

PROCESS AND REACTOR DESIGN STUDY  
OF LIGNIN PROPOXYLATION

by

Ana Maria Barbero

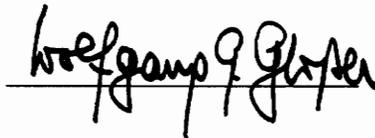
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APPROVED:



W. G. Glasser



D. L. Michelsen



W. H. Velander

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Committe Chairman: Wolfgang G. Glasser

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(ABSTRACT)

Lignin, the second most abundant biopolymer on earth following cellulose, can be described as a million-ton, low cost, under-utilized resource. The use of lignin in polymeric products adds the highest value to the raw material. Production of engineering plastics from lignin is an attractive approach to the utilization of lignin. The use of lignin in structural materials is limited by its insolubility and its failure to undergo melt flow. A promising method to overcome the limitations is to chemically modify lignin by reaction with a low modulus substance, like an aliphatic ether. The reaction of lignin with propylene oxide (PO) produces a copolymer, hydroxypropyl lignin (HPL). Extensive studies have been directed toward the understanding of the chemistry and properties of HPL. A study of the process design is necessary to examine the economics of lignin propoxylation.

This work includes the chemical and kinetic analysis of the lignin propoxylation reaction as well as the modelling of a semibatch polymerization process; the design of a lignin propoxylation pilot plant; and a preliminary study of an industrial plant. Two models for the lignin propoxylation reaction are proposed and analyzed to produce a mathematical description of the reaction

process. The design of the pilot plant involves (a) the process design, which includes a material balance, a flow sheet, and a listing of the equipment; and (b) the economic analysis in which estimates of capital cost and operating costs are discussed. The scale-up to industrial production gives an estimate of the characteristics of a continuous process. This study constitutes a substantial contribution to the development of a new technology dealing with *Engineering Plastics from Lignin*.

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## NOTATION

The notation used in this thesis accompanied by the S.I. units corresponding to each parameter are given next. Other units used in this work are given in parenthesis.

|              |  | S.I. units(other)                     |
|--------------|--|---------------------------------------|
| $a_{gl}$     | surface area of gas bubbles per<br>unit volume of liquid     | $m^{-1}$                              |
| $C_B$        | concentration of B   | $kmol\ m^{-3}$                        |
| $C_{B_g}$    | concentration of B in the gas phase                          | $kmol\ m^{-3}$                        |
| $C_{B_i}$    | concentration of B in the inlet                              | $kmol\ m^{-3}$                        |
| $C_{B_l}$    | concentration of B in the liquid phase                       | $kmol\ m^{-3}$                        |
| $E_a$        | activation energy  | $J\ mol^{-1}$<br>( $kcal\ mol^{-1}$ ) |
| $f_{i_v}$    | partial fugacity of species i,<br>for the vapor phase        | Pa (psia)                             |
| $f_{i_l}$    | partial fugacity of species i,<br>for the liquid phase       | Pa (psia)                             |
| $H_B$        | Henry's law constant ( $C_{B_g}^*/C_{B_l}^*$ of equilibrium) |                                       |
| $t$          | time   | s                                     |
| $K_{B_{gl}}$ | overall gas-liquid mass transfer coefficient                 | $m\ s^{-1}$                           |
| $K_i$        | Raoult's law constant ( $P_i^{sat}/P$ )                      |                                       |
| $k$          | reaction constant (for first order)                          | $s^{-1}$                              |

---

|             |  |                                    |
|-------------|--|------------------------------------|
| $k_g$       | mass transfer coefficient in the gas phase                                   | $\text{m s}^{-1}$                  |
| $k_l$       | mass transfer coefficient in the liquid phase                                | $\text{m s}^{-1}$                  |
| L           | moles of liquid over total moles,<br>with mole fractions $\{x_i\}$           |                                    |
| L(ml)       | liquid volume in milliliters   | ml                                 |
| Mw          | molecular weight   | $\text{kg kmol}^{-1}$              |
| n           | total number of moles  |                                    |
| P           | total pressure   | Pa (psia)                          |
| $P_i^{sat}$ | saturation pressure if species i   | Pa                                 |
| PF          | Poynting Factor  |                                    |
| $Q_g$       | volumetric flow rate of the gas phase  | $\text{m}^3\text{s}^{-1}$          |
| $Q_g^0$     | initial feed rate  | $\text{m}^3\text{s}^{-1}$          |
| $Q_g^1$     | feed rate during the reaction  | $\text{m}^3\text{s}^{-1}$          |
| R           | gas constant   | $\text{kJ kmol}^{-1}\text{K}^{-1}$ |
| $r_B$       | velocity of reaction<br>( $kC_B$ , for an irreversible first-order reaction) | $\text{kmol m}^{-3}\text{s}^{-1}$  |
| St          | Stanton Number $\left(\frac{K_{B_{gl}} a_{gl} V_l}{Q_g H_B}\right)$          |                                    |
| T           | temperature  | K ( $^{\circ}\text{C}$ )           |
| Tg          | glass transition temperature   | K ( $^{\circ}\text{C}$ )           |
| $U_m$       | concentration of species U whose<br>chain length is m                        | $\text{kmol m}^{-3}$               |

---

|          |   |   |
|----------|---|---|
| $u_{1g}$ | superficial velocity of the gas bubbles                           | $\text{m s}^{-1}$                               |
| $V$      | moles of vapor over total moles,<br>with mole fractions $\{y_i\}$ |   |
| $V_l$    | volume of liquid phase  | $\text{m}^3, \text{l}, \text{ml}, (\text{gal})$ |
| $V_l^0$  | initial liquid volume   | $\text{m}^3, \text{l}, \text{ml}, (\text{gal})$ |
| $x_i$    | molar fraction of species $i$ in the liquid phase                 |   |
| $y_i$    | molar fraction of species $i$ in the vapor phase                  |   |
| $z$      | reactor axial coordinate  | $\text{m}$                                      |
| $z_i$    | overall molar fraction of species $i$                             |   |

***Greek Symbols***

|                |   |                    |
|----------------|---|--------------------|
| $\epsilon_g$   | ratio of gas volume to solvent volume   |                    |
| $\rho$         | density   | $\text{kg l}^{-1}$ |
| $\phi_i$       | partial fugacity coefficient of species $i$   |                    |
| $\phi_i^{sat}$ | partial fugacity coefficient of species $i$ ,<br>as saturated vapor                     |                    |
| $\Phi_i$       | fugacity coefficients relation $\left(\frac{\phi_i}{\phi_i^{sat}} (\text{PF})_i\right)$ |                    |
| $\gamma_i$     | activity coefficient of species $i$   |                    |

---

*Subscripts*

- $v$  vapor phase
- $l$  liquid phase
- $c$  critical properties
- $1$  propylene oxide
- $2$  toluene

*Superscripts*

- $0$  initial conditions
- $*$  equilibrium conditions

*Chapter 1*  
*INTRODUCTION*

Lignin behaves like a three dimensional, highly branched polymer that binds cellulose fibers together in wood. It is the second most abundant biopolymer on earth following cellulose. Lignin is one of the major components of wood, occurring in amounts ranging from about 7 to 32 % of the weight of moisture-free wood. Some of the functions of lignin in a plant system are the following (Falkehag, 1975):

- Energy storage system.
- Response to biochemical stresses by inhibiting enzymatic degradation of other components and by displaying low susceptibility to biodegradation itself.
- Response to mechanical stresses; lignin assumes the role of an important mechanical reinforcing agent for the entire tree.
- Control of water balances and plant response to humidity.
- Response to chemical stresses acting as antioxidant, as ultraviolet light stabilizer, and possibly as flame retardant.
- Contributing to soil properties during natural decay.
- Interaction with other systems, like its role in the digestive system of mammals.

Lignin is the "unwanted" constituent of wood because it creates many problems during the pulping process. The main objective of pulping is delignification to liberate cellulosic fibers. If it were not for lignin, it would not be necessary to apply strong alkaline or acidic reagents in the chemical delignification of wood to obtain pulp and paper products (Glasser, 1980). Lignin uses can be classified of the following manner (Falkehag, 1975):

- Energy.
- Paper, board, etc.
- Fragmentation into low molecular weight chemicals, like vanillin, phenols, etc.
- Macromolecular uses in solution systems as dispersants, emulsion

stabilizers, precipitants, etc.

- Macromolecular uses in polymer materials systems.
- Matrix or gel applications involving adsorption, desorption, etc.
- Carbonization and pyrolysis to active carbon and carbon or graphite fibers and foams.
- Soil and fertilizer applications.

