1)
26	2.4955	1.2277	26	2.4908	1.2254	(1)
				2.2695	1.23659	(2)
28	2.7369	1.2503	28	2.7317	1.2479	(1)
30	2.9873	1.2737	30	2.9814	1.2712	(1)
30.10	3	1.2749				(1)
31.77	3.2129	1.2936	31.77	3.2194	1.2962	(3)
35	3.6548	1.3357	35	3.6471	1.3329	(1)
				3.6688	1.36451	(2)
37.42	4	1.3674				(1)
40	4.3871	1.4029	40	4.3774	1.3998	(1)
42.70	4.8247	1.4453	42.70	4.8151	1.4424	(3)
43.85	5	1.4584				(1)
45	5.1909	1.4755	45	5.1785	1.4720	(1)
				6.0458	1.55478	(2)
				7.6154	1.66449	(2)
56.78	7.5258	1.6954	56.78	7.5072	1.6912	(3)
61.97	8.8024	1.8169	61.97	8.7791	1.8121	(3)

Notes :
(1) Gmelins, 1937
(2) Mellor, 1930
(3) Vogel, 1989

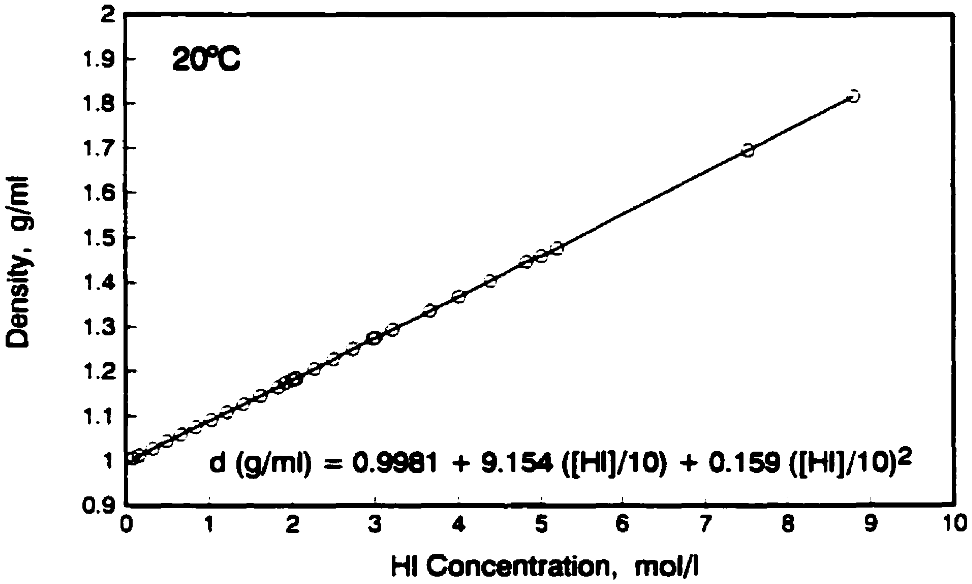

Figure A.1 Density of HI Solution at 20° C

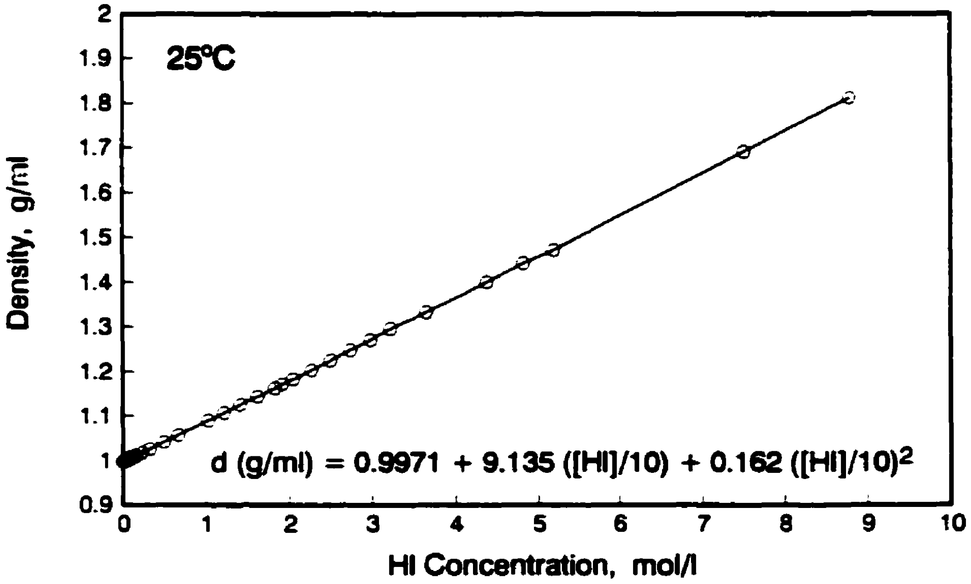

Figure A.2 Density of HI Solution at 25° C

A.3 Stability of 57 wt% HI solution at bubble point

As HI converts slowly to I_2, the stability of 57 wt% HI solution was tested by boiling the solution for 5.75h in a flask with a condenser to return HI-H_2O vapour to the flask. The HI and I_2 concentrations were determined periodically by the methods appearing in Appendix H.1.

Heating Time h	Temperature °C	HI Concentration mol/l	I_2 Concentration mol/l
-	23	7.65	0.0062
0	127	7.58	0.0125
0.25	127	7.46	0.0125
0.50	127	7.43	0.0125
0.75	127	7.37	0.0287
1.25	127	7.41	0.0281
1.75	127	7.35	0.0281
2.25	127	7.37	0.0281
2.75	127	7.33	0.0297
3.75	127	7.29	0.0312
4.75	127	7.29	0.0437
5.75	127	7.35	0.0500

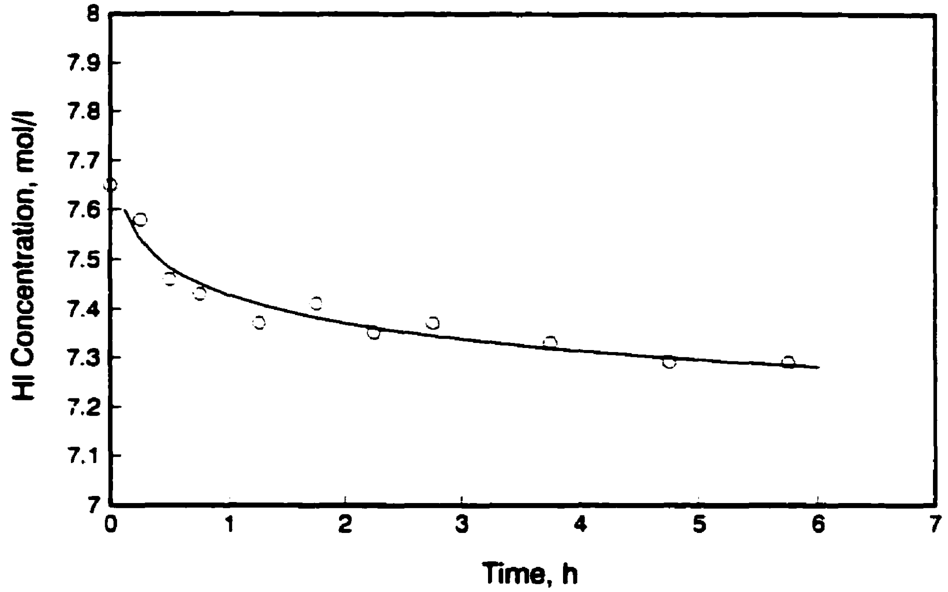

Figure A.3 Stability of HI Solution at Bubble Point: HI Decomposition

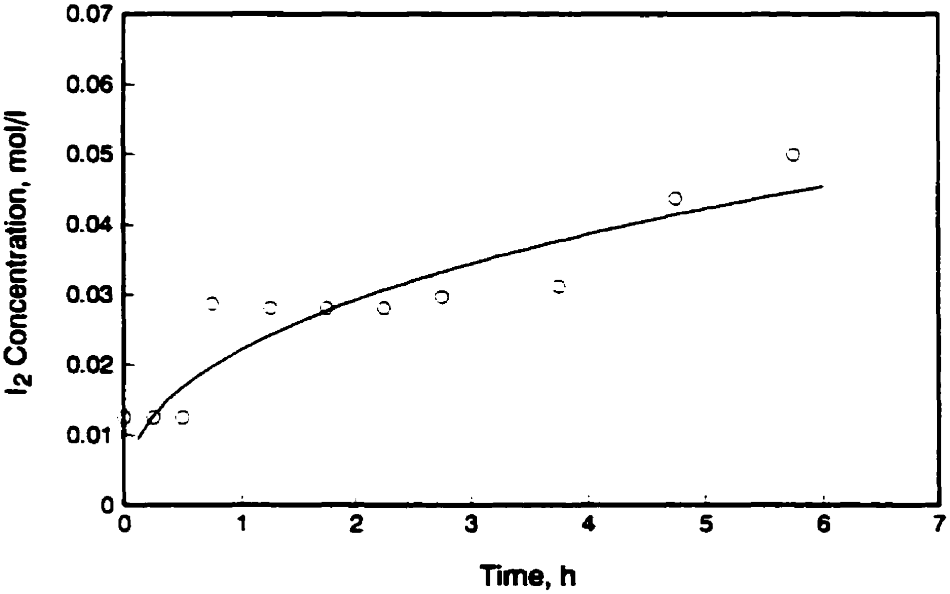

Figure A.4 Stability of HI Solution at Bubble Point: I_2 Produced

A.4 Vapour pressure of hydrogen iodide

Hydrogen iodide is colourless gas at room temperature. Its critical point temperature and pressure are 424.1°K (150.9°C) and 82 atm.

At 222.30°K, (−50.85°C) liquid hydrogen iodide freezes to a colourless solid. The vapour pressure of solid hydrogen iodide is given by the equation

$$\log (P \text{ mmHg}) = 10.493 - 0.003167\ T - 0.377 \log T - 1406/T$$

At 237.75 ± 0.05°K, (−35.40°C), hydrogen iodide condenses to a colourless liquid. The vapour pressure of liquid hydrogen iodide is given by the equation:

$$\log(P \text{ mmHg}) = 7.20883 - 1025.71/T$$

or more accurately, by

$$\log (P \text{ mmHg}) = 26.119 + 0.002293\ T - 7.111 \log(T) - 1636/T$$

Reference:

Mellor, 1930

APPENDIX B

SOLUBILITIES OF IODINE

B.1 Solubility of I_2 in water

Temp. °C	Solubility g/l	Temp. °C	Solubility g/l	Temp. °C	Solubility g/l
0	0.14	40	0.52	90	3.15
10	0.20	50	0.71	100	4.45
20	0.285	60	1.00	106	5.60
25	0.335	70	1.50	112.3	7.29
30	0.385	80	2.25		

Reference:
Stephen and Stephen, 1963

B.2 Solubility of I_2 in HI solution
(Temperature = 25°C)

HI Concentration			I_2 Solubility		I_2/HI	Reference
g/l	mol/l	wt%	g/l	mol/l	mol/mol	
7.73	0.0604	0.735	7.49	0.0295	0.488	(1)
11.79	0.0922	1.09	11.65	0.0459	0.498	
15.46	0.121	1.40	15.48	0.0610	0.504	
26.99	0.211	2.27	28.35	0.112	0.531	
39.90	0.312	3.11	41.45	0.163	0.522	
54.10	0.423	3.91	59.86	0.236	0.558	
63.95	0.500	4.40	76.15	0.300	0.600	
81.22	0.635	5.15	100.3	0.395	0.622	
			kg/l			
682.1	5.33	45.9	2.28	8.98	1.69	(2)
781.6	6.11	50.2	2.84	11.2	1.83	
894.3	6.99	54.4	3.47	13.7	1.96	
1201	9.39	64.0	4.72	18.6	1.98	
1298	10.1	66.7	5.22	20.6	2.03	

References:
(1) Silcock, 1963
(2) Powell and Campbell, 1947

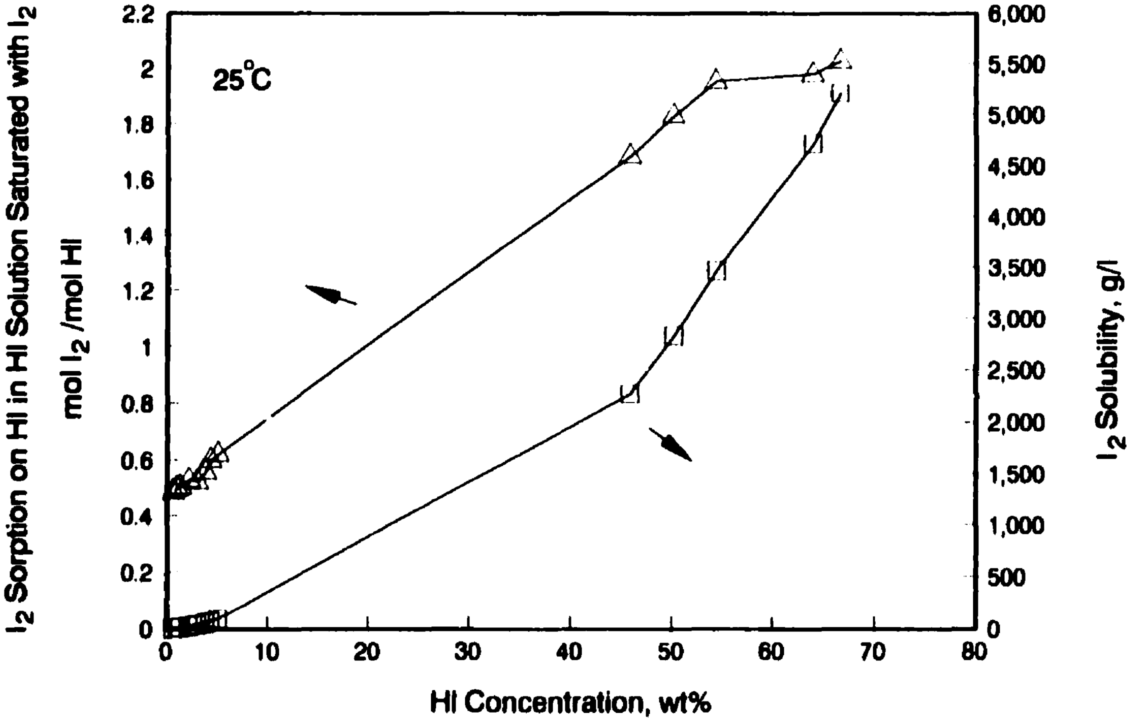

Figure B.1 Solubility of I_2 in HI Solution

B.3 Solubility of I_2 in organic solutions

Solvent	Temp.	Solubility		Solvent	Temp.	Solubility	
	°C	wt%	g/l		°C	wt%	g/l
CS_2 Carbon disulfide	0	7.89		$CHCl_3$ chloroform	10	1.773	
	10	10.51			15	2.129	32.6
	15	12.35			20	2.562	
	20	14.62			25	3.101	45.2
	25	16.92			30	3.693	
	30	19.26					
	35	21.62		CH_2Cl_2 dichloromethane	15		42.2
	40	25.22			25		58.6
	16.6		178.5				
CCl_4 carbon tetrachloride	0	0.728		C_3H_6O acetone	0	2.5	
	15		20.5				
	21		25.1				
	25		29.1	C_6H_6 benzene	20		119.343
	35	2.6			25	14.09	
	50	4.349			30	16.1	
					35	17.9	
$C_2H_4O_2$ acetic acid	20	1.727			40	20.05	
	30	2.706			50	25.51	

order of I_2 solubility:

$$CS_2 > C_6H_6 >> CH_2Cl_2 \sim C_3H_6O > CHCl_3 > C_2H_4O_2 > CCl_4 > H_2O$$

Reference:
Stephen and Stephen, 1963

APPENDIX C

OVERPOTENTIAL RELATIONS FOR I_2 ELECTROCHEMICAL REDUCTION

(personal communication from E.M. Berksoy, McGill University)

C.1 Current density – overpotential relations

The relation between the current density, i, and the overpotential, η, is given by the Butler-Volmer equation (Pletcher and Walsh, 1990),

$$i = i_o \left(\exp\frac{(\alpha_a\, nF\eta)}{RT} - \exp\frac{(-\alpha_c\, nF\eta)}{RT} \right) \qquad \text{(C.1)}$$

where n is the number of electrons transferred, F is the Faraday constant, 96487 $C{\cdot}mol^{-1}$ and R is the gas constant 8.314 $J{\cdot}mol^{-1}{\cdot}k$. This equation shows that the current density at an electrode is a function of overpotential η, exchange current density i_o, and the transfer coefficients α_c of cathode and α_a of anode.