Lignin can be described as a multi-ton, low cost product that is under-utilized. Of the 16 million tons of lignin dissolved in the kraft-pulp industry annually, only a small fraction is recovered. The rest is burned in the recovery units of the kraft mills (Falkehag, 1975). The fuel value of lignin was approximately 3 to 4 cents per lb in the late 1970's (Glasser, 1981). However, lignin can be better utilized in lignin-containing pulps; as low molecular weight chemicals from lignin; and as component of polymeric products (Glasser, 1981). Several references address the conversion of lignin into polymeric products (Falkehag, 1975; Glasser, 1981). Lignin in polymeric products is valued at approximately 20 to 25 cents per lb (Glasser, 1981). Several of the properties of the natural polymer lignin are similar to those required for the so called "Engineering Plastics". Engineering plastics are nonmetallic materials "...which possess physical properties enabling them to perform for prolonged use in structural applications, over a wide temperature range, under mechanical stress, and in difficult chemical and physical environments" (Foy, 1969).

Lignin is used in polymeric form as part of resins, adhesives, and binders; as polyelectrolytic antioxidant and dispersant; as ion exchanger and complexing agent; and as a controlled release agent (Glasser, 1981). Among the more promising applications for lignin in thermosets are those involving phenolic resins, polyurethanes and epoxies. Presently, polyurethane foams and other compounds are made of synthetic organic chemicals. Lignin polyols can be used as a substitute for these synthetic organic chemicals. From a market study of polyhydric alcohols for polyurethanes (Rice, 1988) we extract the following information. The term polyhydric alcohol, or polyol, means an alcohol having more than one hydroxyl group. Polyhydric alcohols are often short-chain polyalcohols that are building blocks to long chain molecules or they serve as

crosslink agents. In 1985 the United States produced more than 2.6 billion kg (5.7 billion lb) of polyols per year. Ethylene glycol comprises more than 70 percent of the total volume of production of polyhydric alcohols, with a bulk price of 0.40 \$/lb. The prices of polyhydric alcohols range from 0.40 to 0.80 \$/lb. One important reaction of polyhydric alcohols is that with isocyanates to form urethanes. Not only can the short chain low molecular weight polyhydric alcohols be used in polyurethane production but specially the higher molecular weight hydroxyl terminated polyethers and polyesters. Most of the polyols used in polyurethane manufacture have average molecular weights between 200 and 10,000 kg/kmol and hydroxyl numbers between 50 and 500. Polyether polyols are manufactured mainly by using PO or ethylene oxide (EO). The most important applications for polyether polyols are in flexible foams, rigid foams, and elastomers and coatings. Polyethers used for flexible foams are linear or slightly branched with molecular weights between 1,000 and 8,000. Rigid foams are obtained through the use of highly branched, short chain polyethers. These have a functionality between 3 and 7, and molecular weights between 250 and 1,000. Polyether polyols can also be used for reactive adhesives, and the most important are polypropoxylene ether polyols. Polyester polyols are used in polyurethane rigid foams, coatings, adhesives, millable gums, and elastomers. In general linear or slightly branched polyesters with molecular weights of 400 to 6,000; with hydroxyl contents between 28 to 300; and with acid numbers of 1 are used in the formulations. The highly branched, aromatic polyester polyols serve primarily as a vehicle for polyurethane coatings and adhesives. The consumption of polyurethane adhesives is growing at a rate of about 8% annually. The entry into the market by polyols from lignin will be successful if they can compete with these synthetic chemicals.

The utilization of lignin in structural material systems is limited by the insolubility and resistance to flow when heated. A promising method to overcome the limitations involves the chemical modification and derivatization of the high-modulus polyaromatic lignin with a low-modulus substituent, such as an aliphatic ether (Glasser, 1984). The polydispersity and multifunctionality of lignin constitutes another limitation for its use in polymeric products.

Consequently, a more uniform, low-modulus derivative needs to be synthesized. The chemical modification of lignin by reaction with alkene oxides, also termed oxyalkylation or alkoxylation, is a technique for overcoming these limitations (Muller, 1983). The reaction of lignin with propylene oxide has been studied at the laboratory scale under different conditions (Wu, 1984) and the product, hydroxypropyl lignin (HPL) has been characterized (Glasser, 1984). HPL derivatives are expected to become components of thermosetting and thermoplastic polymeric materials. The synthesis and characterization of polyurethane films (Saraf, 1984; Rials, 1984, 1985) and foams (Mozheiko, 1981) have been reported. Also wood adhesives from lignin and isocyanates have been analyzed (Newman, 1985). Polymeric products from lignin have been patented by Allan, 1969; Christian, 1971; and Glasser, 1977.

Research is under way to define conditions under which copolymer formation from propylene oxide and lignin can be performed with high efficiency. The conditions under which the homo-polymerization of propylene oxide is prevented are also under investigation.

Despite the significant amount of study that has been directed toward understanding the chemistry and physics of the hydroxypropyl lignin copolymer, a reaction engineering analysis of the polymerization kinetics either in the presence or absence of transport effects has not been presented. Such an analysis would be useful in design, scale-up, troubleshooting and optimization of the HPL polymerization reactor.

*Chapters 3 to 6*, deal with the analysis and modelling of the propoxylation reaction. The chemical and physical description of the propoxylation reaction is presented in *Chapter 3*. An outline of the modelling of the propoxylation reaction and the identification of the required variables is given at the end of *Chapter 3*. A vapor-liquid equilibrium analysis of the system solvent-reactant is given in *Chapter 4*. This thermodynamic analysis gives the PO distribution in the two phases. The analysis and design of a semibatch polymerization reactor is presented in *Chapter 5*. First, the model equations for a gas-liquid semibatch polymerization reactor are formulated. Then, the model equations for a liquid semibatch polymerization reactor are solved. Finally, the liquid and the gas-

liquid models are compared. In *Chapter 6*, the experimental data is presented and analysed. The liquid model equation is included in a computer program that simulates the semibatch polymerization and the results are correlated with the experimental data. From the conclusions drawn in the previous section a temperature gradient process is proposed to improve the reaction rate. Experimental data is obtained and the liquid model is applied following the new process conditions. Finally, a technique for the prediction of the optimum temperature gradient is proposed.

*Chapter 7* deals with the design of a lignin propoxylation pilot plant. The pilot plant is to be installed at the Thomas M. Brooks Forest Products Center of Virginia Polytechnic Institute & State University, Blacksburg, Virginia. The pilot plant will be constructed using some equipment already available like a 37.8 liters (10 gallon) reactor and a rotary evaporator. Having the reactor size fixed the amount of raw materials that can be processed is the following: 6.25 kilograms (13.75 pounds) of lignin and 5.45 kilograms (12 pounds) of propylene oxide per batch. Additional materials used in the process include: potassium hydroxide as catalyst; toluene as solvent; and ethylene oxide, ethyl iodide, and epichlorohydrin as optional capping, blocking, or functionalization reagents. The product of the reaction is a mixture of hydroxypropyl lignin (HPL) and polypropylene oxide (PPO). The amount of product per batch is approximately 8 kilograms (17.6 pounds) of copolymer and 3 kilograms (6.6 pounds) of homopolymer. A Wood Fractionation Pilot Plant will also be installed at the Thomas M. Brooks Forest Products Center which will produce Steam Explosion Lignin which will be used in the present process. This Plant using the Steam Explosion technology has been designed in a Master Thesis (Avellar, 1989). The methods of isolation and purification of lignin are described by Avellar, (1989).

This project will make available good quantities of HPL for testing in various end-use applications. However, the small size of this pilot plant and the characteristics of the equipment included in the plant will not give the exact information for a direct scale-up. An option could be the design of a second, larger pilot plant with equipment that can be easily scaled-up, before a full scale design is approached. In this work a preliminary design of an industrial plant

with capacity of 2 tons of lignin per hour, or approximately 10 thousands tons of lignin per year, is discussed. It is important to note that for a full scale plant the characteristics of the lignin used should be fairly constant to get a product of constant quality. The process should be designed to use a certain type of lignin, and if a new type of lignin needs to be used the process should be adjusted to the new conditions.

## *Chapter 2*

### *LITERATURE REVIEW*

In this chapter, a review of the state-of-the-art of the lignin propoxylation reaction as well as the homo-polymerization of propylene oxide is presented.

Lignin, the phenolic polymer matrix in which cellulose fibers are embedded in wood, is a high-impact strength, thermally resistant thermoset polymer which performs best in combination with highly crystalline cellulosic fibers (Wu, 1984). Lignin formation, chemistry, structure, analysis, and utilization is discussed in several texts and reports (Sarkanen, 1968; Freudenberg, 1968; Glasser, 1980). The development of lignin-containing copolymers has substantial potential, mainly due to the possibility of biodegradation of the plastics derived from lignin. The ever increasing difficulties associated with solid refuse disposal is one of the concerns that is driving this area of research.

The complex and heterogeneous nature of lignin is now well recognized. This complex nature has its origin in the complex mechanism of formation, the coupling of radical isomers and secondary condensation reactions. Additional complications for the characterization of lignin result during the isolation of lignin from the tree. All isolation processes are a balance between two goals, high yield and representative chemical structure, both mutually exclusive.

An incomplete knowledge of the exact chemical structure of lignins has hampered its utilization. Better methods for analyzing lignin, both quantitatively and qualitatively are needed. Also, the ultrastructural distribution of lignin in the cell wall needs yet to be elucidated. Fortunately, for the utilization of lignin and its derivatives the uncertainties about structure are not as much of a handicap as they are for the research in synthesis, biological role in the plant, or degradation of native lignin. Lignin derivatives are formulated to overcome the insoluble nature of isolated lignin. The most common industrial derivative is a lignin sulfonate, a water soluble by-product of sulfite pulping. Lignin can also be

modified by oxyalkylation giving polyols which can become components of polyurethanes network polymers. The conversion of lignin into polyol can be achieved by treatment with 1,2 alkene oxide, 1,2 alkene sulfide, or 1,2 alkene carbonate (Glasser, 1982).

### 2.1 Hydroxypropyl lignin

Oxyalkylation of lignin with propylene oxide (PO), or hydroxypropylation, has been performed under different conditions. Hydroxypropylation of lignin is a modification reaction that gives a more uniform product while, at the same time, reducing the modulus of lignin by its combination with PO. Hydroxypropyl lignins, HPLs, are soluble in most polar or protic organic solvents; they contain a single functional group (secondary hydroxyls); and they possess a lower glass transition temperature than the parent lignin (Wu, 1984). The synthesis of poly(oxyalkylene) polyols from lignin and tannin was patented in 1971, by Christian et al. In that process lignin was treated with PO at 150°C and then the polyol was mixed with CFCL<sub>3</sub>, diethylethanolamine, and phenyl isocyanate giving a foam. In 1977, Glasser and Hsu, patented the synthesis of polyurethanes from lignin. They treated lignin first with maleic anhydride and then with PO, followed by reaction with 2,4 toluene diisocyanate.

In 1979, Mozheiko et. al., published the preparation of polyurethanes from oxypropylated lignin. They reacted hydrolysis lignin and lignosulfonates with PO, using glycerol as solvent, and potassium hydroxide as catalyst. The reaction was carried out in a stainless steel autoclave at 140 °C and a pressure up to 25 atm. (374 psi). Hydroxypropyl lignin was then reacted with phenylisocyanate and the reactivity of modified lignins was shown to be significantly increased with respect to parent lignins, which means that hydroxypropyl lignins are suitable for use in the preparation of polyurethane foams and coatings. In this work, the following overall kinetic equation is given for the reaction of PO with guaiacol, in the presence of glycerol:

$$-\frac{d[\text{PO}]}{dt} = \{ k_1 [\text{ArOH}] + k_2 [\text{ROH}] \} [\text{ArONa}] [\text{PO}], \quad 2.0$$

where  $k_1$  is the reaction constant for the interaction between PO and guaiacol and  $k_2$  is the reaction constant for the interaction between PO and the solvent, glycerol.  $k_1$  is approximately 35 times higher than  $k_2$ .

The kinetics of the propoxylation reaction has been studied by Glasser and Wu, in 1984. They studied the reaction of lignin model compounds and parent lignin with PO. According to the results obtained, the compounds analyzed can be arranged in three groups. In the first group, where benzoic acid was used, no reaction was observed due to the neutralization of KOH by the acidic functionality; in the second group, where guaiacol, vanillyl alcohol, or cinnamyl alcohol was used, the reaction was very rapid; and in the third group, where vanillic, syringic, or p-hydroxybenzoic acid was used, the reaction showed two distinct phases, a slow copolymerization phase that ended when the acidic functionality had been consumed, and a rapid homo-polymerization phase. The reaction of PO with these lignin-like model compounds had the following overall kinetic equation,

$$-\frac{d[\text{PO}]}{dt} = \sum_i k_i [\text{R}_i\text{O}^-] [\text{PO}], \quad 2.1$$

where  $k_i$  is the rate of propoxylation of the  $\text{R}_i\text{O}^-$  anionic species. The reaction of PO with lignin followed this last sequence that is, a minor initial copolymerization and a major subsequent rapid homo-polymerization reaction. The acidic functionality of lignin retarded the onset of the homo-polymerization reaction. Hydroxypropylation of kraft lignin was done in a batch reactor under alkaline conditions at 180 °C, using KOH as a catalyst. A 1-1.5 mL PO/g lignin was enough to produce a propoxylated lignin. The isolation of the copolymer was possible by liquid-liquid extraction.

In 1987, Glasser reported the kinetics of the propoxylation reaction for organosolv lignin. An amount of organosolv lignin equivalent to 120 meq of OH was reacted with PO in the presence of 120 mmole of KOH in an inert solvent (toluene) at 120 °C. It was found that the lignin propoxylation is a first order reaction in PO, with three distinct reaction phases, an 'induction period', an 'initial phase' and a 'final phase'. The induction period decreases as the

temperature and/or the amount of catalyst increases. The induction period, which is not related to KOH dissolution, could be related to the formation of oxyanion species reactive with PO. In the initial phase, the rate constant of the reaction varies with temperature and KOH concentration. The rate constant of the final phase is about four times that of the initial phase, and it varies significantly with temperature. It has an activation energy of  $42.7 \cdot 10^3$  J/mol (10.2 kcal/mol) (Zhang and Glasser, 1987). The rate of reaction does not depend upon the amount of catalyst below or above equimolar KOH:OH ratios (Zhang and Glasser, 1987). The following values of the constant of reaction were reported:

$k_i = 1.54 \cdot 10^{-3} \text{ hr}^{-1} = 4. \cdot 10^{-7} \text{ sec}^{-1}$  for the initial phase, and

$k_{f1} = 4.4 \cdot 10^{-6} \text{ sec}^{-1}$ ,

$k_{f2} = 4.9 \cdot 10^{-6} \text{ sec}^{-1}$ ,

$k_{f3} = 6.2 \cdot 10^{-6} \text{ sec}^{-1}$ ,

$k_{f4} = 7.4 \cdot 10^{-6} \text{ sec}^{-1}$ ,

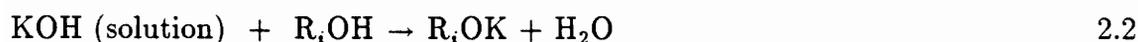
$k_{f5} = 8.8 \cdot 10^{-6} \text{ sec}^{-1}$ ,

$k_{f6} = 9.6 \cdot 10^{-6} \text{ sec}^{-1}$ , and

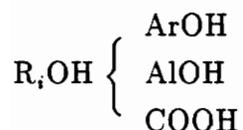
$k_{f7} = 1.14 \cdot 10^{-5} \text{ sec}^{-1}$  for each one of the final phases.

This report stated that it is possible to propoxylate lignin to any degree of molar substitution without requiring an intermediate isolation of the reaction product. It is important to point out that the physical characteristics of the HPLs obtained are somewhat dependent on the lignin origin and the extraction process. The pilot plant here designed can be used to characterize, under identical conditions, the different products obtained as different types of lignin are reacted. Bagasse lignins have the highest acidic functional and they produce the highest HPL conversion.

Following is given the reaction mechanism for the lignin propoxylation reaction. First, lignin is contacted with a KOH solution, that is,



where  $\text{R}_i\text{OH}$  can be an aliphatic hydroxyl group, a phenolic hydroxyl group or a carboxy group.



At this point water is removed by azeotropic distillation. Then, PO is injected and the following reaction takes place,



Phenolic hydroxyls are the most reactive. After they are consumed, carboxyl groups and aliphatic hydroxyls react with PO. If there were water in the system the following reaction can take place,



This reaction produces free KOH which can initiate the PO homopolymerization.

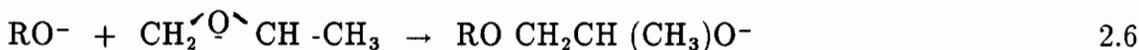
## 2.2 Polypropylene Oxide

In the production of HPL, the homo-polymerization of PO is a competitive reaction. A review of the homo-polymerization process is given next. The ring-opening polymerization of cyclic monomers, such as PO, proceeds either by step- or chain-growth mechanism, depending on the reaction conditions and the initiator employed (O'dian, 1981). The polymer obtained is the same regardless of the polymerization mechanism. Ring-opening polymerizations can be initiated by ionic initiators or by molecular species. Ionic initiators are usually more reactive than molecular ones. The chain growth process in ionic ring-opening polymerization shows similar characteristics to ionic chain polymerization, only monomers add to the growing chain. However, ring-opening polymerization can also have same characteristics of step-growth polymerization. The classification of a ring-opening polymerization as a chain- or step-growth polymerization can be made on two bases. One is the distribution of the polymer molecular weight with time. On this basis, ring-opening polymerization is similar to step-growth polymerization, in that the polymer molecular weight increases

slowly. The other basis is the kinetic law that describes the reaction. On this second basis, many ring-opening polymerizations have kinetic expressions that follow those of either chain- or step-growth polymerization. Epoxide polymerizations can be described in terms of three different mechanisms: anionic (base catalysis), cationic (acid catalysis), and coordinate. Following is reviewed the anionic homo-polymerization.