For large cathodic polarization the first term in Equation C.1 becomes negligible.

$$-i = i_o \exp\left(\frac{-\alpha_c\, nF\eta}{RT}\right) \qquad \text{(C.2)}$$

Equation C.2 can be written as

$$\log(\, -i \,) = \log(\, i_o \,) - \frac{\alpha_c\, nF\eta}{2.303RT} \qquad \text{(C.3)}$$

which is known as the cathodic Tafel equation.

Similarly for large positive overpotentials, the second term in Equation C.1 becomes negligible and this leads to the anodic Tafel equation

$$\log(i) = \log(i_o) + \frac{\alpha_a nF\eta}{2.303RT} \qquad \text{(C.4)}$$

For $\eta > 52$ mV. Equations C.3 and C.4 are good approximations to Equation C.1. The term 2.303RT/αnF is known as the Tafel slope.

However for the case of small polarization, $\eta \approx 0$, the Equation C.1 relation between current density and overpotential, with $\alpha_a = \alpha_c = 0.5$ mV, becomes

$$i = i_o \frac{nF}{RT} \eta \qquad \text{(C.5)}$$

which shows that for $\eta \approx 0$, current density i depends linearly on overpotential η.

C.2 Cathodic overpotential: I_2/I^- overpotential on platinum

For the I_2/I^- redox couple, with the transfer coefficient taken as 0.5, the standard exchange current density was found to be 0.4A/cm^2 (Dane, et al., 1968). The standard exchange current density is the exchange current density of I_2/I^- at which the concentrations of I^- and I_2 are 1M. The exchange current density was 0.049 A/cm^2 for $[I^-] = 0.033$M and $[I_2] = 0.0369$M at 25°C.

For typical conditions of the present process the cathodic overpotential can be estimated from the Tafel Equation C.3 as:

$$\log(i) = \log(i_o) - \{1/(\text{Tafel slope})\}\ \eta_c \qquad \text{(C.6)}$$

where the Tafel slope is 0.12 V for T = 25°C and can be expected to be 0.16 V for T = 120°C. Because the exchange current density i_o is a function of $[I^-]$, $[I_2]$ and temperature, it will increase with temperature and with concentration of I^- for concentrations of I_2 in the range of 0.01 M − 1 M. For the conditions of T = 120°C and $[I^-] = 7.5M$. i_o is expected to be higher than 0.049 A/cm^2. However this value may be used to find the upper limit of the I_2/I^- overpotential. Therefore for the cathodic current density of −0.68 A/cm^2 (14.7 cm^2 effective area of the sheet cathode and 10A cell current) the overpotential calculated by the relation

$$\log(\ -(-0.68)\ ) = \log(\ 0.049\ ) - (1/0.16)\ \eta_c$$

is $\eta_c = -0.18$ V. which is the upper limit for $|\eta_c|$ the typical conditions here.

For calculation of the overpotential for very large exchange current density (0.4 A/cm^2 for I_2 and I^- concentrations each of 1 M) for which the overpotential is very small. the linear relation of the Tafel Equation C.5 can be used at $i = -0.68$ A/cm^2 (14.7 cm^2 effective area of the sheet cathode and 10 A cell current) as:

$$-0.68 = 0.4\ (nF/RT)\ \eta_c$$

where n = 2. The calculated overpotential is $\eta_c = -0.03$V. which may be taken as its lower limit. Then the cathodic overpotential range is:

$$-0.03 \text{ V} > \eta_c > -0.18 \text{ V}$$

In general the concentration overpotential should be considered but here it will be quite small (about −0.01 V) due to the high rotational speed of the cathode. Thus cathodic overpotential range becomes:

$$-0.04 \text{ V} > \eta_c > -0.19 \text{ V} \qquad \text{(at I = 10 A)}$$

When the circuit current is only 0.1 A. the cathodic current density is −0.0068 A/cm^2 for the cathode effective area of 14.7 cm^2. Using Equation C.5. with the exchange current density of 0.049 A/cm^2, the overpotential can be calculated by the relation

$$-0.0068 = 0.049\ (nF/RT)\eta_c^{1\to0}$$

to be $\eta_c^{1\to0} = -0.002$ V.

C.3 Anodic overpotential: O_2 overpotential on lead

The anode compartment contains 38 wt% H_2SO_4 as anolyte and a lead anode to electrolyse water to produce the H^+ ions required in the cathode compartment, plus oxygen as an associated product. In sulphuric acid solution the anode surface is covered first with $PbSO_4$, which is oxidized further to a brown layer of PbO_2 when the electrode is polarized at higher potentials. When conversion of $PbSO_4$ to PbO_2 is near completion, O_2 evolution starts on the PbO_2 surface.

For β-PbO_2 the Tafel slope is 0.12 V at 25°C and can be expected to be 0.13 V at 60°C, and exchange current density is $6.2\cdot10^{-10}$ A/cm^2 (Hoare, 1968). Taking these values of Tafel slope and exchange current density, the oxygen overpotential of the anode of 25 cm^2 surface area and at a typical current of 10 A, i.e. 0.4 A/cm^2 current density, is calculated using the Tafel Equation C.4 as

$$\log(\ 0.4\ ) = \log(\ 6.2\cdot10^{-10}\ ) + (1/0.13)\ \eta_a$$

to be 1.15V.

At a very low cell current, 0.1 A, i.e. 0.004 A/cm^2 anodic current density (25 cm^2 anode area), using Equation C.4, the anodic overpotential is calculated by the relation

$$\log(0.004) = \log(6.2\cdot 10^{-10}) + (1/0.13)\,\eta_a^{1\rightarrow 0}$$

to be 0.89 V.

C.4 Calculation of the ohmic drop

For the ECLR cells separated by the semipermeable membrane. the ohmic drop. V^{ohm}. has the following components:

$$V^{ohm} = V_c^{ohm} + V_m^{ohm} + V_a^{ohm} + V^{ohm}(\text{bubble-effect}) + V^{ohm}(\text{hardware}) \qquad (C.7)$$

Each of these components is now treated.

V_c^{ohm} of the cathode compartment. the ohmic drop between the cathode surface and the membrane. can be estimated from the equation given for cylindrical electrodes (Pickett.1977)

$$V_c^{ohm} = -i_c\, r_c\, \frac{S_c}{\kappa_c\, r_{c/m}} \qquad (C.8)$$

where the mean radius. $r_{c/m}$ is

$$r_{c/m} = \frac{S_c}{\ln\left(1 + \frac{S_c}{r_c}\right)} \qquad (C.9)$$

and

i_c the cathodic current density. taken as −0.68 A/cm² (where the average current is taken as 10 A and the effective surface area of the continuous smooth cylindrical cathode is taken as 14.7 cm². Section 4.2)

S_c the closest distance between the cathode and the membrane (2.0 cm)

κ_c the conductivity of 57 wt% aqueous HI, (0.74 mho cm^{-1}) (Weast, 1977)

r_c the radius of the cathode (1.25 cm)

Therefore the V_c^{ohm} is calculated to be 1.10 V.

V_m^{ohm}, the ohmic drop by the membrane, is

$$V_m^{ohm} = i_m \rho_m \tag{C.10}$$

where ρ_m, the specific resistance of NAFION 324 membrane, is given as 4.5 ohm·cm^2 by DuPont (NAFION perfluorinated membranes, Product Bulletin) and i_m is the current density 0.42 A/cm^2 at the membrane of 5.5 cm diameter and 10 A cell current. V_m^{ohm} is calculated to be 1.89 V.

V_a^{ohm} of the anode compartment, the ohmic drop between the surface of the anode plate and membrane is

$$V_a^{ohm} = i_a \frac{S_a}{\kappa_a} \tag{C.11}$$

where

i_a is the anodic current density (0.4 A/cm^2, when I = 10 A and surface area of anode that views the cathode is 25 cm^2)

S_a is the distance between the anode surface and the membrane (2.0 cm)

κ_a the conductivity of 38 wt% H_2SO_4 solution is about 0.5 mho·cm^{-1} (Weast, 1977 and Pletcher and Walsh, 1990).

V^{ohm}(bubble-effect), the ohmic drop by O_2 evolution at the lead anode is very small, about 0.01 V ohmic drop (Hine,1985).

V^{ohm}(hardware), the ohmic drop of the electric circuit, including the sliding contact for the rotating cathode is measured to be about 0.1 V between cathode and anode.

Inserting these values into Equation C.8, total ohmic voltage drop of the system is

$$V^{ohm} = 1.10\ V + 1.89\ V + 1.60\ V + 0.01\ V + 0.1\ V = 4.70\ V.$$

The major contribution to the total voltage drop is the membrane resistance, constituting 40% of the total.

C.5 Competitive H^+/H_2 overpotential on platinum

The exchange current density i_o of H^+/H_2 on smooth platinum cathode is 10^{-3} A/cm^2 (Prentice, 1991). The overpotential can be estimated from the Tafel Equation C.6. The Tafel slope is 0.12 at 25°C, and 0.16 at 120°C. For the typical conditions of T = 120°C, $[H^+] = 7.5$ M and -0.68 A/cm^2 current density (10 A cell current, 14.7 cm^2 cathode effective area), the overpotential $\eta_{H^+-H_2}$ determined from Equation C.6

$$\log(\ -\ (-0.68)\ ) = \log(\ 10^{-3}\ ) - (1/0.16)\eta_{H^+-H_2}$$

is -0.46 V.

C.6 Voltage at very low cell current with the mesh cathode

The voltage at very low cell current with the sheet cathode is discussed in Section 3.2.3.

When the circuit current is only 0.1 A, the cathodic current density is -0.0096 A/cm^2 for the mesh cathode effective area of 10.4 cm^2. Using Equation C.5, with the exchange current density of 0.049 A/cm^2, the overpotential can be calculated by the relation

$$-0.0096 = 0.049\ (nF/RT)\eta_c^{m\ I\rightarrow 0}$$

to be $\eta_c^{m\ I\to 0} = -0.003$ V.

At the very low cell current the anodic overpotential, $\eta_a^{I\to 0}$ is 0.89 V, Appendix C.3. Therefore the total voltage at the low cell current with the mesh cathode

$$V_T^{m\ I\to 0} = -0.83\ \mathrm{V} - |-0.003|\ \mathrm{V} - |0.89|\ \mathrm{V}$$

is -1.72 V, where -0.83 V is the thermodynamic minmum required potential.

C.7 Voltage range for I_2 reduction without H_2 generation

The voltage range of -0.80 V for I_2 reduction without H_2 generation at the continuous sheet cathode of 14.7 cm^2 effective surface area is described in Section 3.2. For the mesh cathode of 10.4 cm^2 effective surface area, this voltage range is calculated here.

At the same typical conditions as described in Section C.2 and -0.96 A/cm^2 cathode current density (10 A cell current and 10.4 effective cathode surface area) the cathodic overpotential, η_c^m for I_2 reduction from Equation C.6 as

$$\log(\ -(-0.96\ ) = \log(\ 0.049\ ) - (1/0.16)\ \eta_c^m$$

is -0.21 V. The anodic overpotential η_a is 1.15 V. For the ohmic drop, only the item of cathode cell ohmic drop is changed for cathode current density of -0.96 A/cm^2, the radius of the mesh cathode of 0.65 cm and the closest spacing between the mesh cathode and membrane of 2.5 cm. By calculation from Equations C.8 and C.9 with the above values, the cathode cell ohmic drop with the mesh cathode, $V_{c_m}^{m,ohm}$, is 1.33 V. Therefore the total ohmic drop, from Equation C.7, $V^{m,ohm}$, is 4.93 V. The total required voltage for I_2 reduction with the mesh cathode, by Equation 3.7, is

$$V^{m}_{T} = -0.83 \text{ V} - |-0.21| \text{ V} - |1.15| \text{ V} - 4.93 \text{ V}$$

is −7.12 V. where −0.83 V is the thermodynamic minimum required potential for I_2 reduction. Section 3.2.3.

With the mesh cathode of 10.4 cm^2 effective surface area the overpotential for H_2 generation from Equation C.6 at 0.96 A/cm^2 cathode current density (10 A cell current) by the relation

$$\log(-(-0.96)) = \log(10^{-3}) - (1/0.16)\eta^{m}_{H-H_2}$$

is −0.48 V. The total required voltage for H_2 generation with the mesh cathode by Equation 3.10

$$V'^{m}_{T} = -1.36 \text{ V} - |-0.48| \text{ V} - |1.15| \text{ V} - 4.93 \text{ V}$$

is −7.92 V. where −1.36 V is the thermodynamic minimum required potential for H_2 generation. Section 3.2.4.

Therefore the voltage range for I_2 reduction without H_2 generation at the mesh cathode is (−7.92 − (−7.12) =) −0.80 V. which is the same at the sheet cathode.

APPENDIX D

CALIBRATION OF WOOD FEEDER

Controller speed rpm	Wood flow rate g/min	Controller speed rpm	Wood flow rate g/min
10	0.042	150	0.794
20	0.097	180	0.949
30	0.166	210	1.084
40	0.231	240	1.216
50	0.299	270	1.353
60	0.334	300	1.492
70	0.398	330	1.602
80	0.444	360	1.694
90	0.496	390	1.846
100	0.546	400	1.871
110	0.596	420	1.953
120	0.646	450	2.100
		480	2.218