Many epoxide reactions are initiated by the hydroxide group of an alcohol. An exchange reaction occurs between the alcohol and the propagating chain. The initiation step is slow under this conditions. The degree of polymerization increases, and the molecular weight distribution broadens. The polymerization rate, however, is not affected. The reaction mechanism is the following, (Gee, 1961):

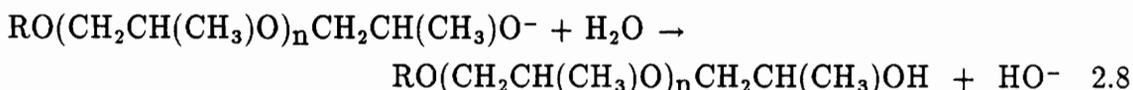
Initiation:



Propagation:



Termination:



Chain transfer:



Byproducts:



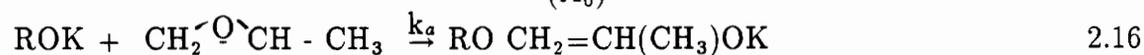
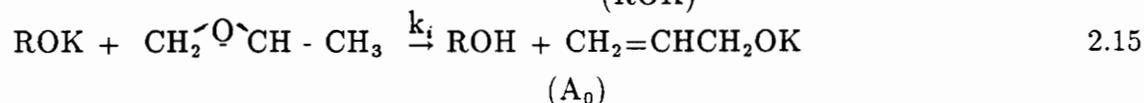
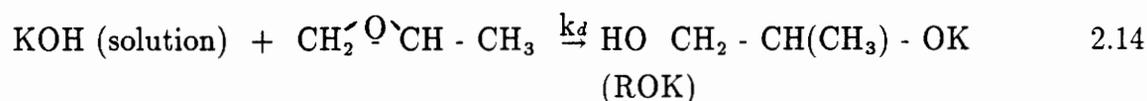
In the reaction of higher alcohols with epoxides employing different kinds of alkoxide catalysts, various rate constants are observed (McAdams, 1985). Higher rate constants are obtained with the more basic alkoxides  $\text{tert-C}_4\text{H}_9\text{OK} > \text{tert-C}_4\text{H}_9\text{ONa} > \text{KOH} > \text{RONa}$ . The following rate equation,

$$-\frac{[\text{PO}]}{dt} = k [\text{cat}] [\text{PO}] \quad 2.12$$

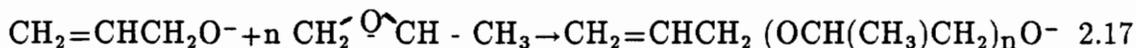
holds for a wide range of catalysts and monomer concentration. It was demonstrated that the formation of unsaturation is a consequence of the isomerization of PO to allyl alcohol. The amount of unsaturation increases with temperature rising and catalyst concentration declining. Monofunctional polyethers with unsaturation act as plasticizers in urethanes and adversely affect polyurethane foam properties. For the manufacture of these polyols, continuous tubular reactors or semibatch autoclaves are used (McAdams, 1985). In a semibatch operation, initiator and catalyst are charged into the reactor and PO is added continuously until the desired molecular weight is obtained. The batch autoclave is the more versatile, while the tubular reactor needs to be inconveniently long. In order to make the polyol in a reasonable amount of time, high temperatures and pressures are used. Glycerol or another initiator system is charged to the autoclave. KOH is then added, and the reactor is pressurized with nitrogen to 446 kPa (50 psig). Then, the reactor is evacuated to 8 kPa (60 mm Hg), heated to 105 °C, and the required amount of water is removed by stripping. PO is added at constant rate (600-900 g oxide per hour per mole initiator) in 5 hours: the pressure is not allowed to exceed 722 kPa (90 psig). The mixture is kept for 3 more hours after the addition is complete, and the time-temperature curve should become constant. The mixture is cooled to 50 °C and discharged into a nitrogen filled bottle. The catalyst can be removed by ion-exchange resin or by neutralization. The polyol is passed through a column packed with an ion-exchange resin to remove the potassium hydroxide. This method can be applied to virtually all polyols, but it is more effective for low molecular weight polyols. Alternatively, residual PO and alkali can be removed by neutralization with an organic or an inorganic acid such as  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , or carbonic acid (Gehm, 1974) followed by filtration. This method is efficient and

removes the catalyst to a concentration of less than 2 ppm. However, the disposal of the filter cake, which contains an equal weight of polyol, makes this method less attractive. This method is not as effective with low molecular weight or hydrophilic polyols. However, it is used when the viscosity of the polyol permits rapid filtration of the polyol. In contrast, the method of ion-exchange reduces the problem of disposal, but a solvent is required which must be removed. A third alternative is to use water to remove the catalyst. The polyol is dissolved in toluene, the KOH is dissolved in water, and the organic and aqueous phases are separated in a continuous centrifuge. The methods for the catalyst removal are discussed for their application in the separation of the HPL from the catalyst in *Chapter 8, Process Selection*.

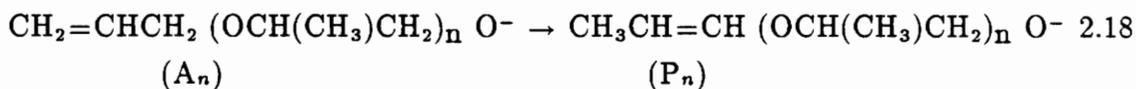
In 1956, Dege proposed the generalized mechanism of polymerization on commercial scale. Another way of polymerization of alkene oxides involves use of anhydrous KOH, in the absence of hydroxylic initiators, Pierre 1956. Several features of the polymerization in the presence of anhydrous KOH are different from the commercial process: (1) the polymerization rate is much higher; (2) the average molecular weight is relatively constant throughout the polymerization; (3) NaOH and LiOH are ineffective catalyst while KOH, RbOH, and CsOH are effective (Snyder, 1961). The following reaction sequence was proposed by Steiner (1964). They showed that no basic change in mechanism is necessary to account for the change in characteristics of the two polymerization systems. The mechanism includes initiation,



propagation,



and isomerization,



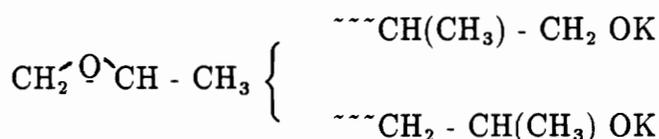
The reaction kinetics proposed by Steiner is the following:

$$-\frac{d[\text{PO}]}{dt} = k_d [\text{KOH}] [\text{PO}] + k_i [\text{ROH}] [\text{PO}] + k_i [\text{A}_0] [\text{PO}] + k_a [\text{PO}] [\text{ROK}] + \\ + \sum_{n=1}^6 k_a [\text{PO}] \text{A}_n + \sum_{n=1}^6 k_a [\text{PO}] \text{P}_n \quad 2.19$$

The reaction proceeds readily at room temperature. PO was polymerized using powdered, anhydrous KOH which was placed in a stainless steel bomb. The bomb was flushed with nitrogen capped and maintained at 30°C. After the desired amount of time (usually the reaction is completed in 60 hours) the mixture was neutralized with hydrochloric acid. After complete neutralization, the volatile materials were removed by evaporation using a rotative evaporator. The residue was dissolved in hexane and centrifuged to remove KCl. This procedure eliminates the possibility of hydrolysis of propenyl ethers since the mixture never becomes acidic, and contact with water is minimal. It was reported that the rate of polymerization is independent of amount of solid catalyst, as long as there is an excess of catalyst. The conversion of the reagents for different mole ratio of KOH to PO was computed, and no significant change in the reaction rate was found. This situation rules out the possibility of any significant amount of surface catalysis. The polymer obtained was a viscous tar with an average molecular weight of 2000-3000. The molecular weight distribution was extremely broad. The lowest molecular weight was about 600 kg/kmol and the highest 31000 kg/kmol. No undissolved KOH was detected after the reaction. The catalyst concentration seems to be a rate determining factor in PO homo-polymerization. However, if the amount of KOH is higher than 2.6 mmol/mol PO no further increase in reaction rate was observed. A competing

reaction occurs in the base-catalyzed polymerization of PO, and this is the formation of an unsaturated end group. The amount of unsaturation formed increases as the temperature increases and as the molecular weight of the polymer increases.

Since PO is an unsymmetrical epoxide its polymerization can follow two different ways of propagation:



The final structure will be the same for both cases, except at the end groups. Some studies indicate that when the epoxide ring is opened using an alkaline catalyst a secondary alcohol is formed almost exclusively. Primary hydroxyls are much more reactive than secondary hydroxyls.

Other natural polymers are modified by grafting polymerization. Grafting of cellulose, starch, amylose, wool, silk, rubber, etc. with vinyl monomers has been studied extensively (Millich, 1977). Grafting is an effective means of increasing wet-tenacity, wash-and-wear property, and rot and mildew resistance of cellulosic materials. The most important practical problem concerns the homo-polymerization which takes place simultaneously with graft polymerization. The application of interfacial polymerization eliminates under appropriate conditions the problem of homo-polymerization. But interfacial polymerization produces only superficially modified polymers, then it is not an appropriate method of reaction for our system.

To favor copolymerization over homo-polymerization, and to reduce the unsaturation, it is convenient to perform the polymerization reaction: (a) at low temperature; (b) with a minimal amount of PO; and (c) using a lignin with a high content of acidic functionality.

### Chapter 3

## CHEMICAL AND PHYSICAL DESCRIPTION OF THE PROPOXYLATION REACTION

This chapter describes the chemical and physical characteristics of the lignin propoxylation reaction and it outlines the process model. The chemical composition and structure of lignin and hydroxypropyl lignin are given first. The characteristics of the propoxylation reaction are presented next, and these are followed for a compilation of reaction conditions that minimize the effect of a competitive reaction. Then, the physical description of the reaction process is presented. The steps that conduct to the design of the polymerization process are finally enumerated.

### 3.1 Chemical Description

The multifunctional polydisperse nature of lignin makes the reaction with propylene oxide (PO) a very complicated one. Lignin can be represented by a monomeric phenylpropane unit, called the C<sub>9</sub>-unit, which is shown in Figure 3.1. The composition of an average C<sub>9</sub>-unit, in terms of functionality is summarized below for steam explosion lignin.

Table 3.1 Composition of the average phenylpropane unit  
( C<sub>9</sub>-unit basis)

|        | Total<br>H | Aromat.<br>H | Total<br>OH | Phe.<br>OH | OCH <sub>3</sub> | Total<br>CO |
|--------|------------|--------------|-------------|------------|------------------|-------------|
| barley | 8.42       | 1.98         | 1.12        | 0.61       | 0.64             | 0.33        |
| poplar | 7.75       | 2.01         | 1.11        | 0.48       | 0.97             | 0.21        |
| aspen  | 7.00       | 2.10         | 1.14        | 0.49       | 1.11             | 0.15        |

A C<sub>9</sub>-unit is composed of approximately eight hydrogen atoms, two of which are aromatic; one hydroxyl group, which sometimes is an aromatic hydroxyl

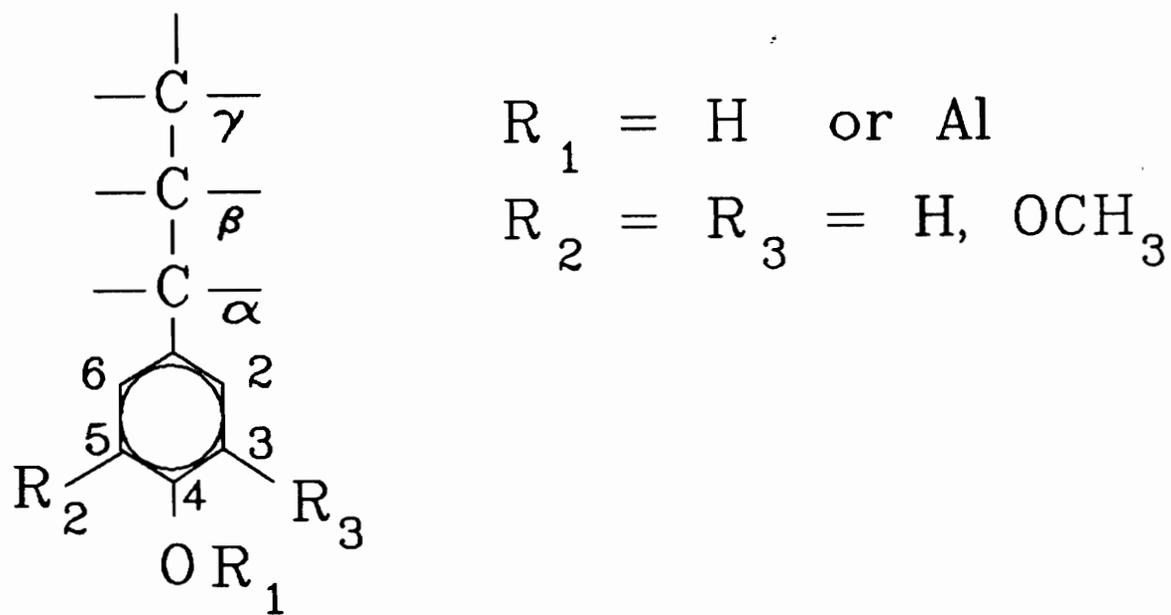


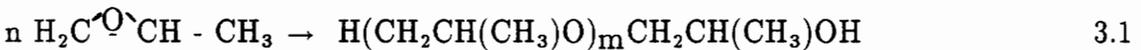
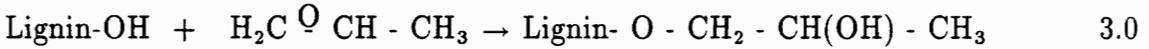
Figure 3.1 Structure of a monomeric  $C_9$ -unit.

group; one methoxyl group; and one of every five C<sub>9</sub>-units has a carbonyl group. These C<sub>9</sub>-units are linked together by different bonds forming the lignin molecule. The approximate linkage distribution per 100 C<sub>9</sub>-units is given below (Glasser, 1983). Al-5 represents a linkage between an aliphatic carbon atom and a carbon-5 in the aromatic ring. Al-2/6 represents a linkage between an aliphatic carbon and a carbon-2 or -6 in the aromatic ring. 1/5-5 is a biphenyl connection of the type 1-5 or 5-5. Al-O-4 represents an alkyl aryl ether linkage.

Table 3.2 Approximate linkage distribution of steam explosion lignins per 100 C<sub>9</sub>-units

|        | Al - 5 | Al - 2/6 | 1/5 - 5<br>4 - O - 5 | Al - O - 4 |
|--------|--------|----------|----------------------|------------|
| barley | 5 - 8  | 8 - 12   | 25 - 35              | 4 - 8      |
| poplar | 2 - 6  | 4 - 6    | 15 - 20              | 8 - 12     |
| aspen  | 2 - 5  | 6 - 8    | 17 - 22              | 28 - 32    |

The reaction between PO and lignin produces a copolymer hydroxypropyl lignin (HPL) plus a homopolymer polypropylene oxide (PPO). That is,



The schematic structure of an HPL molecule is given in Figure 3.2. This schematic structure was constructed based on the composition of a typical steam explosion lignin. The lignin composition, in terms of functionality is given below.

Table 3.3 Composition of the lignin model ( Mw : 905 kg/kmol)

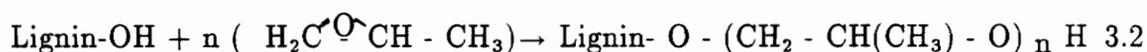
|                        | Total<br>H | Aromat.<br>H | Total<br>OH | Phe.<br>OH | OCH <sub>3</sub> | Total<br>CO |
|------------------------|------------|--------------|-------------|------------|------------------|-------------|
| 5 C <sub>9</sub> units | 50         | 13           | 4           | 3          | 5                | 1           |
| 1 C <sub>9</sub> unit  | 10         | 2.6          | 0.8         | 0.6        | 1                | 0.20        |



Table 3.4 Composition of the HPL model ( Mw : 1,200 kg/kmol).  
Structure of Figure 3.2

|                        | Total<br>H | Aromat.<br>H | Total<br>OH | Phe.<br>OH | OCH <sub>3</sub> | Total<br>CO |
|------------------------|------------|--------------|-------------|------------|------------------|-------------|
| 5 C <sub>9</sub> units | 85         | 13           | 5           | 0          | 5                | 1           |
| 1 C <sub>9</sub> unit  | 17         | 2.6          | 1           | 0          | 1                | 0.20        |

The degree of substitution, defined as the average number of separate functional groups that react with PO per C<sub>9</sub>-unit, is between 0.9 and 2.6. The molar substitution, defined as average number of moles of PO per hydroxyl functional group, is approximately 1.0 (Glasser, 1984). These low substitution levels imply that only between one and two functional groups per average phenylpropane lignin building unit react with PO, and that no chain extension occurs. It is apparent that carboxy and phenoxy groups react prior to other groups. If more than one PO reacts with each hydroxide group, the reaction is:



The product is chain extended hydroxypropyl lignin (CEHPL). Its structure is given in Figure 3.3.