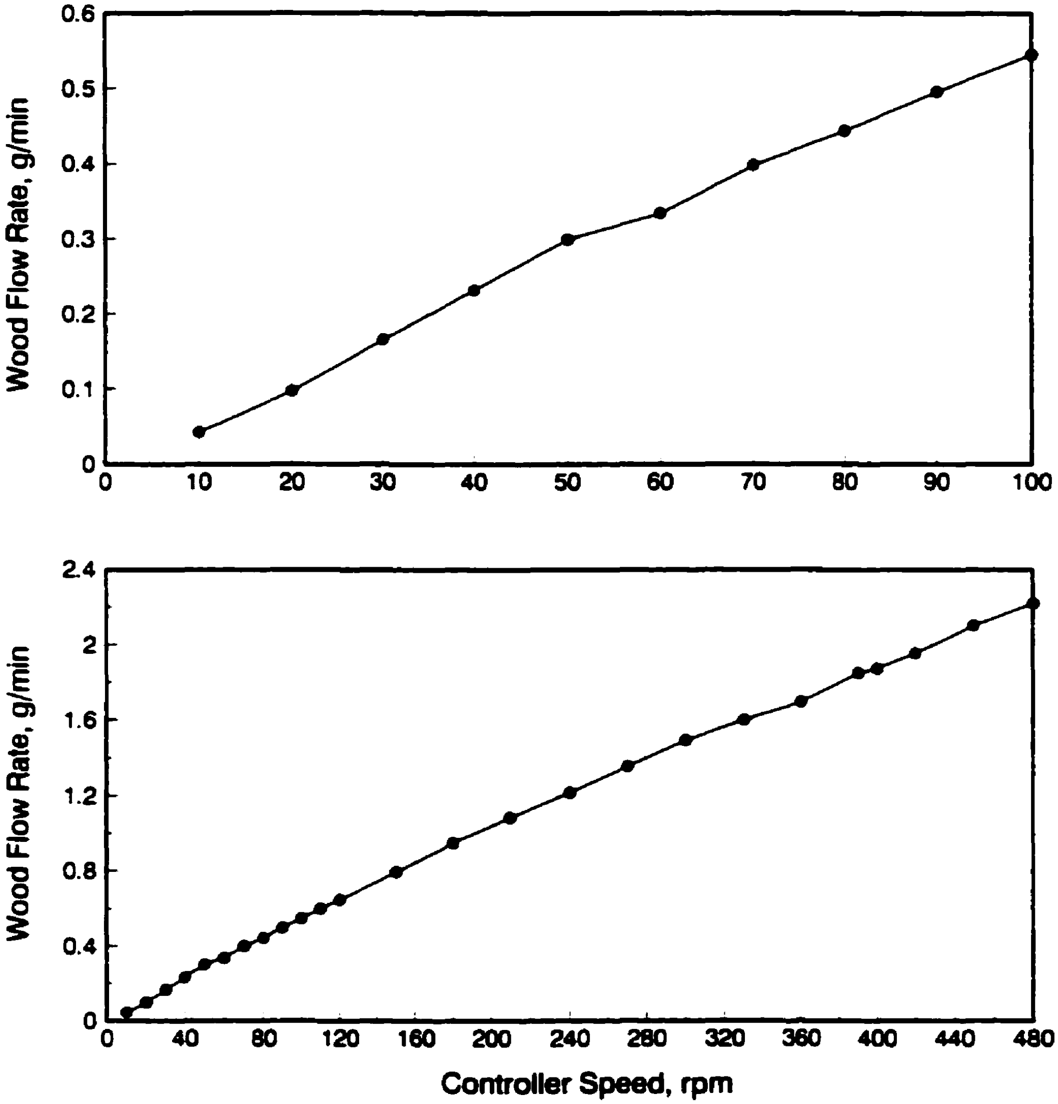

Figure D.1 Wood Feeder Calibration

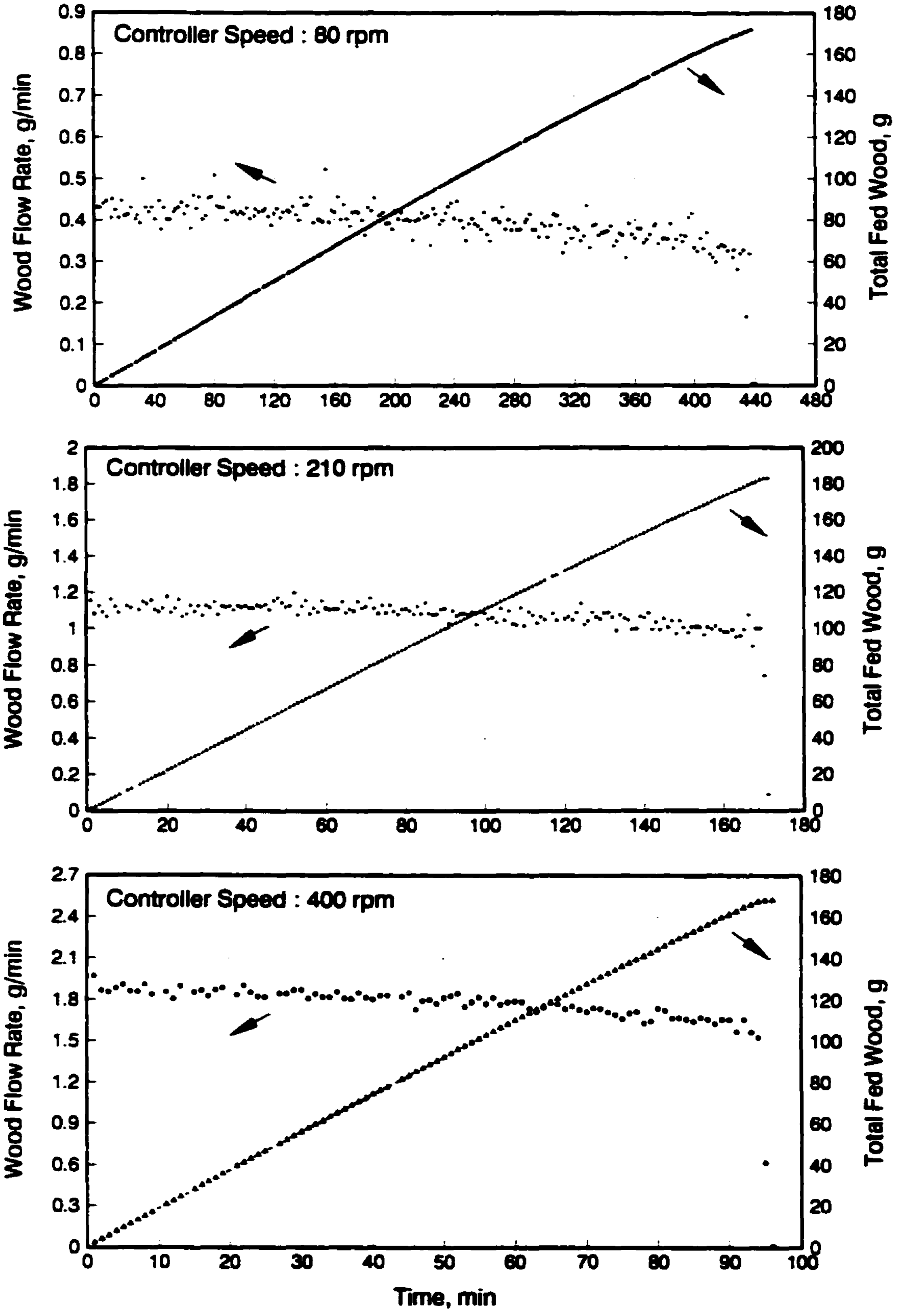

Figure D.2 Stability of Wood Flow Rate

APPENDIX E

OPERATION OF HI GAS SUPPLY SYSTEM

E.1 General operation procedures for HI gas supply

Each time before HI gas flow, the system must be purged with nitrogen. After HI gas flow, the system must be purged with nitrogen first, the purged with dry air, finally purged with nitrogen again.

HI gas flow

Start-up

1. Check that the following valves are closed: 21, 20, 18, 13, 12, 11, 9, 4.
2. All outlet lines must be immersed in the HI absorber. The three-way glass stop-cock 22 must be closed to the reactor, must be open to the HI absorber.
3. The purging three-way glass stop-cock 23 must be open.
4. Open valve 14 on the HI cylinder (in the freezer)
5. Open (slowly) the following valves by order: 1, 2, 5, 7, 8, 3 and 10
6. Flush with HI for 5 minutes

HI gas supply

1. Close valves 3 and 10
2. Close the purging three-way glass stop-cock 23
3. Regulate HI flow with valve 7
4. Open the three-way glass stop-cock 22 to the reactor, close the connection to the HI

absorber.

Shut-down

1. Close the three-way glass stop-cock 22 to the reactor, open the connection to the HI absorber.
2. Close valves in the order 8, 7, 5, 4, 2, 1 and 14.

Purging with N_2

Stage I

1. The main valve 14 (HI gas) must be closed. Check that 21, 20 and 18 valves are closed.
2. All outlet lines must be immersed in the HI absorber. The purging valve 23 must be open. The three-way glass stop-cock 22 to the reactor must be closed and the connection to the HI absorber opened.
3. Open valve 11 on the N_2 cylinder
4. With regulator 12, set the purging pressure below 100 kPa
5. Open valve 13 on the N_2 cylinder
6. Open the following valves by order: 9, 1, 2, 5, 7, 8, 4, 3 and 10
7. Flush with nitrogen for 5 – 30 minutes, depending on the flowrate

Stage II

1. Close valves 4, 3 and 10.
2. Close the purging glass stop-cock 23
3. Flush with nitrogen for 15 – 60 minutes, depending on the flowrate
4. Reduce pressure of N_2 to 50 kPa with regulator 12
5. Close valves in the order: 8, 7, 5, 2, 1 and 9
6. Check again the pressure of N_2, if necessary reduce to 50 kPa
7. Close valves in the order: 13, 12 and 11 on the N_2 cylinder

Purging with dry air

Stage I

1. The main valve 14 (HI gas) must be closed.
2. Check that the following valves are closed in the order: 13, 12, 11, 10, 9, 4,3 and 1.
3. All outlet lines must be immersed in the HI absorber. The purging valve 23 must be open. The glass valve 22 to the reactor must be closed, the connection to the HI absorber open.
4. Open valve 18 on the air line
5. Set the air purging pressure below 20 kPa
6. Open valves 21 and 20
7. Open (slowly) the following valves in the order: 2, 5, 7, 8 and 3
8. Flush with air for 0.5h – 2h, depending on the flowrate

Stage II

1. Close the purging glass valves 3 and 23
2. Flush with air for 1 – 6 minutes, depending on the flowrate
3. Close valves in the order 8, 7, 5 and 2
4. Reduce the air pressure to zero
5. Close valves in the order 21, 20 and 18 on the air line

E.2 General operation procedures for checking HI cylinder

Each time after checking the HI cylinder to prevent corrosion deposits from accumulating and plugging the main HI cylinder valve, the system must be purged with nitrogen. Experience indicates that this operation should be carried out each three months.

Stage I - checking HI gas flow in the cylinder

1. Check that the following valves are closed: 22, 21, 20, 18, 13, 12, 11, 9, 8, 7, 5, 4,

3, 2 and 1

2. The purging three-way glass stop-cock 23 must be open to the HI absorber.

4. Open valve 14 on the HI cylinder (in the freezer)

5. Open (slowly) the valve 10

6. Flush with HI for 5 minutes

Stage II - shut-down

1. Close the three-way valve 23

2. Close valves 10 and 14

Stage III - purging with N_2

1. The purging three-way glass stop-cock 23 must be open to the HI absorber.

2. Open valve 11 on the N_2 cylinder

3. With regulator 12, set the purging pressure below 100 kPa

4. Open valve 13 on the N_2 cylinder

5. Open the valves 9 and 10

7. Flush with nitrogen for 30 minutes

8. Close the three-way valve 23

9. Close valves 10 and 9

10. Close valves in the order: 13, 12 and 11 on the N_2 cylinder

APPENDIX F

ELECTROCHEMICAL PERFORMANCE CHARACTERISTICS

F.1 Platinum mesh cathode/lead anode mode ECLR

(Voltage = 8 V, Cathode rotation speed = 2000 rpm)
(Spacing: cathode-membrane-anode = 25/20 mm)

Time min	Current A	I_2 concentration M	Reduction rate g/min	Current efficiency %
0	16.5	0.51		
2	15	0.46	1.59	
7	19.5	0.34	1.52	96.71
12	19	0.23	1.40	95.04
17	18.5	0.13	1.27	96.13
22	17	0.02	1.15	95.04
24.5	15	0.0075	0.32	96.13
27.5	15	0.007	0.19	95.04
29.5	12	0.005	0.063	82.86
36.5	12	0.003	0.018	86.17

F.2 Platinum sheet cathode/lead anode mode ECLR

(Voltage = 3 V, Cathode rotation speed = 500 rpm)
(Spacing: cathode-membrane-anode = 20/20 mm)

Time min	Current A	I_2 concentration M	Reduction rate g/min	Current efficiency %
0	2.6	0.39		
15	3.0	0.37	0.28	
20	3.8	0.3	0.29	96.71
36	3.6	0.23	0.27	95.04
50	2.9	0.18	0.22	96.13
65	2.8	0.12	0.21	95.04
80	2.9	0.086	0.22	96.13
90	2.8	0.083	0.21	95.04
100	2.6	0.054	0.17	82.86
110.5	2.5	0.024	0.17	86.17
117	2.1	0.0079	0.14	84.48
120.5	1.7	0.0014	0.10	74.54
124	1.8	0.0014	0.00	0.00

(Voltage = 6 V, Cathode rotation speed = 0 rpm)
(Spacing: cathode-membrane-anode = 20/20 mm)

Time min	Current A	I_2 concentration M	Reduction rate g/min	Current efficiency %
0	8.7	0.27		
4.5	11.6	0.22	0.81	88.49
10	11.7	0.15	0.80	86.65
15	10.8	0.099	0.63	73.92
19	10.2	0.065	0.52	64.60
23	10	0.041	0.36	45.62
27.1	9.9	0.025	0.23	29.44
30	9.7	0.018	0.15	19.60
33	9.9	0.012	0.12	15.36
36	9.7	0.0089	0.06	7.84
39	9.7	0.0061	0.06	7.84
46.3	9.3	0.0046	0.01	1.36

(Voltage = 6 V, Cathode rotation speed = 500 rpm)
(Spacing: cathode-membrane-anode = 20/20 mm)

Time min	Current A	I_2 concentration M	Reduction rate g/min	Current efficiency %
0	10.3	0.31		
3.2	13.1	0.26	0.92	
6	13.3	0.22	0.92	89.00
9	13.3	0.17	0.98	87.66
12	13	0.13	0.93	93.37
15	12.9	0.081	0.96	90.66
18.1	11.7	0.041	0.75	94.31
21	10.9	0.015	0.53	81.23
24.05	10.5	0.0026	0.24	61.62
27	10.5	0.0020	0.01	28.97

(Voltage = 6 V, Cathode rotation speed = 1000 rpm)
(Spacing: cathode-membrane-anode = 20/20 mm)

Time min	Current A	I_2 concentration M	Reduction rate g/min	Current efficiency %
0	15.5	0.30		
3	15.6	0.25	1.17	95.04
6	15.8	0.19	1.24	99.45
9	16	0.13	1.24	98.21
12	16	0.073	1.18	93.46
14	15.1	0.034	1.18	99.03
16.5	13.8	0.0041	0.71	65.20
18.5	13.8	0.0011	0.11	10.10
20.5	13.8	0.00068	0.02	1.84

(Voltage = 6 V, Cathode rotation speed = 1500 rpm)
(Spacing: cathode-membrane-anode = 20/20 mm)

Time min	Current A	I_2 concentration M	Reduction rate g/min	Current efficiency %
0	8.6	0.23		
3	11.8	0.20		
6	15.2	0.14	1.18	98.38
8	15.4	0.10	1.17	96.28
10	15.4	0.063	1.07	88.05
12	14.7	0.028	0.99	85.34
14	14	0.010	0.51	46.16
15.5	13.8	0.0013	0.32	29.39

(Voltage = 7V, Cathode rotation speed = 500 rpm)
(Spacing: cathode-membrane-anode = 20/20 mm)

Time min	Current A	I_2 concentration M	Reduction rate g/min	Current efficiency %
0	13.8	0.36		
2	17.6	0.32	1.25	
4	17.6	0.27	1.38	99.36
6	17.6	0.23	1.36	97.92
8	17.6	0.18	1.36	97.92
10	17.2	0.14	1.31	96.52
13	16.3	0.073	1.26	97.96
15	15.6	0.041	1.11	90.17
17	15.3	0.022	0.71	58.81
19	15	0.0065	0.42	35.48
21	14.7	0.0029	0.1	8.62
24	14.6	0.0014	0.03	2.60

(Voltage = 7V, Cathode rotation speed = 500 rpm)
(Spacing: cathode-membrane-anode = 20/30 mm)

Time min	Current A	I_2 Concentration M	Reduction Rate g/min	Current Efficiency %
0	15.5	0.14		
2	16.6	0.1	1.09	83.21
4	16.1	0.063	1.11	87.37
6.5	15.7	0.03	0.76	61.34
8.5	15.5	0.014	0.46	37.61
10	15.5	0.0061	0.3	24.53
12	15.4	0.0029	0.09	7.41

APPENDIX G

COMPOSITION OF SUBSTRATES

Standard wood certificate

The certificate of hybrid poplar was supplied by the National Research Council in 1985.

Constituents:

Alpha Cellulose	43.30 %
Hemicellulose	32.70 %
Pentosan	19.4 %
Klason Lignin	21.52 %
Soluble Lignin	2.7 %

Elemental Analysis, weight %

C	48.2
H	6.4
O	45.3
N	0.09
S	0.05

Elemental composition

$CH_{1.59}O_{0.70}$

Cellulose

Standard cellulose is $(C_6H_{10}O_5)_n$, i.e. $CH_{1.67}O_{0.83}$

Xylan (Aldrich)

The composition is as analyzed by the pregl type microcombution in Department of Chemical Engineering of McGill University.

Elemental Analysis, weight %

C	44.89
H	6.02
O	47.08

Elemental composition

$CH_{1.61}O_{0.79}$

Alkali Lignin (Sigma)

The composition is analyzed by the pregl type microcombution in Department of Chemical Engineering of McGill University.

Elemental Analysis, weight %

C	63.50
H	6.07
O	27.80

Elemental composition

$CH_{1.15}O_{0.33}$

Alcell Lignin (Repap)

The composition is analyzed by the pregl type microcombution in Department of Chemical Engineering of McGill University.

Elemental Analysis, weight %

C	67.42
H	6.44
O	27.64

Elemental composition

$CH_{1.15}O_{0.31}$

APPENDIX H

ANALYSIS METHODS

H.1 Solution analysis

Iodine in the aqueous phase

Molecular iodine in the aqueous phase was determined with a standard solution of sodium thiosulphate.

$$I_2 + 2\ S_2O_3^{2-} = S_4O_6^{2-} + 2\ I^- \tag{H.1}$$

A 20 ml aliquot of the 50 times diluted aqueous phase (2 ml), in a 250-ml Erlenmeyer flask, was titrated with 0.03 M $Na_2S_2O_3$ to determine the iodine content. Double determinations were made. The endpoint was established by means of a starch solution indicator.