It is desirable to avoid the formation of all PPO. To decrease the amount of PPO homopolymer formed in favor of HPL formation, it is necessary to perform the reaction with a minimum amount of KOH, or to avoid the presence of free KOH. The homo-polymerization occurs at temperatures higher than 85°C, and it is very fast at 150°C (Wu, 1984). It is therefore convenient to work at low temperatures. Lower temperatures are also conducive to keeping PO dissolved in the liquid phase; and they help reduce the amount of unsaturation. But the reaction gets very slow at low temperatures which calls for a compromise between expediency and side reactions.

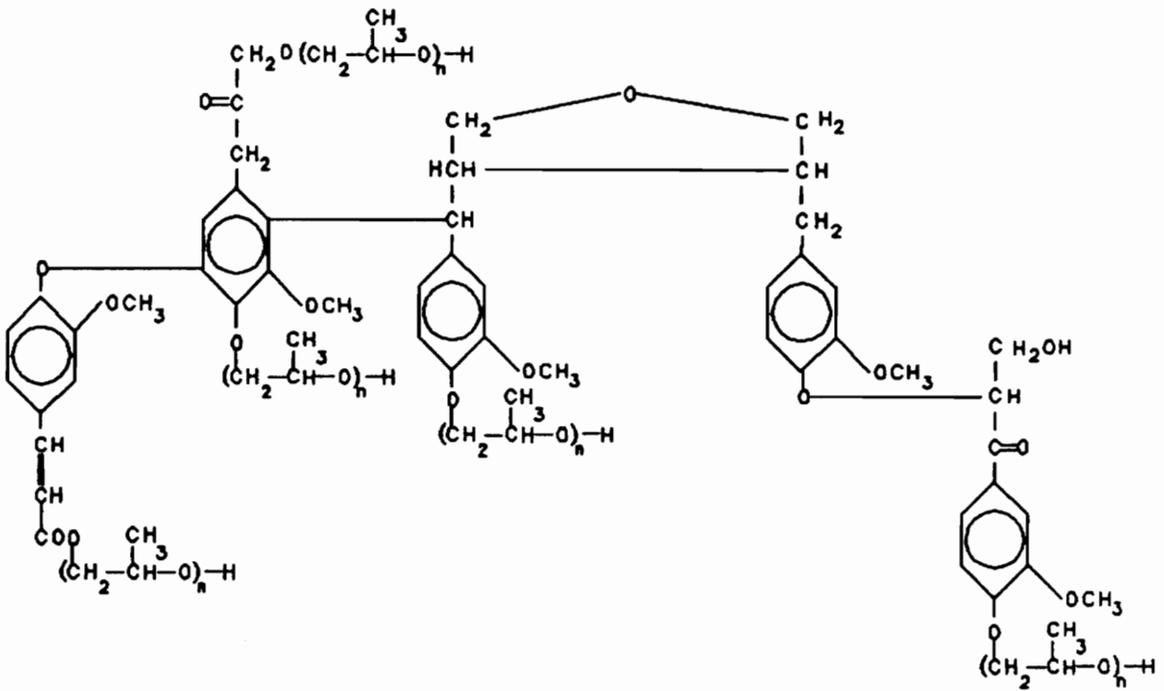


Figure 3.3 Structural scheme of chain extended hydroxypropil lignin (CEHPL).

The reactions that take place can be described as,



where A is lignin, B is PO,  $P_1$  is HPL, and  $P_2$  is PPO. Several kinetic equations have been presented in the *Literature Review*. The overall kinetic equation for the reaction of PO with lignin-like model compounds has the character of a second order reaction, first order in PO and first order in the anionic species. A report by Zhang and Glasser (1987), provides a kinetic equation for the reaction of lignin with PO, and this is a first order reaction in PO. We will consider the two reactions combined, that is,



where P is the reaction product, including HPL and PPO. Since lignin, (A), is in excess and it was found that there is no catalyst effect on the rate, (over a limit of 1mmol of KOH per meq HPL<sub>OH</sub> the rate is independent of catalyst) the reaction results in a pseudo-first order reaction in PO, component B, that is,

$$-\frac{d C_B}{dt} = k C_B . \quad 3.6$$

This kinetic equation will be the basis for the kinetic process model.

### 3.2 Physical Description

The physical system considered in this study is an Isothermal Stirred Tank Reactor. The temperature is constant throughout the reaction; or it is set constant for each reaction phase. A liquid phase, maintained batchwise within the reactor, is contacted with gaseous PO supplied intermittently at a rate approximately equal to PO-consumption. The reagent delivery system consists of a pressure transducer in combination with an electronic process controller, three reagent cylinders connected through a 4-way valve, and a strip chart recorder monitoring temperature and pressure. A schematic drawing of the reactor is given in Figure 3.4. Initially, the reactor is loaded with lignin (component A) and KOH (catalyst) suspended in toluene. Another alternative is to stir lignin

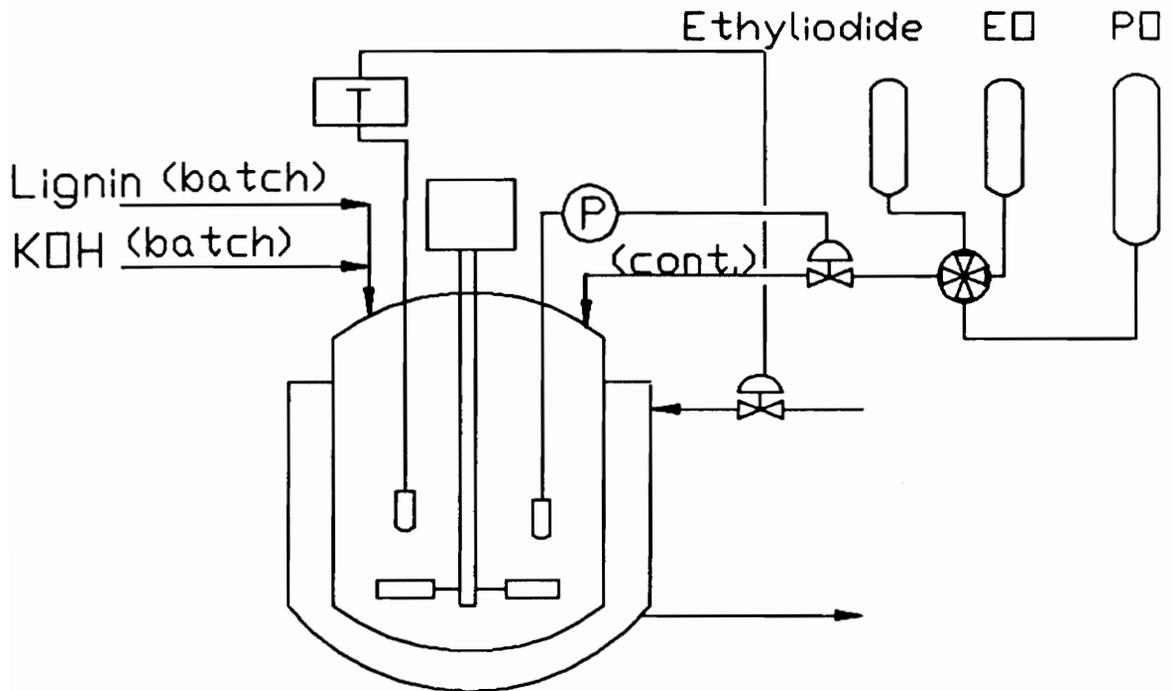


Figure 3.4 HPL polymerization reactor.

into an aqueous KOH solution to a target final pH, for example pH 11.5, followed by neutralization of the KOH with CO<sub>2</sub>, and spray drying. This mixture is distilled azeotropically to remove water. The reactor is then evacuated. Finally, the reactor is closed and the injections of PO start. Other reagents, like ethylene oxide, can be added as different options. When the reagent gas is added to the reactor, it is transported by gas-to-liquid transfer to the liquid phase where chemical reactions occur. After the first PO injection, a pressure limit is reached, and the following injections maintain this pressure.

The lignin propoxylation reaction is an exothermic reaction. When the reaction is carried out in a batch mode it is difficult to maintain a constant temperature. On the contrary, the heat removal is not a problem under the present conditions, that is using a semibatch process.