The iodine concentration in the aqueous phase is

$$[I_2] = \frac{1}{2} \times \frac{100}{2} \times \frac{[Na_2S_2O_3]\ V_{Na_2S_2O_3}\ (ml)}{20\ (ml)}\ (M) \tag{H.2}$$

Total iodine in the aqueous phase

The total iodine and iodide content of the aqueous phase was titrated in the presence of a high concentration of hydrochloric acid, with a standard solution of potassium iodate.

$$IO_3^- + 2\ I^- + 6\ Cl^- + 6\ H^+ = 3\ ICl_2^- + 3\ H_2O \tag{H.3}$$

$$IO_3^- + 2\ I_2 + 10\ Cl^- + 6\ H^+ = 5\ ICl_2^- + 3\ H_2O \tag{H.4}$$

A 20 ml aliquot of the 50 times diluted aqueous phase (2 ml) was added to about 50 ml concentrated hydrochloric acid in a 250-Erlenmeyer flask. The resulting mixture was titrated with 0.075 M KIO_3. The endpoint is determined by the disappearance of the purple colour and the imparting of a yellowish colour by the p-ethoxychrysoidine (4-(ethoxyphenylazo)-m-phenylenediamine monohydrochloride) indicator. Double determinations were made. The iodide content of the aqueous phase was obtained by difference between the determination of total iodine and iodide and determination of iodine.

The total iodine concentration in the aqueous phase is

$$[I] = \frac{100}{2} \times \frac{[KIO_3]\ V_{KIO_3}\ (ml)}{20\ (ml)}\ (M) \tag{H.5}$$

H⁺ in the aqueous phase

A 20 ml aliquot of the 50 times diluted aqueous phase (2 ml) was alkalimetric analyzed with 0.15 N standard NaOH to determine H^+ concentration. The endpoint was determined with phenolphthalein indicator.

The H^+ concentration in the aqueous phase is

$$[H^+] = \frac{100}{2} \times \frac{[NaOH]\ V_{NaOH}\ (ml)}{20\ (ml)}\ (M) \tag{H.6}$$

HI concentration

The HI concentration was determined for H^+ in the HI solution by Equation H.6. The weight concentration of HI solution is

$$[HI] = \frac{[HI]\ (M)\ M_{HI}}{1000\ d(g/ml)} \times 100\ wt\% \qquad (H.7)$$

where d : density of HI solution, g/ml

[HI] (M) : molar concentration of HI solution, mol/l

M_{HI} : molecular weight of HI, 127.9 g/mol

H.2 Substrates and product analyses

Carbon, hydrogen and oxygen elemental analysis

Substrates and product fractions OP (or OA and ON) and AP were analyzed for carbon, hydrogen and oxygen by pregl type microcombustion, using the elemental analysis facility of the McGill Department of Chemical Engineering.

The standard chemical to determine C, H, O contents of organic compounds is acetanelide, of elemental composition 71.09 wt% C, 6.71 wt% H, and 11.84 wt% O. The measurement error is

C, wt%	H, wt%	O, wt%
±0.9	±0.07	±0.35

Iodine elemental analysis

The total iodine in the products was determined after oxygen flask combustion on the micro scale (Mazor, 1975). Hydrogen iodide and iodine vapour were dissolved as iodide ions and hypoiodite ions in alkaline (KOH) absorption solution.

$$I_2\ (g) + H_2O = OI^- + I^- + 2\ H^+ \qquad (H.8)$$

$$HI\ (g) = I^- + H^+ \qquad (H.9)$$

Hypoiodite ions were oxidized to iodate ions by bromine.

$$OI^- + 2\ Br_2 + 2\ H_2O = IO_3^- + 4\ Br^- + 4\ H^+ \qquad (H.10)$$

The iodine was liberated on addition of iodide (KI)

$$IO_3^- + 5\ I^- + 6\ H^+ = 3\ H_2O + 3\ I_2 \qquad (H.11)$$

The six-fold amount of iodine was titrated with standard sodium thiosulphate solution.

$$3\ I_2 + 6\ S_2O_3^{2-} = 3\ S_4O_6^{2-} + 6\ I^- \qquad (H.12)$$

An accurately weighed 5 -10 mg of the sample was placed on an L-shaped piece of ashless filter paper. Add 10 ml of water and 2 ml of 2 N potassium hydroxide solution to the 500 ml combustion flask as the absorption solution. Blow oxygen into flask for two minutes, then immediately ignite the top of filter paper and insert into combustion flask tightly. After burning, lubricate the ground-glass joint with union water. Complete absorption of hydrogen iodide and iodine by diffusion alone required 1 hr with shaking the flask.

When the gases had been completely absorbed, wash the collar of the flask, the joint, and the basket with 15 - 20 ml deionized water. Add 10 ml of buffer solution (10 g of potassium acetate in 100 ml of glacial acid) and 5 ml of saturated bromine water and allow to stand for 1 - 2 minutes with shaking. Dilute to about 50 ml and add 10 drops of formic acid for reduce excess bromine. Leave until the disappearance of the yellow colour of bromine.

Acidify the solution with 5 ml of 4 N sulphuric acid. Add 0.2 g of potassium iodide and immediately titrate the iodine liberated with standard 0.03 M sodium thiosulphate solution to a pale yellow colour. Add about 2 ml of starch solution and continue the titration to the disappearance of the blue colour.

The iodine content of product is

$$I,\ wt\% = \frac{1}{6} \times \frac{253.8 \times 10^{-3}\ [Na_2S_2O_3]\ (M)\ V_{Na_2S_2O_3}\ (ml)}{W_{sample}\ (g)} \times 100\% \qquad \text{(H.13)}$$

The standard chemical to determine organic iodine content is iodobenzic acid with 51.17 wt% I content. The measure error is ±1.0 wt%.

Methoxy groups

The content of methoxy groups present in wood was determined by the Zeisel method (Browning, 1967), in which the methoxy groups are converted to methyl iodide upon boiling with strong hydriodic acid

$$ROCH_3 + HI = ROH + CH_3I \qquad \text{(H.14)}$$

The volatile methyl iodide was swept from the reaction mixture and absorbed in an acetic acid solution containing potassium acetate and bromine. The iodine was oxidized to iodate according to the reaction

$$CH_3I + Br_2 = CH_3Br + IBr \qquad \text{(H.15)}$$

$$IBr + 2\ Br_2 + 3\ H_2O = HIO_3 + 5\ HBr \qquad \text{(H.16)}$$

The excess bromine was destroyed by addition of formic acid, and the iodate equivalent of the original methoxy content was determined by titration with standard sodium thiosulphate of the six fold amount of iodine liberated in the reaction.

$$HIO_3 + 5\ HI = 3\ I_2 + 3\ H_2O \qquad \text{(H.17)}$$

The methoxy group (CH_3O-) in hybrid poplar was determined to be 4.7% on the carbon basis in this laboratory.

APPENDIX I

EXPERIMENTAL DATA OF NONELECTROCHEMICAL LIQUEFACTION

I.1 Amount of charges

Run #	Substrate	Charge g	HI solution g	HI solution ml	HI g
36	xylan	5.522	259.2	152.0	147.3
37	xylan	2.882	189.3	110.8	107.5
38	cellulose	4.309	201.9	117.8	115.3
39	cellulose	3.493	234.0	137.4	132.7
56	hybrid poplar	7.216	300.1	204.0	132.8
57	hybrid poplar	7.559	391.4	266.3	169.4
59	hybrid poplar	3.841	287.8	226.8	86.4
60	hybrid poplar	1.577	248.8	224.1	36.5
62	Alcell lignin	7.513	332.6	192.1	189.5
63	Alcell lignin	8.460	304.8	176.1	174.2
64	Alcell lignin	13.297	330.8	193.7	188.9
65	xylan	8.596	247.7	145.0	141.2
66	xylan	10.356	243.9	142.8	138.8
67	xylan	16.500	266.2	156.0	151.7
68	xylan	6.636	234.2	137.5	133.3
72	hybrid poplar	14.453	423.6	233.1	262.4
73	hybrid poplar	24.678	205.3	134.0	125.8
74	hybrid poplar	31.499	237.1	119.4	162.0
75	hybrid poplar	17.865	268.8	134.8	184.3
76	hybrid poplar	15.716	177.4	88.9	121.6
77	hybrid poplar	8.508	142.8	79.3	87.1
78	hybrid poplar	6.075	239.2	139.7	137.4
79	hybrid poplar	7.357	231.3	134.6	133.3
80	hybrid poplar	9.773	254.0	147.7	145.9
81	hybrid poplar	14.961	266.5	155.1	154.5
82	hybrid poplar	4.356	217.9	126.7	126.4
83	cellulose	11.835	211.1	122.7	122.3
84	cellulose	8.404	201.2	117.3	115.7
85	cellulose	7.004	203.2	118.2	116.8
86	cellulose	4.762	171.9	100.5	98.9
87	hybrid poplar	2.336	271.1	158.4	156.2
89	Alkali lignin	10.856	255.9	149.4	145.7
90	Alkali lignin	6.689	226.0	132.3	129.1
91	Alkali lignin	6.272	261.7	152.8	148.1
92	Alkali lignin	4.674	242.2	142.3	136.4
93	Alkali lignin	2.649	250.4	146.3	142.4
94	Alkali lignin	2.727	181.8	132.3	103.4
95	Alcell lignin	4.242	235.7	138.0	133.6
96	Alcell lignin	2.066	146.4	85.7	83.0
97	Alcell lignin	1.672	167.2	94.5	95.7
98	hybrid poplar	3.965	287.3	168.1	162.7
99	hybrid poplar	7.039	280.7	164.9	159.2
101	hybrid poplar	12.677	506.9	296.4	286.9
105	cellulose	9.991	368.5	215.6	208.1

cellulose – oven dried for 2 h at 80°C, 0.12 wt% moisture
xylan – oven dried for 2 h at 80°C, 1.55 wt% moisture
h.p. – oven dried for 2 h at 80°C, 0.26 wt% moisture
Alkali – oven dried for 2 h at 80°C, 0.81 wt% moisture
Alcell – oven dried for 2 h at 80°C, 0.81 wt% of moisture

I.2 Experimental conditions

Run	[HI] wt%	[Substrate] wt%	Liquor/Substrate ml/g	R_w g/g	R mol/mol	Temperature* °C	Time min
36	56.9	2.1	27.5	27.2	5.7	126	15
37	56.8	1.5	38.5	38.0	8.0	125	15
38	57.1	2.1	27.3	26.9	5.7	124	15
39	56.7	1.5	39.3	38.2	8.0	126	15
56	44.3	2.4	28.3	18.5	3.6	114	15
57	43.3	1.9	35.2	22.5	4.4	114	15
59	30.0	1.3	59.0	22.7	4.4	106	15
60	14.3	0.6	142.2	22.7	4.4	102	15
62	57.0	2.3	25.6	25.5	3.6	119	15
63	57.2	2.8	20.8	20.8	2.9	117	15
64	57.1	4.0	14.6	14.3	2.0	117	15
65	57.0	3.5	16.9	16.7	3.5	122	15
66	56.9	4.3	13.8	13.6	2.9	120	15
67	57.0	6.2	9.5	9.4	2.0	116	15
68	57.0	2.8	20.7	20.4	4.3	122	15
72	61.9	3.4	16.1	18.2	3.5	123	15
73	61.3	12.0	4.6	5.1	1.0	104	15
74	68.3	13.3	3.8	5.2	1.0	102	15 (+5)
75	68.6	6.6	7.5	10.3	2.0	116	15 (+5)
76	68.5	8.9	5.7	7.8	1.5	109	15 (+5)
77	61.0	6.0	9.3	10.2	2.0	115	15
78	57.4	2.5	23.0	22.7	4.4	122	15
79	57.6	3.2	18.3	18.2	3.5	120	15
80	57.4	3.9	15.1	15.0	2.9	118	15
81	58.0	5.6	10.4	10.4	2.0	113	15
82	58.0	2.0	29.1	29.2	5.7	123	15
83	58.0	5.6	10.4	10.4	2.0	117	15
84	57.5	4.2	14.0	13.9	2.9	118	15
85	57.5	3.5	16.9	16.7	3.5	120	15
86	57.5	2.8	21.1	20.8	4.4	122	15
87	57.6	0.9	67.8	67.2	13.0	126	15
89	57.0	4.2	13.8	13.6	2.0	120	15
90	57.1	3.0	19.8	19.5	2.9	122	15
91	56.6	2.4	24.4	23.9	3.6	123	15
92	56.3	1.9	30.4	29.5	4.4	125	15
93	56.9	1.1	55.3	54.4	8.1	126	15
94	56.9	1.5	39.1	38.4	5.7	125	15
95	56.7	1.8	32.5	31.9	4.5	125	15
96	56.7	1.4	40.9	40.2	5.6	125	15
97	57.2	1.0	58.6	58.0	8.1	126	15
98	56.6	1.4	42.4	41.3	8.0	126	15
99	56.7	2.5	23.4	22.7	4.4	123	15
101	56.6	2.5	23.4	22.7	4.4	124	2
105	56.5	2.7	21.6	20.9	4.0	123	15

* reaction temperature at end of reaction time

I.3 HI and I_2 concentration in the aqueous phase and stoichiometric coefficients

Run	Before Reaction				After Reaction					Stoichiometric Values		
#	HI Sol. ml	[HI] wt%	[HI] M	[I_2] M	HI Sol. ml	[HI] wt%	[HI] M	[I_2] M	Δ[HI] wt%	a	c	X_{HI} %
36	152.0	56.9	7.55	0.06	154.8	50.0	6.11	0.63	6.9	1.00	0.44	17.5
37	110.8	56.8	7.53	0.06	112.8	51.8	6.47	0.51	5.0	0.99	0.48	12.5
38	117.8	57.1	7.60	0.04	119.2	49.8	6.07	0.71	7.3	1.08	0.50	19.1
39	137.4	56.7	7.51	0.05	137.9	51.7	6.45	0.55	5.0	1.11	0.54	13.8
56	204.0	44.3	5.09	0.02								
57	266.2	43.3	4.98	0.018	269.3	42.1	4.72	0.12	1.1	0.18	0.09	4.1
59	226.8	30.0	2.98	0.01	227.5	29.9	2.97	0.01	0.1	0.00	0.0	0.0
60	224.1	14.3	1.24	0.00	224.1	14.3	1.24	0.00	0.0	0.00	0.0	0.0
62	192.0	57.6	7.71	0.05	195.6	55.8	7.30	0.16	1.8	0.13	0.05	3.5
63	176.1	57.7	7.74	0.05	178.8	55.3	7.21	0.16	2.4	0.16	0.04	5.4
64	193.7	57.2	7.63	0.03	194.7	54.1	6.95	0.12	3.1	0.17	0.02	8.4
65	145.0	57.0	7.58	0.03	148.8	47.3	5.61	0.83	9.4	0.84	0.38	24.0
66	142.8	56.9	7.56	0.03	146.8	45.4	5.27	0.97	11.5	0.80	0.36	28.2
67	156.0	57.0	7.58	0.03	162.0	42.3	4.75	1.12	14.7	0.68	0.29	34.8
68	137.5	56.9	7.56	0.03	140.4	48.6	5.85	0.73	8.5	0.83	0.38	19.5
72	233.1	61.9	8.79	0.015	245.7	52.5	6.60	0.88	9.5	0.74	0.37	21.0
73	113.9	61.3	8.62	0.015	117.4	41.8	4.67	1.35	19.5	0.44	0.16	44.4
74	119.4	68.3	10.63	0.015	122.7	44.0	5.03	1.98	24.3	0.52	0.19	51.8
75	134.7	68.6	10.70	0.015	137.7	49.5	6.02	1.78	19.1	0.86	0.34	42.7
76	88.9	68.5	10.69	0.015	90.4	45.5	5.28	1.97	23.0	0.75	0.28	50.0
77	79.3	61.0	8.54	0.026	80.6	46.4	5.44	1.19	14.6	0.70	0.27	35.3
78	139.7	57.4	7.68	0.03	142.1	51.1	6.32	0.60	6.3	0.72	0.33	16.4
79	134.6	57.6	7.72	0.015	137.7	49.6	6.04	0.68	8.0	0.70	0.31	20.0
80	147.7	57.4	7.68	0.016	150.3	48.6	5.85	0.77	8.8	0.65	0.29	22.5
81	155.1	58.0	7.81	0.017	159.3	45.1	5.21	0.91	12.9	0.64	0.24	31.7
82	126.7	58.0	7.81	0.015	129.1	51.1	6.53	0.48	6.9	0.84	0.35	14.9
83	122.7	57.9	7.80	0.015	128.5	42.6	4.80	1.19	15.3	0.78	0.35	35.7
84	117.3	57.5	7.70	0.017	121.5	44.8	5.17	1.09	12.7	0.90	0.43	30.5
85	118.2	57.5	7.69	0.018	121.7	46.1	5.40	0.98	11.3	0.98	0.45	27.7
86	100.5	57.5	7.70	0.02	101.7	48.6	5.85	0.86	8.9	1.02	0.49	23.2
87	158.4	57.6	7.72	0.02	159.9	55.1	7.16	0.26	2.5	0.83	0.41	6.4
89	149.4	57.0	7.57	0.05	148.6	53.6	6.84	0.19	3.3	0.20	0.04	10.0
90	132.2	57.1	7.61	0.03	130.4	55.6	7.27	0.12	1.5	0.17	0.03	5.8
91	152.8	56.6	7.49	0.05	152.9	55.1	7.16	0.14	1.5	0.15	0.04	4.3
92	142.3	56.3	7.43	0.05	142.1	55.4	7.23	0.15	0.9	0.12	0.06	2.8
93	146.3	56.9	7.55	0.06	147.9	55.3	7.20	0.13	1.6	0.29	0.08	3.6
94	106.8	57.1	7.58	0.06	108.7	55.1	7.15	0.17	2.0	0.22	0.09	3.9
95	138.0	56.7	7.51	0.05	138.0	54.4	7.00	0.16	2.3	0.30	0.06	6.7
96	85.7	56.7	7.51	0.05	86.0	54.7	7.06	0.17	2.0	0.31	0.09	5.6
97	98.0	57.2	7.63	0.03	97.9	56.0	7.35	0.13	1.2	0.30	0.11	3.8
98	168.1	56.6	7.50	0.05	169.0	53.2	6.75	0.39	3.5	0.76	0.36	9.5
99	164.9	56.7	7.52	0.052	166.7	51.0	6.31	0.60	5.7	0.67	0.33	15.2
101	296.4	56.6	7.49	0.051	303.3	50.7	6.25	0.54	5.9	0.64	0.29	14.5
105	215.6	56.5	7.46	0.071	225.7	46.1	5.39	0.83	10.5	0.98	0.43	10.4

I.4 Amount of substrate and products

RUN	SUBSTRATE		PRODUCT		
#	species	amount*(g)	fraction	weight(g)	Yield,$Y_{C/j}$
36	xylan	5.425	OA	3.817	77.3
			ON	0	0
37	xylan	2.830	OA	1.864	72.7
			ON	0.007	0.2
38	cellulose	4.292	OA	2.640	64.3
			ON	0.028	0.7
39	cellulose	3.472	OA	1.760	54.4
			ON	0.023	0.7
56	h.p.	7.180	OA	1.156	16.6
			ON	3.454	51.8
57	h.p.	7.521	OA	1.345	19.3
			ON	3.001	41.7
59	h.p.	3.814	OA	0.465	11.4
			ON	1.893	49.8
60	h.p.	1.572	OA	0.042	2.6
			ON	0.883	55.6
62	Alcell	7.437	OP	6.783	74.1
63	Alcell	8.377	OP	8.424	82.2
64	Alcell	13.173	OP	16.793	97.0
65	Xylan	8.451	OA	6.528	77.4
			ON	0.352	5.9
66	Xylan	10.183	OA	8.429	70.5
			ON	0.996	13.8
67	Xylan	16.232	OA	12.104	57.4
			ON	3.292	28.1
68	Xylan	6.522	OA	5.047	79.1
			ON	0.101	2.3
72	h.p.	14.399	OA	12.758	91.1
			ON	0.021	0.1
73	h.p.	24.576	OA	20.535	71.3
			ON	6.747	33.2
74	h.p.	31.417	OA	25.914	81.8
			ON	6.284	22.8
75	h.p.	17.819	OA	18.832	99.7
			ON	0.060	0.3
76	h.p.	15.675	OA	16.403	95.7
			ON	1.491	12.5
77	h.p.	8.547	OA	7.629	86.5
			ON	0.659	7.7
78	h.p.	6.044	OA	4.861	82.6
			ON	0.031	0.7
79	h.p.	7.322	OA	6.791	89.4
			ON	0.088	1.6
80	h.p.	9.731	OA	10.215	87.2
			ON	0.596	8.1
81	h.p.	14.900	OA	13.372	77.7
			ON	2.448	21.4
82	h.p.	4.332	OA	3.067	74.4
			ON	0.038	0.9
83	Cellulose	11.803	OA	10.810	88.1
			ON	1.032	10.1
84	Cellulose	8.290	OA	7.856	86.5
			ON	0.194	3.2
85	Cellulose	6.981	OA	6.253	84.5
			ON	0.118	2.4
86	Cellulose	4.744	OA	3.333	72.2
			ON	0.026	0.5
87	h.p.	2.322	OA	1.301	61.1
			ON	0	
89	Alkali	10.754	OP	16.155	97.6
			ON	2.656	24.4

90	Alkali	6.623	OP	10.719	94.6
			ON	1.493	21.8
91	Alkali	6.208	OP	9.724	89.7
			ON	1.619	25.7
92	Alkali	4.623	OP	6.339	87.7
			ON	1.314	27.6
93	Alkali	2.618	OP	2.481	73.0
			ON	0.242	8.9
94	Alkali	2.695	OP	2.733	79.0
			ON	0.053	19.0
95	Alcell	4.194	OP	4.409	73.2
96	Alcell	2.066	OP	1.929	66.7
97	Alcell	1.649	OP	1.325	62.2
98	h.p.	3.938	OA	2.715	70.1
			ON	0	0
99	h.p.	7.002	AP	1.007	15.9
105	Cellulose	9.962	AP	2.285	29.2

Notes :

h.p. : Hybrid poplar
* : Moisture-free basis

I.5 Elemental composition of product fractions ($Z_{i/j}$)

Run	Product fraction	Elemental content, wt%					Elemental composition			Hydrogen retention	Oxygen removal
#	(j)	C	H	O	I	Total	H/C	O/C	I/C	%	%
36	OA	49.35	5.57	6.25	44.89	106.06	1.36	0.095	0.086	84.2	88.0
	OP	33.56	3.93	4.83	54.82	97.14	1.41	0.108	0.155	87.4	86.4
37	OA	49.56	5.62	5.34	43.42	103.94	1.36	0.081	0.083	84.6	89.8
	OP	34.10	4.20	4.40	55.92	98.62	1.48	0.097	0.155	91.9	87.7
38	OA	46.48	5.26	5.51	42.83	100.08	1.36	0.089	0.087	81.4	89.3
39	OA	47.74	5.54	5.20	42.31	100.79	1.39	0.082	0.084	83.5	90.1
56	OA	49.84	4.82	16.54	27.52	98.72	1.16	0.249	0.052	73.0	64.4
	ON	51.92	6.08	36.65	2.46	97.11	1.41	0.530	0.0045	88.5	24.3
	OP	50.69	5.54	30.77	12.18	99.18	1.31	0.456	0.023	82.6	34.9
57	OA	52.00	4.97	16.42	26.48	99.87	1.15	0.237	0.048	72.2	66.1
	ON	50.42	6.01	36.37	2.31	95.11	1.43	0.541	0.0043	90.0	22.6
	OP	48.49	4.94	31.53	10.70	95.66	1.22	0.488	0.021	77.0	30.3
59	OA	45.04	4.68	15.06	40.59	105.37	1.25	0.251	0.085	78.5	64.1
	ON	48.32	6.32	41.10	2.41	98.15	1.46	0.638	0.0047	91.9	8.8
	OP	43.35	5.43	35.58	14.19	98.55	1.50	0.616	0.031	94.6	12.0
60	OA	46.93	5.77	18.31	34.76	105.77	1.48	0.293	0.071	92.9	58.2
	ON	47.70	6.12	41.62	1.61	97.05	1.54	0.655	0.0032	96.9	6.4
	OP	47.69	6.18	41.00	3.61	98.48	1.56	0.645	0.0072	97.9	7.8
62	OP	54.74	4.74	19.22	21.30	100.00	1.04	0.264	0.037	90.4	15.0
63	OP	55.13	4.77	17.00	23.10	100.00	1.04	0.231	0.040	90.4	25.3
64	OP	51.30	4.61	20.22	24.14	100.27	1.08	0.296	0.045	93.8	4.6
65	OA	44.98	5.06	8.91	45.16	104.11	1.35	0.149	0.095	83.9	81.2
	ON	63.41	5.99	10.51	20.66	100.57	1.13	0.124	0.031	70.5	84.3
66	OA	38.23	4.29	6.11	48.72	97.35	1.35	0.120	0.121	83.7	84.8
	ON	63.41	5.99	11.56	18.51	99.47	1.13	0.137	0.028	70.5	82.7
	OP	33.40	3.63	6.13	55.15	98.31	1.31	0.138	0.156	81.1	82.6
67	OA	34.55	4.13	5.87	50.51	95.06	1.44	0.128	0.138	89.2	83.9
	ON	62.13	5.53	12.89	17.64	98.19	1.07	0.156	0.027	66.4	80.3
	OP	31.49	3.27	7.59	52.80	95.15	1.25	0.181	0.159	77.5	77.1
68	OA	45.87	5.01	5.51	44.43	100.82	1.31	0.090	0.092	81.5	88.6
	ON	65.33	6.07	9.32	18.88	99.60	1.12	0.107	0.027	69.3	86.4
	OP	32.89	3.70	5.99	54.72	97.30	1.35	0.137	0.158	83.9	82.7
72	OA	49.56	5.65	6.61	39.26	101.08	1.37	0.100	0.075	86.1	85.7
	OP	38.18	3.98	9.22	56.39	107.77	1.25	0.181	0.140	78.7	74.1
73	OA	41.13	4.66	8.77	45.61	100.17	1.36	0.160	0.105	85.6	77.1
	ON	58.31	5.68	16.66	18.91	99.56	1.17	0.214	0.031	73.6	69.4
	OP	38.67	3.80	11.84	52.91	107.22	1.18	0.230	0.130	74.2	67.2
74	OA	47.80	5.53	7.35	45.39	106.07	1.39	0.115	0.109	87.4	83.5
	ON	54.93	5.55	17.84	22.82	101.14	1.21	0.244	0.039	76.3	65.2
	OP	30.95	2.90	7.35	64.13	105.33	1.13	0.178	0.196	70.8	74.5
75	OA	45.47	5.11	7.40	48.50	106.48	1.35	0.122	0.101	84.9	82.5
	OP	29.65	3.41	6.53	66.26	105.85	1.38	0.165	0.211	86.9	76.4
76	OA	44.08	4.81	7.18	48.95	105.02	1.31	0.122	0.105	82.4	82.5
	ON	63.43	5.24	12.10	23.44	104.21	0.99	0.143	0.035	62.4	79.5
	OP	28.75	2.89	6.70	64.96	103.30	1.21	0.175	0.214	75.9	75.0
77	OA	46.71	4.98	9.51	46.65	107.85	1.28	0.153	0.094	80.5	78.2
	OP	32.60	3.03	7.71	58.55	101.89	1.12	0.178	0.170	70.2	74.6
78	OA	49.50	5.38	9.63	38.94	103.45	1.31	0.146	0.075	82.1	79.1
	OP	37.83	3.64	8.11	49.54	99.12	1.16	0.161	0.124	73.0	77.0
79	OA	46.46	5.06	10.18	41.25	102.95	1.31	0.164	0.084	82.3	76.5
	ON	63.45	5.65	16.60	13.41	99.11	1.07	0.196	0.020	67.3	71.9
	OP	36.31	3.35	8.34	51.69	99.69	1.11	0.172	0.135	69.7	75.4
80	OA	40.04	4.61	8.74	46.80	100.19	1.38	0.164	0.111	87.0	76.6
	ON	64.05	5.78	16.40	13.06	99.29	1.08	0.192	0.019	68.2	72.5
	OP	36.10	3.28	8.51	54.68	102.57	1.09	0.177	0.143	68.6	74.7
81	OA	41.73	5.03	7.17	45.22	99.15	1.45	0.129	0.103	91.0	81.6
	ON	62.91	5.29	16.54	21.23	105.97	1.01	0.197	0.032	63.5	71.8
	OP	30.95	2.69	7.52	55.32	96.48	1.04	0.182	0.169	65.7	73.9
82	OA	50.65	5.56	9.42	38.16	103.79	1.32	0.140	0.071	76.0	74.6
	OP	41.25	4.24	9.08	45.61	100.18	1.23	0.165	0.105	73.9	80.1
83	OA	42.76	5.32	7.55	44.51	100.14	1.49	0.133	0.099	89.5	84.0
	ON	51.51	5.37	14.12	24.63	95.63	1.25	0.206	0.045	75.0	75.2
	OP	27.22	3.26	6.55	64.11	101.14	1.44	0.181	0.223	86.1	78.2

84	OA	40.56	4.89	7.17	48.75	101.37	1.45	0.133	0.114	86.7	84.0
	ON	61.29	5.81	7.75	27.83	102.68	1.14	0.095	0.043	68.2	88.6
	OP	28.20	3.35	6.15	63.10	100.80	1.43	0.164	0.212	85.4	80.3
85	OA	41.93	5.03	6.37	48.50	101.83	1.44	0.114	0.110	86.3	86.3
	ON	62.27	5.88	7.81	25.25	101.21	1.13	0.094	0.038	67.9	88.7
86	OA	45.72	5.31	6.08	44.43	101.54	1.39	0.100	0.092	83.5	88.0
	OP	30.62	3.81	5.81	61.68	101.92	1.49	0.142	0.191	89.5	82.8
87	OA	52.55	5.65	8.80	38.85	105.85	1.29	0.126	0.070	81.2	82.0
89	OP	41.25	3.89	14.25	38.28	97.67	1.13	0.259	0.088	98.5	21.4
	ON	62.67	5.92	19.70	9.49	97.06	1.00	0.236	0.014	86.7	28.5
90	OP	37.12	3.70	13.21	44.45	98.48	1.20	0.267	0.113	100	19.1
	ON	61.45	5.77	21.11	9.80	98.13	1.13	0.258	0.015	98.1	21.4
91	OP	36.35	3.60	13.01	44.27	97.23	1.19	0.269	0.115	100	18.6
	ON	62.60	5.91	21.97	7.22	97.70	1.13	0.263	0.011	98.6	20.2
92	OP	40.63	3.70	14.51	38.17	97.01	1.09	0.268	0.089	95.1	18.8
	ON	61.66	5.81	21.30	11.72	100.49	1.13	0.259	0.018	98.4	21.4
93	OP	48.92	4.49	16.08	29.94	99.43	1.10	0.247	0.058	95.9	25.2
	ON	60.92	5.45	21.19	11.19	98.75	1.07	0.261	0.017	93.4	20.9
94	OP	49.47	4.53	16.14	28.25	98.35	1.11	0.245	0.054	95.6	25.8
95	OP	46.96	4.58	15.25	32.68	99.47	1.17	0.244	0.066	100	21.4
96	OP	48.16	4.55	15.69	31.00	99.40	1.13	0.245	0.061	98.7	21.1
97	OP	52.19	4.93	16.54	26.68	100.34	1.13	0.238	0.048	98.7	23.3
98	OA	49.00	5.37	9.35	36.84	97.56	1.32	0.143	0.071	82.8	79.5
	OP	37.87	3.81	8.96	49.64	100.28	1.21	0.178	0.124	76.0	74.6
99	OA	52.72	5.66	9.72	33.16	101.26	1.30	0.138	0.060	81.1	80.2
	OP	38.05	3.65	8.61	50.03	100.34	1.15	0.170	0.124	72.5	75.7
	AP	53.34	6.97	14.51	23.45	98.27	1.57	0.204	0.042	98.7	70.8
105	AP	56.68	7.67	18.27	15.86	98.48	1.63	0.242	0.027	97.3	70.8