### *3.3 Conclusions*

The reaction of lignin with PO giving HPL and PPO can be considered a first order reaction under present conditions. The existing process is semibatch. Lignin, the catalyst, and the solvent are conducted in a batchwise manner with PO and eventually EO being injected over the course of the reaction. The temperature needs to be kept as low as possible, at a compromise value resulting in a balance between reaction rate and PPO formation. Depending upon pressure and temperature, PO and toluene are distributed in the two phases, vapor and liquid. The lignin propoxylation reaction occurs in the liquid phase, only.

A model of the reaction process is developed in *Chapters 4 to 6*. To solve the model equations for the process modelling it is necessary to know:

- The reaction kinetics.
- The process characteristics.
- The reagents initial concentration in the two phases.

The chemical description of the reaction, the kinetic equation and the physical description of the reaction process were presented in this chapter. The concentration distribution of the reagents must be determined in order to model the process. Since the kinetic equation is dependent only upon PO, the balance equations will be developed for this component. The PO-toluene vapor-liquid

equilibrium needs to be solved in order to determine the PO concentration. The vapor-liquid equilibrium analysis is given in *Chapter 4*. The equations for modelling a semibatch polymerization process are presented in *Chapter 5*. Finally, the predicted response of process variables is correlated with experimental data in *Chapter 6*.

*Chapter 4*  
**VAPOR-LIQUID EQUILIBRIUM ANALYSIS**

Two phases, vapor and liquid, are present in the lignin propoxylation reaction, at the temperature-pressure conditions of the process. In this chapter the vapor-liquid equilibrium of the lignin propoxylation reaction is analyzed. Although the system is out of equilibrium during the reaction, it is important to know the equilibrium composition for different pressure and temperature conditions, at each point in time. The process model of the reaction requires knowledge of the composition in both phases of the system, which can be calculated solving the vapor-liquid equilibrium. The results of this study will also contribute to the determination of the optimum working conditions for the lignin propoxylation reaction.

Several assumptions are made to allow the application of classical vapor-liquid equilibrium theory to the complicated reaction system. The assumptions are as follows:

- First the system analyzed is propylene oxide (PO) - toluene. It is assumed that the presence of lignin and catalyst does not have any influence on the equilibrium.
- It is also assumed that the pressure of the system is due to PO and toluene only. If there were nitrogen pressure, the vapor-liquid equilibrium must consider this third component as well.
- During the reaction a polymer soluble in toluene is produced and the results obtained here are no longer applicable. Phase equilibrium behavior involving polymers has not yet been well quantified in thermodynamic terms, but efforts are being made. A modified *fluid-lattice model* for vapor-polymeric liquid equilibrium is presented by Panayiotou (1986).
- After all PO has been injected, ethylene oxide feeding starts. The new two phases in equilibrium are the vapor, ethylene oxide-toluene, and the polymeric toluene solution. A vapor-polymeric liquid equilibrium has to be applied to the

new system to calculate the ethylene oxide concentration in both phases.

For a non-reacting system, the phase rule gives the number of variables that must be specified in order to fix the intensive state of a system at equilibrium. For a binary system ( $N=2$ ), with 2 phases ( $\pi=2$ ), the phase rule gives:

$$F = 2 - \pi + N = 2 - 2 + 2 = 2.$$

Two degrees of freedom, or two variables must be set to define the system. Given pressure and temperature at each point, by using the vapor-liquid equilibrium theory, the composition of the system can be computed in both the liquid and the vapor phase.

#### 4.1 Propylene oxide - toluene vapor-liquid equilibrium (ideal behavior)

First, let's assume an ideal liquid and an ideal gas. Then Raoult's law applies,

$$y_i P = x_i P_i^{sat} \quad i = 1, 2 \quad 4.0$$

where  $y_i$  is the molar fraction in the vapor phase,  $P$  is the total pressure,  $x_i$  is the molar fraction in the liquid phase, and  $P_i^{sat}$  is the saturation pressure of species  $i$ . In Equation 4.0  $i=1$  for PO and  $i=2$  for toluene. The saturation pressure is calculated using the Antoine vapor pressure equation,

$$\log P_i^{sat} = A - \frac{B}{T+C} \quad 4.1$$

where  $A$ ,  $B$ , and  $C$  are the Antoine constants. The Antoine constants for PO and toluene are taken from the literature (Gmehling). The experimental data was obtained by Glubbov (1977). The boiling points at different pressures can be calculated using the Antoine vapor pressure equation.

From Table 4.1, considering each component independently, at a work pressure in the range between  $2 \cdot 10^5$  and  $4.8 \cdot 10^5$  Pa (29 and 70 psia), and at a temperature in the range between 70 and 130°C, both toluene and PO are a mixture of

saturated liquid and saturated vapor.

Table 4.1 PO and toluene boiling points from the Antoine vapor pressure equation

| Pressure<br>atm/psia/bar | Boiling Points (°C) |       |
|--------------------------|---------------------|-------|
|                          | toluene             | PO    |
| 1/ 14.7 / 1.013          | 110.61              | 34.23 |
| 2/ 29.4 / 2.026          | 136.95              | 54.86 |
| 3/ 44.1 / 3.040          | 154.41              | 68.51 |
| 4/ 58.8 / 4.053          | 167.87              | 79.02 |
| 5/ 73.5 / 5.066          | 179.00              | 87.70 |

Actually, PO is injected at much more pressure,  $6.5 \cdot 10^5$  Pa (80 psig), at which it is in liquid phase. As it fills the head space of the reactor, it will reach its equilibrium composition according to the pressure and the temperature in the reactor.

Let's calculate the quantities and compositions of liquid and vapor phases making up a two-phase system at known pressure, temperature, and overall composition. The material balance equations are,

$$L + V = 1 \quad \text{and,} \quad 4.2$$

$$z_i = x_i L + y_i V \quad i = 1, 2, \quad 4.3$$

where,

$z_i$  : overall molar fraction,

$x_i$  : molar fraction in the liquid phase,

$y_i$  : molar fraction in the vapor phase,

L: moles of liquid over total moles, with mole fractions  $\{x_i\}$ , and

V: moles of vapor over total moles, with mole fractions  $\{y_i\}$ .

As a matter of convenience Raoult's law is written as,

$$y_i = K_i x_i \quad i = 1, 2, \quad 4.4$$

where,

$$K_i = P_i^{sat} / P.$$

Using these equations the molar fraction in the vapor can be written as,

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)}. \quad 4.5$$

Since  $\sum y_i = 1$ ,

$$\sum_i \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \text{ with } i = 1, 2. \quad 4.6$$

In a flash calculation temperature, pressure, and  $\{z_i\}$  are known. Therefore, the only unknown in Equation 4.6 is  $V$ , which can be obtained by trial. The solution to this ideal system for different sets of pressure and temperature is given below for a system with the following overall composition:  $z_1 = 0.3$  (or 6 moles of PO over 20 moles total) and  $z_2 = 0.7$  (or 14 moles of toluene over 20 moles total). The following table gives the vapor fraction,  $V$ ; the PO molar fraction in the vapor,  $y_1$ ; the liquid fraction,  $L$ ; and the PO molar fraction in the liquid,  $x_1$ . The toluene composition can be calculated as:  $y_2 = 1 - y_1$  for the gas phase, and  $x_2 = 1 - x_1$  for the liquid phase.

| Table 4.2 Results from the V-L flash calculation (ideal behavior) |                   |       |        |       |        |
|---|-------------------|-------|--------|-------|--------|
| Pressure<br>psia  | Temperature<br>°C | V     | $y_1$  | L     | $x_1$  |
| 44.1  | 110               | 0.058 | 0.7686 | 0.942 | 0.2714 |
| 44.1  | 120               | 0.245 | 0.6488 | 0.755 | 0.1872 |
| 44.1  | 130               | 0.467 | 0.5062 | 0.533 | 0.1195 |
| 44.1  | 140               | 0.892 | 0.3285 | 0.108 | 0.0642 |
| 58.8  | 130               | 0.186 | 0.6678 | 0.804 | 0.2102 |
| 58.8  | 140               | 0.403 | 0.5371 | 0.597 | 0.1399 |

Let's read at 44.1 psia and 130°C, the number of moles in the vapor is the total number of moles multiplied by the vapor fraction,  $V : 20 (0.467) = 9.34$  moles.

The number of moles in the liquid is the total number of moles multiplied by the liquid fraction,  $L: 20 (0.533) = 10.66$  moles.

The number of moles of PO in the liquid is the total number of moles in the liquid multiplied by the PO liquid fraction, that is:  $20 L x_1 = (20)(0.533)(0.1195) = 1.274$ .

The number of moles of PO in the vapor is the total number of moles in the vapor multiplied by the PO vapor fraction, that is:  $20 V y_1 = (20)(0.467)(0.5062) = 4.726$ .