I.6 Iodine balance in aqueous HI solution

Run	Before Reaction			After Reaction			Iodine Balance
No.	Iodine amount			Iodine amount			in
	as HI	as I_2	Total	as HI	as I_2	Total	aqueous HI
	g	g	g	g	g	g	%
36	145.6	2.3	147.9	120.0	24.8	144.8	97.9
37	105.9	1.7	107.6	92.6	14.6	107.2	99.6
38	113.6	1.2	114.8	91.8	21.5	113.3	98.7
39	130.9	1.7	132.7	112.9	19.2	132.1	99.6
41	152.4	0.4	152.8	117.8	31.0	148.8	97.4
42	175.5	0.5	176.0	145.9	26.2	172.1	97.8
43	178.0	0.5	178.5	151.8	22.8	174.7	97.9
44	176.0	0.5	176.5	149.1	25.2	174.4	98.8
45	180.3	1.0	181.3	142.6	30.7	173.3	95.6
46	178.3	0.5	178.8	142.3	30.2	172.5	96.5
47	181.6	2.0	183.7	148.1	30.2	178.3	97.1
48	179.5	1.0	180.5	147.8	28.5	176.2	97.7
52	199.5	0.6	200.1	188.1	11.8	199.9	99.9
56	131.8	1.0	132.8				
57	168.3	1.2	169.5	161.3	8.2	169.5	100.0
59	85.8	0.5	86.3	85.7	0.6	86.3	100.0
60	35.3	0.0	35.3	35.3	0.0	35.3	100.0
62	187.9	2.4	190.3	181.2	7.9	189.1	99.4
63	172.9	2.2	175.2	163.6	7.3	170.8	97.5
64	187.5	1.5	189.0	171.7	5.9	177.6	94.0
65	139.5	1.1	140.6	105.9	31.3	137.3	97.6
66	137.0	1.1	138.1	98.2	36.1	134.3	97.3
67	150.1	1.2	151.3	97.6	46.0	143.7	95.0
68	131.9	1.0	133.0	104.2	26.0	130.2	97.9
73	124.7	0.4	125.1	69.6	40.2	109.8	87.7
74	161.1	0.5	161.5	78.3	61.7	140.0	86.7
75	182.9	0.5	183.5	105.2	62.2	167.4	91.2
76	120.6	0.3	121.0	60.6	45.2	105.8	87.4
77	86.0	0.5	86.5	55.6	24.3	80.0	92.5
78	136.2	1.1	137.2	114.0	21.6	135.6	98.8
79	131.8	0.5	132.3	105.5	23.8	129.3	97.7
80	143.9	0.6	144.5	111.6	29.4	140.9	97.5
81	153.7	0.7	154.4	105.3	36.8	142.1	92.1
82	125.6	0.5	126.0	107.0	15.7	122.7	97.4
83	121.4	0.5	121.9	78.3	38.8	117.1	96.1
84	114.6	0.5	115.1	79.7	33.6	113.3	98.4
85	115.4	0.5	115.9	83.4	30.3	113.6	98.0
86	98.2	0.5	98.7	75.5	22.5	97.7	99.0
87	155.1	0.8	155.9	145.3	10.6	155.8	99.9
89	143.5	1.9	145.4	129.0	7.2	136.1	93.6
90	127.7	0.9	128.6	120.3	4.0	124.3	96.7
91	145.3	1.9	147.2	138.9	5.4	144.4	98.1
92	134.1	1.8	136.0	130.4	5.4	135.8	99.9
93	140.2	2.1	142.3	135.1	4.9	140.0	98.4
94	102.7	1.5	104.2	98.6	4.7	103.3	99.2
95	131.5	1.9	133.4	122.6	5.6	128.2	96.1
96	81.7	1.2	82.8	77.0	3.7	80.8	97.5
97	94.9	0.7	95.6	91.3	3.2	94.5	98.9
98	160.0	2.1	162.1	144.8	16.7	161.5	99.6
99	157.4	2.2	159.6	133.5	25.4	158.9	99.6
101	281.7	3.8	285.6	240.6	41.6	282.2	98.8
105	204.1	3.9	208.0	154.3	47.5	201.9	97.0

APPENDIX J
TYPICAL INVESTIGATION OF NONELECTROCHEMICAL LIQUEFACTION

J.1 Effect on wood liquefaction of initial HI concentration: 14 – 68 wt%

Reaction Conditions

Reaction Time, min	15		15	15			15			15			
HI/Wood Ratio, R	1.0		1.5	2.0			3.5			4.4			
Experiment No.	73	74	76	81	77	75	56	79	72	60	59	57	78
Initial [HI], wt%	61.3	68.3	68.5	58.0	61.0	68.6	44.3	57.6	61.9	14.3	30.0	43.3	57.4
Initial [Wood], wt%	12.0	13.3	8.9	5.6	6.0	6.6	2.4	3.2	3.4	0.6	1.3	1.9	2.5
Liquor/Wood, ml/g	4.6	3.8	5.7	10.4	9.3	7.5	28.3	18.3	16.1	142.1	59.0	35.2	23.0
Initial Temperature, °C	112	20	20	126	112	20	114	126	112	102	106	114	126
Final Temperature, °C	104	102	109	113	115	116	114	120	123	102	106	114	122

Reaction Stoichiometry

HI/Wood Ratio, R	1.0		1.5	2.0			3.5			4.4			
Experiment No.	73	74	76	81	77	75	56	79	72	60	59	57	78
a mol HI reacted/mol C	0.44	0.52	0.75	0.64	0.70	0.86		0.70	0.74	0.00	0.00	0.18	0.72
c mol I_2 produced/mol C	0.16	0.19	0.28	0.24	0.27	0.34		0.31	0.37	0.00	0.00	0.09	0.33
I Balance in solution, %	87.7	86.7	87.4	92.1	92.5	91.2		97.7		100	100	100	98.8
X_{HI}, % (HI Conversion)	44.4	51.8	50.0	31.7	35.3	42.7		20.0	21.0	0.01	0.02	4.1	16.4
Initial [HI], wt%	61.3	68.3	68.5	58.0	61.0	68.6	44.3	57.6	61.9	14.3	30.0	43.3	57.4
Final [HI], wt%	41.8	44.0	45.5	45.1	46.4	49.5		49.6	52.5	14.3	29.9	42.1	51.1
Drop [HI], wt%	19.5	24.3	23.0	12.9	14.6	19.1		8.0	9.4	0	0.1	1.1	6.3
Initial [I_2], M	0.015	0.015	0.015	0.017	0.026	0.015	0.02	0.015	0.015	0.00	0.01	0.018	0.03
Final [I_2], M	1.35	1.98	1.97	0.91	1.19	1.78		0.68	0.88	0.00	0.01	0.12	0.60

Yields

HI/Wood Ratio, R	1.0		1.5	2.0			3.5			4.4			
Experiment No.	73	74	76	81	77	75	56	79	72	60	59	57	78
Initial [HI], wt%	61.3	68.3	68.5	58.0	61.0	68.6	44.3	57.6	61.9	14.3	30.0	43.3	57.4
Y_{CON}, %	33.2	22.8	12.5	21.4	7.7	0.3	51.8	1.6	0.1	55.6	49.8	41.7	0.7
Y_{COA}, %	71.3	81.8	95.7	77.7	86.5	99.7	16.6	89.4	91.1	2.6	11.4	19.3	82.6
$Y_{C/OP}$, %	100	100	100	99.1	94.2	100	68.4	91.0	91.2	58.2	61.2	61.0	83.3
$Y_{C/AP}$, %	0	0	0	0.9	5.8	0	31.6	9.0	8.8	41.8	38.8	39.0	16.7

Elemental Analyses

HI/Wood Ratio, R	1.0		1.5	2.0			3.5			4.4			
Experiment No.	73	74	76	81	77	75	56	79	72	60	59	57	78
Initial [HI], wt%	61.3	68.3	68.5	58.0	61.0	68.6	44.3	57.6	61.9	14.3	30.0	43.3	57.4
OA Elemental Comp.													
C, %	41.13	47.80	44.08	41.73	46.71	45.47	49.84	46.46	49.56	46.93	45.04	52.00	49.50
H, %	4.66	5.53	4.81	5.03	4.98	5.11	4.82	5.06	5.65	5.77	4.68	4.97	5.38
O, %	8.77	7.35	7.18	7.17	9.51	7.40	16.54	10.18	6.61	18.31	15.06	16.42	9.63
I, %	45.61	45.39	48.95	45.22	46.65	48.50	27.52	41.25	39.26	34.76	40.59	26.48	38.94
H/C	1.36	1.39	1.31	1.45	1.28	1.35	1.16	1.31	1.37	1.48	1.25	1.15	1.31
O/C	0.160	0.115	0.122	0.129	0.153	0.122	0.249	0.164	0.100	0.293	0.251	0.237	0.146
I/C	0.105	0.090	0.105	0.103	0.095	0.101	0.052	0.084	0.075	0.071	0.085	0.048	0.075
Hydrogen Retention,%	85.6	87.4	82.4	91.0	80.5	84.9	73.0	82.3	86.1	92.9	78.5	72.2	82.1
Oxygen Removal,%	77.1	83.5	82.5	81.6	78.2	82.5	64.4	76.5	85.7	58.2	64.1	66.1	79.1
ON Elemental Comp.													
C, %	58.31	54.93	63.43	62.91			51.92	63.45		47.70	48.32	50.42	
H, %	5.68	5.55	5.24	5.29			6.08	5.65		6.12	5.88	6.01	
O, %	16.66	17.84	12.10	16.54			36.65	16.60		41.62	41.10	36.37	
I, %	18.91	22.82	23.44	21.23			2.46	13.41		1.61	2.41	2.31	
H/C	1.17	1.21	0.99	1.01			1.41	1.07		1.54	1.46	1.43	
O/C	0.214	0.244	0.143	0.197			0.530	0.196		0.655	0.638	0.541	
I/C	0.031	0.039	0.035	0.032			0.005	0.020		0.003	0.005	0.004	
Hydrogen Retention,%	73.6	76.3	62.4	63.5			88.5	67.3		96.9	91.9	90.0	
Oxygen Removal, %	69.4	65.2	79.5	71.8			24.3	71.9		6.4	8.8	22.6	
OP Elemental Comp.													
C, %	38.67	30.95	28.75	30.95	32.60	29.65	50.69	36.31	38.18	47.69	43.35	48.49	37.83
H, %	3.80	2.90	2.89	2.69	3.03	3.41	5.54	3.35	3.98	6.18	5.43	4.94	3.46
O, %	11.84	7.35	6.70	7.52	7.71	6.53	30.77	8.34	9.22	41.00	35.58	31.53	8.11
I, %	52.91	64.13	64.96	55.32	58.55	66.26	12.18	51.69	56.39	3.61	14.19	10.70	49.54
H/C	1.18	1.13	1.21	1.04	1.12	1.38	1.31	1.11	1.25	1.56	1.50	1.22	1.16
O/C	0.230	0.178	0.175	0.182	0.178	0.165	0.456	0.172	0.181	0.645	0.616	0.488	0.161
I/C	0.130	0.196	0.214	0.169	0.170	0.211	0.023	0.135	0.140	0.007	0.031	0.021	0.124
Hydrogen Retention,%	74.2	70.8	75.9	65.7	70.2	86.9	82.6	69.7	78.7	97.9	94.6	77.0	73.0
Oxygen Removal, %	67.2	74.5	75.0	73.9	74.6	76.4	34.9	75.4	74.1	7.8	12.0	30.3	77.0

J.2 Effect on wood liquefaction of initial HI concentration: 57 – 68 wt%

Reaction Conditions

Reaction Time, min	15							15			15		
Initial [HI], wt%	57							61			68		
Experiment No.	81	80	79	78	82	98	87	73	77	72	74	76	75
HI/Wood Ratio, R	2.0	2.9	3.5	4.4	5.7	8.0	13.0	1.0	2.0	3.5	1.0	1.5	2.0
Initial [Wood], wt%	5.6	3.9	3.2	2.5	2.0	1.4	0.9	12.0	6.0	3.4	13.3	8.9	6.6
Liquor/Wood, ml/g	10.4	15.1	18.3	23.0	29.1	42.4	67.8	4.62	9.28	16.1	3.79	5.66	7.54
Initial Temperature, °C	126	126	126	126	126	126	126	112	112	112	20	20	20
Final Temperature, °C	113	118	120	122	123	126	126	104	115	123	102	109	116

Reaction Stoichiometry

Initial [HI], wt%	57							61			68		
HI/Wood Ratio, R	2.0	2.9	3.5	4.4	5.7	8.0	13.0	1.0	2.0	3.5	1.0	1.5	2.0
Experiment No.	81	80	79	78	82	98	87	73	77	72	74	76	75
a mol HI reacted/mol C	0.64	0.65	0.71	0.72	0.84	0.76	0.83	0.44	0.70	0.74	0.52	0.75	0.86
c mol I_2 produced/mol C	0.24	0.29	0.31	0.33	0.35	0.36	0.41	0.16	0.27	0.37	0.19	0.28	0.34
I Balance in solution, %	92.1	97.5	97.7	98.8	97.4	99.6	99.9	87.7	92.5		86.7	87.4	91.2
X_{HI}, % (HI Conversion)	31.7	22.5	20.0	16.4	14.9	9.5	6.4	44.4	35.3	21.0	51.8	50.0	42.7
Initial [HI], wt%	58.0	57.4	57.6	57.4	58.0	56.6	57.6	61.3	61.0	61.9	68.3	68.5	68.6
Final [HI], wt%	45.1	48.6	49.6	51.1	51.1	53.2	55.1	41.8	46.4	52.5	44.0	45.5	49.5
Drop [HI], wt%	12.9	8.8	8.0	6.3	6.9	3.5	2.5	19.5	14.6	9.4	24.3	23.0	19.1
Initial [I_2], M	0.017	0.016	0.015	0.03	0.015	0.05	0.02	0.015	0.026	0.015	0.015	0.015	0.01
Final [I_2], M	0.91	0.77	0.68	0.60	0.48	0.39	0.26	1.35	1.19	0.88	1.98	1.97	1.78

Yields

Initial [HI], wt%	57							61			68		
HI/Wood Ratio, R	2.0	2.9	3.5	4.4	5.7	8.0	13.0	1.0	2.0	3.5	1.0	1.5	2.0
Experiment No.	81	80	79	78	82	98	87	73	77	72	74	76	75
$Y_{C/ON}$, %	21.4	8.1	1.6	0.7	0.9	0	0	33.2	7.7	0.1	22.8	12.5	0.3
$Y_{C/OA}$, %	77.7	87.2	88.4	82.6	74.4	70.1	61.1	71.3	86.5	91.1	81.8	95.7	99.7
$Y_{C/OP}$, %	99.1	95.3	91.0	83.3	75.3	70.1	61.1	100	94.2	91.2	100	100	100
$Y_{C/AP}$, %	0.9	4.7	9.0	16.7	24.7	29.9	38.9	0	5.8	8.8	0	0	0

Elemental Analyses

Initial [HI], wt%	57							61			68		
HI/Wood Ratio, R	2.0	2.9	3.5	4.4	5.7	8.0	13.0	1.0	2.0	3.5	1.0	1.5	2.0
Experiment No.	81	80	79	78	82	98	87	73	77	72	74	76	75
OA Elemental Composition													
C, %	41.73	40.04	46.46	49.50	50.65	49.00	52.55	41.13	46.71	49.56	47.80	44.08	45.47
H, %	5.03	4.61	5.06	5.38	5.56	5.37	5.65	4.66	4.98	5.65	5.53	4.81	5.11
O, %	7.17	8.74	10.18	9.63	9.42	9.35	8.80	8.77	9.51	6.61	7.35	7.18	7.40
I, %	45.22	46.80	41.25	38.94	38.16	36.84	38.85	45.61	46.65	39.26	45.39	48.95	48.50
H/C	1.45	1.38	1.31	1.31	1.32	1.32	1.29	1.36	1.28	1.37	1.39	1.31	1.35
O/C	0.129	0.164	0.164	0.146	0.140	0.143	0.126	0.160	0.153	0.100	0.115	0.122	0.122
I/C	0.103	0.111	0.084	0.075	0.071	0.071	0.070	0.105	0.095	0.075	0.090	0.105	0.101
Hydrogen Retention, %	91.0	87.0	82.3	82.1	82.9	82.8	81.2	85.6	80.5	86.1	87.4	82.4	84.9
Oxygen Removal, %	81.6	76.6	76.5	79.1	80.1	79.5	82.0	77.1	78.2	85.7	83.5	82.5	82.5
ON Elemental Composition													
C, %	62.91	64.05	63.45					58.31			54.93	63.43	
H, %	5.29	5.78	5.65					5.68			5.55	5.24	
O, %	16.54	16.40	16.60					16.66			17.84	12.10	
I, %	21.23	13.06	13.41					18.91			22.82	23.44	
H/C	1.01	1.08	1.07					1.17			1.21	0.99	
O/C	0.197	0.192	0.196					0.214			0.244	0.143	
I/C	0.032	0.019	0.020					0.031			0.039	0.035	
Hydrogen Retention, %	63.5	68.2	67.3					73.6			76.3	62.4	
Oxygen Removal, %	71.8	72.5	71.9					69.4			65.2	79.5	
OP Elemental Comp.													
C, %	30.95	36.10	36.31	37.83	41.25	37.87		38.67	32.60	38.18	30.95	28.75	29.65
H, %	2.69	3.28	3.35	3.64	4.24	3.81		3.80	3.03	3.98	2.90	2.87	3.41
O, %	7.52	8.51	8.34	8.11	9.08	8.96		11.84	7.71	9.22	7.35	6.70	6.53
I, %	55.32	54.68	51.69	49.54	45.61	49.64		52.91	58.55	56.39	64.13	64.96	66.26
H/C	1.04	1.09	1.11	1.16	1.23	1.21		1.18	1.12	1.25	1.13	1.21	1.38
O/C	0.182	0.177	0.172	0.161	0.165	0.178		0.230	0.178	0.181	0.178	0.175	0.165
I/C	0.169	0.143	0.135	0.124	0.105	0.124		0.130	0.170	0.140	0.196	0.214	0.212
Hydrogen Retention, %	65.7	68.6	69.7	73.0	77.6	76.0		74.2	70.2	78.7	70.8	75.9	86.9
Oxygen Removal, %	73.9	74.7	75.5	77.0	76.4	74.6		67.2	74.6	74.1	74.5	75.0	76.4

J.3 Liquefaction of components of wood

($[HI]_{initial}$ = 57 wt%, $T_{initial}$ = 126°C, t = 15 min)

Reaction Conditions

Hybrid Poplar

Experiment No.	81	80	79	78	82	98
Initial [HI], wt%	58.0	57.4	57.6	57.4	58.0	56.6
HI/Substrate Ratio, R (C basis)	2.0	2.9	3.5	4.4	5.7	8.0
HI/Substrate Ratio, R (O basis)	2.9	4.1	5.0	6.3	8.1	11.4
Initial [Substrate], wt%	5.6	3.9	3.2	2.5	2.0	1.4
Liquor/Substrate Ratio, ml/g	10.4	15.1	18.3	23.0	29.1	42.4
Final Temperature, °C	113	118	120	122	123	126

Cellulose

Experiment No.	83	84	85	86	38	39
Initial [HI], wt%	57.9	57.5	57.5	57.5	57.1	56.7
HI/Substrate Ratio, R (C basis)	2.0	2.9	3.5	4.4	5.7	8.0
HI/Substrate Ratio, R (O basis)	2.6	3.5	4.2	5.3	6.8	9.7
Initial [Substrate], wt%	5.6	4.2	3.5	2.8	2.1	1.5
Liquor/Substrate Ratio, ml/g	10.4	14.0	16.9	21.1	27.3	39.3
Final Temperature, °C	117	118	120	122	124	126

Xylan

Experiment No.	67	66	65	68	36	37
Initial [HI], wt%	57.0	56.9	57.0	57.0	56.9	56.8
HI/Substrate Ratio, R (C basis)	2.0	2.9	3.5	4.3	5.7	8.0
HI/Substrate Ratio, R (O basis)	2.5	3.6	4.4	5.4	7.2	10.1
Initial [Substrate], wt%	6.2	4.3	3.5	2.8	2.1	1.5
Liquor/Substrate Ratio, ml/g	9.5	13.8	16.9	20.7	27.5	38.5
Final Temperature, °C	116	120	122	122	126	125

Alkali Lignin

Experiment No.	89	90	91	92	94	93
Initial [HI], wt%	57.0	57.1	56.6	56.3	57.1	56.9
HI/Substrate Ratio, R (C basis)	2.0	2.9	3.6	4.4	5.7	8.1
HI/Substrate Ratio, R (O basis)	6.1	8.8	10.7	13.3	17.3	24.5
Initial [Substrate], wt%	4.2	3.0	2.4	1.9	1.5	1.1
Liquor/Substrate Ratio, ml/g	13.8	19.8	24.4	30.4	39.1	55.3
Final Temperature, °C	120	122	123	125	125	126

ALCELL Lignin

Experiment No.	64	63	62	95	96	97
Initial [HI], wt%	57.1	57.2	57.0	56.7	56.7	57.2
HI/Substrate Ratio, R (C basis)	2.0	2.9	3.6	4.5	5.6	8.1
HI/Substrate Ratio, R (O basis)	6.5	9.5	11.7	14.4	18.2	26.3
Initial [Substrate], wt%	4.02	2.78	2.26	1.80	1.43	1.00
Liquor/Substrate Ratio, ml/g	14.6	20.8	25.6	32.5	40.9	56.5
Final Temperature, °C	117	117	119	125	125	126

Reaction Stoichiometry

HI/Wood Ratio, R	2.0	2.9	3.5	4.4	5.7	8.0
a mol HI reacted/mol C						
Hybrid Poplar	0.64	0.65	0.70	0.72	0.84	0.76
Cellulose	0.78	0.90	0.98	1.02	1.08	1.11
Xylan	0.68	0.80	0.84	0.83	1.00	0.99
Alkali Lignin	0.20	0.17	0.15	0.12	0.22	0.29
Alcell Lignin	0.17	0.16	0.13	0.30	0.31	0.30
a' mol HI reacted/mol O						
Hybrid Poplar	0.90	0.93	1.00	1.02	1.19	1.08
Cellulose	0.93	1.08	1.17	1.22	1.30	1.33
Xylan	0.87	1.02	1.06	1.14	1.26	1.26
Alkali Lignin	0.61	0.51	0.46	0.37	0.68	0.88
Alcell Lignin	0.55	0.51	0.41	0.97	1.02	0.99
c mol I_2 produced/mol C						
Hybrid Poplar	0.24	0.29	0.31	0.33	0.35	0.36
Cellulose	0.35	0.43	0.45	0.49	0.50	0.54
Xylan	0.29	0.36	0.38	0.38	0.44	0.48
Alkali Lignin	0.04	0.03	0.04	0.06	0.09	0.08
Alcell Lignin	0.02	0.04	0.05	0.06	0.09	0.11
c' mol I_2 produced/mol O						
Hybrid Poplar	0.34	0.41	0.44	0.47	0.49	0.52
Cellulose	0.41	0.51	0.54	0.58	0.60	0.64
Xylan	0.37	0.46	0.46	0.51	0.55	0.61
Alkali Lignin	0.11	0.11	0.13	0.18	0.26	0.24
Alcell Lignin	0.08	0.14	0.17	0.20	0.28	0.35
X_{HI}, % (HI Conversion)						
Hybrid Poplar	31.7	22.4	20.0	16.4	14.9	9.5
Cellulose	35.7	30.5	27.7	23.2	19.1	13.8
Xylan	34.8	28.2	24.0	19.5	17.5	12.5
Alkali Lignin	10.0	5.8	4.3	2.8	3.9	3.6
Alcell Lignin	8.4	5.4	3.5	6.7	5.6	3.8
Final [HI], wt%						
Hybrid Poplar	45.1	48.6	49.6	51.1	51.1	53.2
Cellulose	42.6	44.8	46.1	48.6	49.8	51.7
Xylan	42.3	45.4	47.3	48.6	50.0	51.8
Alkali Lignin	53.6	55.6	55.1	55.4	55.1	55.3
Alcell Lignin	54.1	55.3	55.8	54.4	54.7	56.0
Drop [HI], wt%						
Hybrid Poplar	12.9	8.8	8.0	6.3	6.9	3.5
Cellulose	15.3	12.7	11.3	8.9	7.3	5.0
Xylan	14.7	11.5	9.7	8.5	6.9	5.0
Alkali Lignin	3.3	1.5	1.5	0.9	2.0	1.6
Alcell Lignin	3.1	2.4	1.8	2.3	2.0	1.2
Final [I_2], M						
Hybrid Poplar	0.91	0.77	0.68	0.60	0.48	0.39
Cellulose	1.19	1.09	0.98	0.86	0.71	0.55
Xylan	1.12	0.97	0.83	0.73	0.63	0.51
Alkali Lignin	0.19	0.12	0.14	0.15	0.17	0.13
Alcell Lignin	0.12	0.16	0.16	0.16	0.17	0.13

Yields

HI/Wood Ratio, R	2.0	2.9	3.5	4.4	5.7	8.0
$Y_{C/ON}$, %						
Hybrid Poplar	21.4	8.1	1.6	0.8	0.9	0
Cellulose	10.1	3.2	2.4	0.5	0.7	0.7
Xylan	28.1	13.8	5.9	2.3	0	0.2
Alkali Lignin	24.4	21.8	25.7	27.6	19.0	8.9
Alcell Lignin						
$Y_{C/OA}$, %						
Hybrid Poplar	77.7	87.2	88.4	82.6	74.4	70.1
Cellulose	88.1	86.5	84.5	72.2	64.3	54.4
Xylan	57.4	70.5	77.4	79.1	77.3	72.7
Alkali Lignin	74.1	72.8	64.0	60.1	60.0	64.1
Alcell Lignin						
$Y_{C/OP}$, %						
Hybrid Poplar	99.1	95.3	91.0	83.3	75.3	70.1
Cellulose	98.2	89.7	86.9	72.7	65.0	55.1
Xylan	85.5	84.3	83.3	81.3	77.3	72.7
Alkali Lignin	97.6	94.6	89.7	87.7	79.0	73.0
Alcell Lignin	97.0	82.2	74.1	73.2	66.7	62.2
$Y_{C/AP}$, %						
Hybrid Poplar	0.9	4.7	9.0	16.7	24.7	29.9
Cellulose	1.8	10.3	13.1	27.3	35.0	44.9
Xylan	14.5	15.7	16.7	18.7	22.7	27.3
Alkali Lignin	2.4	5.4	10.3	12.3	21.0	27.0
Alcell Lignin	3.0	17.8	25.9	26.8	33.3	37.8

Yield Contributions

(43.3% cellulose, 32.7% xylan, 24% lignin)

HI/Wood Ratio, R	2.0	2.9	3.5	4.4	5.7	8.0
$Y_{C/ON}$, %						
Hybrid Poplar	21.4	8.1	1.6	0.7	0.9	0
Cellulose	4.4	1.4	1.0	0.2	0.3	0.3
Xylan	9.2	4.5	1.9	0.7	0	0
Alkali Lignin	5.8	5.2	6.2	6.6	4.6	2.1
Total	19.4	11.2	9.1	7.6	4.9	2.4
$Y_{C/OA}$, %						
Hybrid Poplar	77.7	87.2	89.4	82.6	74.4	70.1
Cellulose	38.1	37.4	36.6	31.3	27.8	23.6
Xylan	18.8	23.1	25.3	25.9	25.3	23.8
Alkali Lignin	17.6	17.5	15.3	14.4	14.4	15.4
Total	74.5	78.0	77.2	71.6	67.5	62.7
$Y_{C/OP}$, %						
Hybrid Poplar	99.1	95.3	91.0	83.3	75.3	70.1
Cellulose	42.5	38.8	37.6	31.5	28.1	23.9
Xylan	27.9	27.6	27.2	26.6	25.3	23.8
Alkali Lignin	23.4	22.7	21.5	21.1	19.0	17.5
Total	93.9	89.1	86.4	79.2	72.4	65.3
$Y_{C/AP}$, %						
Hybrid Poplar	0.9	4.7	9.0	16.7	24.7	29.9
Cellulose	0.8	4.5	5.7	11.8	15.2	19.4
Xylan	4.8	5.1	5.5	6.1	7.4	8.9
Alkali Lignin	0.6	1.3	2.5	2.9	5.0	6.5
Total	6.1	10.9	13.6	20.8	27.6	34.8

Elemental Analyses

Cellulose

Experiment No.	83	84	85	86	38	39
HI/Wood Ratio, R	2.0	2.9	3.5	4.4	5.7	8.0
OA Elemental Composition						
C, %	42.76	40.56	41.93	45.72	46.48	47.74
H, %	5.32	4.89	5.03	5.31	5.26	5.54
O, %	7.55	7.17	6.37	6.08	5.51	5.20
I, %	44.51	48.75	48.50	44.43	42.83	42.31
H/C	1.49	1.45	1.44	1.39	1.36	1.39
O/C	0.133	0.133	0.114	0.100	0.089	0.082
I/C	0.099	0.114	0.110	0.092	0.087	0.084
Hydrogen Retention, %	89.5	86.7	86.3	83.5	81.4	83.5
Oxygen Removal, %	84.0	84.0	86.3	88.0	89.3	90.1
ON Elemental Composition						
C, %	51.51	61.29	62.27			
H, %	5.37	5.81	5.88			
O, %	14.12	7.75	7.81			
I, %	24.63	27.83	25.25			
H/C	1.25	1.14	1.13			
O/C	0.206	0.095	0.094			
I/C	0.045	0.043	0.038			
Hydrogen Retention, %	75.0	68.2	67.9			
Oxygen Removal, %	75.2	88.6	88.7			
OP Elemental Composition						
C, %	27.22	28.20		30.62		
H, %	3.26	3.35		3.81		
O, %	6.55	6.15		5.81		
I, %	64.11	63.10		61.68		
H/C	1.44	1.43		1.49		
O/C	0.181	0.164		0.142		
I/C	0.223	0.212		0.191		
Hydrogen Retention, %	86.1	85.4		89.5		
Oxygen Removal, %	78.2	80.4		82.8		

Xylan

Experiment No.	67	66	65	68	36	37
HI/Wood Ratio, R	2.0	2.9	3.5	4.3	5.7	8.0
OA Elemental Composition						
C, %	34.55	38.23	44.98	45.87	49.35	49.56
H, %	4.13	4.29	5.06	5.01	5.57	5.62
O, %	5.87	6.11	8.91	5.51	6.25	5.34
I, %	50.51	48.72	45.16	44.43	44.89	43.42
H/C	1.44	1.35	1.35	1.31	1.36	1.36
O/C	0.128	0.120	0.149	0.090	0.095	0.081
I/C	0.138	0.121	0.095	0.092	0.086	0.083
Hydrogen Retention, %	89.2	83.7	83.9	81.5	84.2	84.6
Oxygen Removal, %	83.9	84.8	81.2	88.6	88.0	89.8
ON Elemental Composition						
C, %	62.13	63.41	63.41	65.33		
H, %	5.53	5.99	5.99	6.07		
O, %	12.89	11.56	10.51	9.32		
I, %	17.64	18.51	20.66	18.88		
H/C	1.07	1.13	1.13	1.12		
O/C	0.156	0.137	0.124	0.107		
I/C	0.027	0.028	0.031	0.027		
Hydrogen Retention, %	66.4	70.5	70.5	69.3		
Oxygen Removal, %	80.3	82.7	84.3	86.4		
OP Elemental Composition						
C, %	31.49	33.40		32.89	33.56	34.10
H, %	3.27	3.63		3.70	3.93	4.20
O, %	7.59	6.13		5.99	4.83	4.40
I, %	52.80	55.15		54.72	54.82	55.92
H/C	1.25	1.31		1.35	1.41	1.48
O/C	0.181	0.138		0.137	0.108	0.097
I/C	0.159	0.156		0.157	0.156	0.155
Hydrogen Retention, %	77.5	81.1		83.9	87.4	91.9
Oxygen Removal, %	77.1	82.6		82.7	86.3	87.7

Alkali Lignin

Experiment No.	89	90	91	92	94	93
HI/Wood Ratio, R	2.0	2.9	3.6	4.4	5.7	8.1
OP Elemental Composition						
C, %	41.25	37.12	36.35	40.63	49.47	48.92
H, %	3.89	3.70	3.60	3.70	4.53	4.49
O, %	14.25	13.21	13.01	14.51	16.14	16.65
I, %	38.28	44.45	44.27	38.17	28.25	29.94
H/C	1.13	1.20	1.19	1.09	1.11	1.10
O/C	0.259	0.267	0.269	0.268	0.245	0.247
I/C	0.088	0.113	0.115	0.089	0.054	0.058
Hydrogen Retention, %	98.5	100	100	95.1	95.6	95.9
Oxygen Removal, %	21.4	19.1	18.6	18.8	25.8	25.2
ON Elemental Composition						
C, %	62.67	61.45	62.60	61.66		60.92
H, %	5.92	5.77	5.91	5.81		5.45
O, %	19.70	21.11	21.97	21.30		21.19
I, %	9.49	9.80	7.22	11.72		11.19
H/C	1.10	1.13	1.13	1.13		1.07
O/C	0.236	0.258	0.263	0.259		0.261
I/C	0.014	0.015	0.011	0.018		0.017
Hydrogen Retention, %	86.7	98.1	98.6	98.4		93.4
Oxygen Removal, %	28.5	21.9	20.2	21.4		20.9

Alcell Lignin

Experiment No.	64	63	62	95	96	97
HI/Wood Ratio, R	2.0	2.9	3.6	4.5	5.6	8.1
OP Elemental Composition						
C, %	51.30	55.13	54.74	46.96	48.16	52.19
H, %	4.61	4.77	4.74	4.58	4.55	4.93
O, %	20.22	17.00	19.22	15.25	15.69	16.54
I, %	24.14	23.10	21.30	32.68	31.00	26.68
H/C	1.08	1.04	1.04	1.17	1.13	1.13
O/C	0.296	0.231	0.264	0.244	0.245	0.238
I/C	0.045	0.040	0.037	0.066	0.061	0.048
Hydrogen Retention, %	93.8	90.4	90.4	100	98.7	98.7
Oxygen Removal, %	4.6	25.3	15.0	21.4	21.1	23.3

APPENDIX K

CHARACTERISTICS OF BATCHWISE-CONTINUOUS ELECTROCHEMICAL WOOD LIQUEFACTION

Time, h		0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
#8 ECLR	Current, A		8.7	7.9	8.2	7.8	7.8		7.9		7.2	7.0
	F_{wood}, g/min		0.050	0.050	0.052	0.052	0.044		0.052		0.048	0.053
	$[I_2]$, M	0.006	0.004	0.035	0.024	0.026	0.026		0.036		0.039	0.047
	[HI], M	7.24	6.90	6.82	6.83	6.62	6.48		6.26		6.26	6.11
	[HI], wt%	55.5	53.9	53.5	53.6	52.6	51.9		50.8		50.8	50.0
	Temp., °C	125	125	125	125	124	122	120	118	115	116	116
#9 ECLR	Current, A		10.0	8.7	8.2	7.9	8.5	8.4	7.7	6.4	6.7	7.4
	F_{wood}, g/min		0.047	0.047	0.047	0.046	0.046	0.046	0.048	0.050	0.049	0.045
	$[I_2]$, M	0.021		0.022		0.020		0.022		0.026		0.033
	[HI], M	7.09		6.75		6.64		6.41		6.47		6.51
	[HI], wt%	54.8		53.8		52.7		51.5		51.8		52.0
	Temp., °C	124	125	125	125	123	122	122	122	122	122	122
#11 ECLR	Current, A		9.2	9.2	9.3	10.0	10.8	11.4	11.4	12.1		11.9
	F_{wood}, g/min		0.101	0.081	0.080	0.101	0.101	0.100	0.101	0.101		0.1
	$[I_2]$, M	0.007		0.045		0.090		0.097		0.057		0.060
	[HI], M	7.40		7.17		7.05		6.93		6.32		5.91
	[HI], wt%	56.2		55.2		54.6		54.1		51.1		48.9
	Temp., °C	120	123	122	115	115	114	113	113	113	115	115
#12 ECLR	Current, A		11.2	11.3	11.2	11.3	11.2	11.8	12.0	12.2	11.3	11.7
	F_{wood}, g/min		0.091	0.091	0.091	0.091	0.091	0.091	0.091	0.091	0.091	0.091
	$[I_2]$, M	0.009		0.011		0.026		0.038		0.055		0.045
	[HI], M	7.47		6.75		6.36		5.79		5.38		5.14
	[HI], wt%	56.4		53.2		51.3		48.3		46.0		44.6
	Temp., °C	120	120	120	115	118	118	118	115	115	115	115
#14 ECLR	Current, A		10.5	10.6	10.6	11.2	11.2	11.5	12.2	12.0	12.0	11.9
	F_{wood}, g/min		0.095	0.095	0.095	0.095	0.095	0.095	0.095	0.095	0.095	0.095
	$[I_2]$, M	0.004		0.018		0.039		0.050		0.052		0.048
	[HI], M	6.42		6.09		5.60		5.38		5.38		5.11
	[HI], wt%	51.6		49.9		47.3		46.0		46.0		44.5
	Temp., °C	110	115	118	118	118	118	115	115	115	115	115

Time, h		0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
'15 ECLR	Current, A		10.4	10.8	11.8	11.8	11.9	12.1	12.2	12.3	11.9	12.5
	F_{wood},g/min		0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
	$[I_2]$, M	0.003		0.025		0.027		0.027		0.067		0.074
	[HI], M	7.28		6.75		6.09		5.81		5.51		5.01
	[HI], wt%	55.7		53.1		50.0		48.4		46.8		43.9
	Temp., °C	105	110	112	118	120	118	118	115	115	115	114
'16 ECLR	Current, A		13.9	15.0	15.1	15.2	15.2	14.5	14.7	14.0	14.5	15.3
	F_{wood},g/min		0.101	0.099	0.100	0.100	0.101	0.100	0.103	0.099	0.099	0.100
	$[I_2]$, M	0.005		0.017		0.017		0.027		0.060		0.063
	[HI], M	7.56		6.84		6.33		5.85		5.43		5.20
	[HI], wt%	56.9		53.6		51.1		48.6		46.3		44.0
	Temp., °C	110	119	118	115	115	115	116	116	115	115	115
'17 ECLR	Current, A		10.7	9.8	9.1	8.9	8.7	8.6	8.8	8.7	8.7	8.6
	F_{wood},g/min		0.050	0.050	0.050	0.050	0.051	0.050	0.050	0.050	0.050	0.050
	$[I_2]$, M	0.0004		0.0015		0.0063		0.011		0.018		0.026
	[HI], M	7.49		6.92		6.56		6.29		5.97		5.81
	[HI], wt%	56.6		54.0		52.3		50.9		49.3		48.4
	120	120	120	122	122	120	120	120	120	120	120	118
'18 ECLR	Current, A		9.8	9.8	9.2	9.3	9.3	9.2				
	F_{wood},g/min		0.150	0.150	0.150	0.150	0.150	0.150				
	$[I_2]$, M	0.0016		0.0061		0.068		0.092				
	$[I^-]$, M	7.51		6.85		6.21		5.82				
	[HI], M	7.37		6.68		6.25		5.87				
	[HI], wt%	56.1		52.9		50.7		48.7				
	Temp., °C	118	120	122	122	120	118	118				
'19 ECLR	Current, A		10.3	10.5	10.5	10.4	10.3	10.4				
	F_{wood},g/min		0.102	0.100	0.100	0.100	0.100	0.100				
	$[I_2]$, M	0.001		0.041		0.074		0.098				
	[HI], M	8.22		7.34		6.84		6.39				
	[HI], wt%	59.7		55.9		53.6		51.4				
	Temp., °C	118	124	125	125	123	121	121				
'20 ECLR	Current, A		11.8	11.8	13.4	13.0	12.4	12.4				
	F_{wood},g/min		0.086	0.086	0.086	0.086	0.086	0.086				
	$[I_2]$, M	0.0064		0.026		0.009		0.048				
	[HI], M	8.58		7.52		7.19		6.61				
	[HI], wt%	61.1		56.7		55.3		52.5				
	Temp., °C	110	117	115	120	119	116	115				

APPENDIX L

EXPERIMENTAL DATA FOR SOLVENT EXTRACTION OF PHYSICALLY ASSOCIATED I_2

CS_2 Solvent Extraction of I_2 Associated on OP Product

(Run '14ECLR)
(5.0 g OP sample)

Time		With Charge-Transfer Complex I_2 and Organic Iodide									With I_2 but Without Organic Iodide		
Time (h)	Time (day)	Elemental Analysis, wt%				Atomic Ratio			Hydrogen Retention %	Oxygen Removal %	Elemental Analysis, wt%		Formula
		C	H	O	I	H/C	O/C	I/C			C	I_{I_2}	I_{I_2}/C
0	0	46.38	4.39	14.04	35.19	1.25	0.23	0.072	78.6	67.1	46.38	28.81	0.059
11	0.46	49.91	4.61	19.33	26.15	1.11	0.29	0.050	69.8	58.6		19.77	0.040
18	0.75	50.88	4.74	18.87	25.51	1.12	0.28	0.047	70.4	60.0		19.13	0.039
25	1.04	51.05	4.72	18.76	25.47	1.11	0.28	0.047	69.8	60.0		19.09	0.039
32	1.33	52.08	4.73	19.71	23.48	1.09	0.28	0.043	68.6	60.0		17.10	0.035
42	1.75	54.09	4.80	20.85	20.26	1.07	0.29	0.035	67.3	58.6		13.88	0.028
58	2.42	54.76	5.12	21.70	18.42	1.12	0.30	0.032	70.4	57.1		12.04	0.025
72	3.00	55.68	5.00	23.43	15.89	1.08	0.32	0.027	67.9	54.3		9.51	0.019
88	3.67	56.43	4.94	23.38	15.20	1.05	0.31	0.025	66.0	55.7		8.82	0.018
112	4.67	57.63	5.17	23.00	14.20	1.08	0.30	0.023	67.9	57.1		7.82	0.016
136	5.67				11.47								
178	7.42	60.14	5.23	20.41	11.35	1.04	0.25	0.018	65.4	64.3		4.97	0.010
233	9.71				8.08								
263	10.96	59.84	5.33	23.02	6.38	1.07	0.29	0.010	67.3	58.6		0	0

APPENDIX M

MATERIAL BALANCES IN CONTINUOUS WOOD LIQUEFACTION REACTOR

(The according values for following calculations are recorded in Chapter 7.)

TOTAL MASS BALANCE			
Before Reaction:			
Pure HI Solution:	371.80	g	{= 220 ml × 1.69 g/ml}
I_2 in Solution:	0.21	g	{= 0.0037 mol/l × 0.22 l × M_{I_2}}
HI Make-up Gas:	120	g	{= 0.40 g/min × 300 min}
Wood:	27.0	g	{= 0.090 g/min × 300 min}
Total mass in:	519.01	g	
After Reaction:			
Pure HI Solution:	531.06	g	{= 318 ml × 1.67 g/ml}
I_2 in Solution:	7.59	g	{= 0.094 mol/l × 0.318 l × M_{I_2}}
Product OP:	23.798	g	
Product AP:	2.542	g	
Product GP:	7.56	g	
Inventory at End:	572.55	g	
Water Transferred:	63.95	g	
Total Mass Balance:	98.0	%	{= (572.55 g − 63.95 g)/519.01 g}

WATER BALANCE			
Before Reaction:			
H_2O in Solution:	161.73	g	{= 220 ml × 1.69 g/ml × (1 − 0.565)}
Total H_2O in:	161.73	g	
After Reaction:			
H_2O in Solution:	237.38	g	{= 318 ml × 1.67 g/ml × (1 − 0.553)}
Inventory at End:	249.28	g	
H_2O Produced:	11.70	g	{= b ($M_{H_2O}/M_{CH_{[illegible]}O_{[illegible]}}$) W_{wood}} {= 0.60 × 18/24.92 × 27.0 g}
Water Transferred:	63.95	g	{= 237.38 g − 161.73 g − 11.70}

HI BALANCE

Before Reaction:		
HI in Solution:	210.07 g	{= 220 ml × 1.69 g/ml × 56.5%}
HI make-up:	120.0 g	{= 0.40 g/min × 300 min}
Total HI in:	330.07 g	
After Reaction:		
HI in Solution:	293.68 g	{= 318 ml × 1.67 g/ml × 55.3%}
Inventory at End:	293.68 g	
Net Reacted HI:	21.45 g	{= (a − 2cE$_T$)(M$_{HI}$/M$_{CH_1}$ [illegible] W$_{wood}$} {= (1.07 − 2 × 0.52 × 88%) (127.9/24.92) 27.0g}
Total HI Balance:	95.5 %	{= (293.68 + 21.45 g)/330.07 g}

CARBON BALANCE

Before Reaction:		
Carbon in Wood:	13.014 g	{= 27.0 g × 48.2%}
Total C in:	13.014 g	
After Reaction:		
C in OP Product:	10.954 g	{= 23.798 g × 46.03%}
C in AP Product:	1.397 g	{= 2.542 g × 54.96%}
C in GP Product:	0.638 g	{= 27.0 g × 48.2% × 4.9%}
Inventory at End:	12.989 g	
Carbon Balance:	99.8 %	{= 12.989 g/13.014 g}

HYDROGEN BALANCE

Before Reaction:		
H in Solution:	19.613 g	{= 220 l × 1.69g/ml [A$_H$/M$_{HI}$ 56.5%+2A$_H$/M$_{H_2O}$ 43.5%]}
H in Make-up HI Gas:	0.938 g	{= 0.40 g × 300 min × A$_H$/M$_{HI}$}
H in Wood:	1.728 g	{= 27.0 g x 6.4%}
Total H in:	22.279 g	
After Reaction:		
H in Solution:	28.672 g	{= 318 l × 1.67g/ml [A$_H$/M$_{HI}$ 55.3% + 2A$_H$/M$_{H_2O}$ 44.7%}
H in OP Product:	1.252 g	{= 23.798 g × 5.26%}
H in AP Product:	0.168 g	{= 2.542 g × 6.60%}
H in GP Product:	0.159 g	{= 27.0 g × 48.2% × 4.9% × 3A$_H$/A$_C$}
Inventory at End:	30.251 g	
Water Transferred:		
H in H_2O Transferred:	7.106 g	{= 63.95 g × 2A$_H$/M$_{H_2O}$}
Hydrogen Balance:	103.9 %	{= (30.251 g − 7.106 g)/22.279 g}

OXYGEN BALANCE

Before Reaction:		
O in Solution:	143.76 g	{= 220 ml × 1.69 g/ml A_O/M_{H_2O} 43.5%}
O in Wood:	12.23 g	{= 27.0 g × 45.3%}
Total O in:	155.99 g	
After Reaction:		
O in Solution:	211.01 g	{= 318 ml × 1.67 g/min A_O/M_{H_2O} 44.7%}
O in OP Product:	1.62 g	{= 23.798 g × 6.81%}
O in AP Product:	0.20 g	{= 2.542 g × 7.77%}
Inventory at End:	212.83 g	
Water Transferred:		
O in H_2O Transferred:	56.84 g	{= 63.95 g × A_O/M_{H_2O}}
Oxygen Balance:	100.0 %	{= (212.83 g − 56.84 g)/155.99 g}

TOTAL IODINE BALANCE AND DISTRIBUTION

Before Reaction:			
I in Solution as HI:	208.27 g	(63.6 %)	{= 0.22 l × 7.46 mol/l × A_I}
I in Solution as I_2:	0.21 g	(0.1 %)	{= 0.22 l × 0.0037 mol/l × M_{I_2}}
I in Make-up HI:	119.06 g	(36.3 %)	{= 0.40 g/min × 300 min × A_I/M_{HI}}
Total I in:	327.54 g		
After Reaction:			
I in Solution as HI:	290.55 g	(92.0 %)	{= 0.318 l × 7.20 mol/l × A_I}
I in Solution as I_2:	7.59 g	(2.4 %)	{= 0.318 l × 0.094 mol/l × M_{I_2}}
I in OP Product:	10.30 g	(3.3 %)	{= 23.798 g × 43.28%}
I in AP Product:	0.79 g	(0.3 %)	{= 2.542 g × 31.04%}
I in GP Product:	6.74 g	(2.1 %)	{= 27.0 g × 48.2% × 4.9% × A_I/A_C}
Inventory at End:	315.97 g		
Total Iodine Balance:	96.5 %		{= 315.97 g/327.54 g}

MOLECULAR IODINE BALANCE AND DISTRIBUTION

Before Reaction:			
I_2 in Solution:	0.207 g		{= 0.22 l × 0.0037 mol/l × M_{I_2}}
Total I_2 in:	0.207 g		
I_2 Produced:	144 g		{= 0.48 g/min × 300 min}
After Reaction:			
I_2 in Solution:	7.587 g	(43.3 %)	{= 0.318 l × 0.094 mol/l × M_{I_2}}
I_2 in OP Product:	9.29 g	(53.0 %)	{= 23.798 g × (43.28 − 6.98)/(100 − 6.98)}
I_2 in AP Product:	0.66 g	(3.7 %)	{= 2.542 g × (31.04 − 6.6)/(100 − 6.6)}
Inventory at End:	17.54 g		
I_2 Reduced:	126 g		{= 0.42 g/min × 300 min}
Molecular Iodine Balance:	99.5 %		{= (17.54 g + 126 g)/(0.207g + 144 g)}