The sum of the moles of PO in both phases gives the total PO in the system, that is :  $1.274 + 4.726 = (20)(0.3) = 6$ .

Similarly, the number of moles of toluene in the liquid is,

$$20 x_2 L = (20)(0.533)(0.8805) = 9.388,$$

which added to the moles in the vapor phase,

$$20 V y_2 = (20)(0.467)(0.4938) = 4.612,$$

gives the total toluene in the system, that is:  $9.388 + 4.612 = (20)(0.7) = 14$ , that we started with. Using the density of PO and toluene, we can calculate the approximate liquid volume. Then, we can obtain the vapor volume by subtracting the liquid volume from the total volume of the reactor, 1 gallon. Note that it is here assumed that the liquid density is constant with pressure, and that the volumes are additive. That is, the volume of PO in the liquid phase is:

$$\text{Volume of PO} = 1.274 \text{ MwPO} / \rho_{\text{PO}} = 87.2 \text{ ml},$$

and the volume of toluene in the liquid phase is:

$$\text{Volume of toluene} = 9.388 \text{ MwT} / \rho_{\text{T}} = 1061.8 \text{ ml},$$

giving a total liquid volume of:  $87.2 \text{ ml} + 1061.8 \text{ ml} = 1149 \text{ ml}$

and a total vapor volume of:  $3785 \text{ ml} - 1149 \text{ ml} = 2636 \text{ ml}$

It is then possible to calculate the concentration of PO in the liquid phase:

$$C_{\text{PO}} = 1.274 \text{ moles} / 1149 \text{ ml} = 1.189 \cdot 10^{-3} \text{ kmol/m}^3.$$

Using vapor-liquid equilibrium the composition of a system in equilibrium can be

calculated. The next step is to introduce non-ideal vapor-liquid equilibrium behavior.

#### 4.2 Propylene oxide - toluene vapor-liquid equilibrium (non-ideal behavior)

The equilibrium between phases requires equality of temperature, pressure, and partial fugacities of individual components throughout the system (Walas, 1985). That is:

$$T_v = T_l \quad 4.7$$

$$P_v = P_l \quad 4.8$$

$$f_{i,v} = f_{i,l} \quad 4.9$$

where  $i = 1$  for PO and  $i = 2$  for toluene. The partial fugacity for the vapor phase,  $f_{i,v}$ , is given by:

$$f_{i,v} = y_i \Phi_i P \quad 4.10$$

where ,

$$\Phi_i = \frac{\phi_i}{\phi_i^{sat}} (PF)_i.$$

$\phi_i$  is the partial fugacity coefficient which can be derived from the equation of state applied to the system;  $\phi_i^{sat}$  is the fugacity coefficient of  $i$  as a saturated vapor;  $y_i$  is the molar fraction in the vapor phase;  $P$  the total pressure; and  $(PF)_i$  is the Poynting Factor defined as:

$$(PF)_i = \exp \left( \int_{P_i^{sat}}^P \frac{V_{i,l}}{RT} dP \right) \quad 4.11$$

which can be set equal to

$$(PF)_i = \exp \left( \frac{V_{i,l}}{RT} (P - P_i^{sat}) \right), \quad 4.12$$

for conditions remote from critical, which is the case analyzed here. In the equations above,  $V_{i,l}$  is the molar volume of  $i$ . The values of the Poynting Factor

(PF) for PO and toluene are calculated for different temperatures and low values of pressure using Equation 4.12 .

| Table 4.3 PO and toluene Poynting Factors. |        |      |        |       |        |
|--|--------|------|--------|-------|--------|
| Propylene Oxide                            |        |      |        |       |        |
| 80°C                                       |        | 90°C |        | 120°C |        |
| P(bar)                                     | PF     | P    | PF     | P     | PF     |
| 1  | 0.9924 | 1    | 0.9898 | 1     | 0.9790 |
| 10   | 1.0141 | 10   | 1.0109 | 10    | 0.9988 |
| Toluene                                    |        |      |        |       |        |
| 80°C                                       |        | 90°C |        | 120°C |        |
| P(bar)                                     | PF     | P    | PF     | P     | PF     |
| 1  | 1.0002 | 1    | 1.0016 | 1     | 0.9989 |
| 10   | 1.0355 | 10   | 1.0340 | 10    | 1.0288 |

As a good approximation the Poynting Factor can be taken equal to unity (ie., 1.0) for the range of pressure of 1 to 5 bars as in the present case . The partial fugacity for the liquid phase,  $f_{i,l}$ , is given by:

$$f_{i,l} = x_i \gamma_i P_i^{sat} \quad 4.13$$

where  $x_i$  is the molar fraction in the liquid phase,  $\gamma_i$  is the activity coefficient of component  $i$ , and  $P_i^{sat}$  is the saturation pressure of the component  $i$ . The equilibrium relation results then,

$$y_i \Phi_i P = x_i \gamma_i P_i^{sat}. \quad 4.14$$

At low to moderate pressures the partial fugacity of each component of the

mixture in the vapor phase and the fugacity of saturated vapor can be calculated from the simplest form of the virial equation of state (Smith and Van Ness, 1987). The partial fugacity for a binary system is,

$$\Phi_1 = \exp \frac{B_{11} (P - P_1^{sat}) + P y_2^2 \delta_{12}}{RT} \text{ and,} \quad 4.15$$

$$\Phi_2 = \exp \frac{B_{22} (P - P_2^{sat}) + P y_1^2 \delta_{12}}{RT} \quad 4.16$$

where  $\delta_{12} = 2 B_{12} - B_{11} - B_{22}$ . Values of the virial coefficients come from a generalized correlation, such as,

$$B_{ij} = \frac{R T_{ijc}}{P_{ijc}} (B^0 + w_{ij} B^1)$$

where,

$$w_{ij} = \frac{w_i + w_j}{2},$$

$$T_{ijc} = (T_{ic} T_{jc})^{1/2},$$

$$P_{ijc} = \frac{Z_{ijc} R T_{ijc}}{V_{ijc}},$$

$$Z_{ijc} = \frac{Z_{ic} + Z_{jc}}{2},$$

$$V_{ijc} = \left( \frac{V_{ic}^{1/3} + V_{jc}^{1/3}}{2} \right)^3,$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}, \text{ and}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}.$$

The physical and critical properties for PO are:

Mw : 58.08 kg/kmol.

$$T_{1c} = 482.2 \text{ K}$$

$$P_{1c} = 4.92 \text{ MPa (713.6 psia)}$$

$$V_{1c} = 186 \text{ m}^3/\text{kmol}$$

$$V_{1l} = 70.75 \text{ m}^3/\text{kmol},$$

and for toluene,

$$\text{Mw: } 92.14 \text{ kg/kmol.}$$

$$T_{2c} = 593.1 \text{ K}$$

$$P_{2c} = 4.21 \text{ MPa (610.6 psia)}$$

$$V_{2c} = 316.6 \text{ m}^3/\text{kmol}$$

$$V_{2l} = 106.85 \text{ m}^3/\text{kmol}.$$

The activity coefficients are calculated from the Wilson equation,

$$\gamma_1 = \exp \left( - \text{Ln} ( x_1 + \lambda_{12} x_2 ) + x_2 \left( \frac{\lambda_{12}}{x_1 + \lambda_{12}x_2} - \frac{\lambda_{21}}{\lambda_{21}x_1 + x_2} \right) \right) \quad 4.17$$

$$\gamma_2 = \exp \left( - \text{Ln} ( x_2 + \lambda_{21} x_1 ) - x_1 \left( \frac{\lambda_{12}}{x_1 + \lambda_{12}x_2} - \frac{\lambda_{21}}{\lambda_{21}x_1 + x_2} \right) \right) \quad 4.18$$

$$\text{where } \lambda_{12} = (V_{2l}/V_{1l}) \exp ( - A_{12} / R T ),$$

$$\text{and } \lambda_{21} = (V_{1l}/V_{2l}) \exp ( - A_{21} / R T ).$$

The parameters  $A_{12}$  and  $A_{21}$  are obtained from the literature (Gmehling et al). The Wilson equation serves very well in representing experimental data. Compared to the Van Laar equation, or the two-parameter Margules equation, the Wilson equation always gives as good results as the last two, and in many cases it even gives better results. The Wilson equation does not apply for immiscible liquids. This limitation has no significance in the present case.

For all compositions the system PO-toluene has boiling points between those of the pure substances. The experimental values of PO vapor-phase molar fraction versus the PO liquid-phase molar fraction at constant pressure, 1 atmosphere, are given in Figure 4.1. The experimental values of temperature versus PO molar fraction are given in Figure 4.2. In Figure 4.2  $x$  is the PO

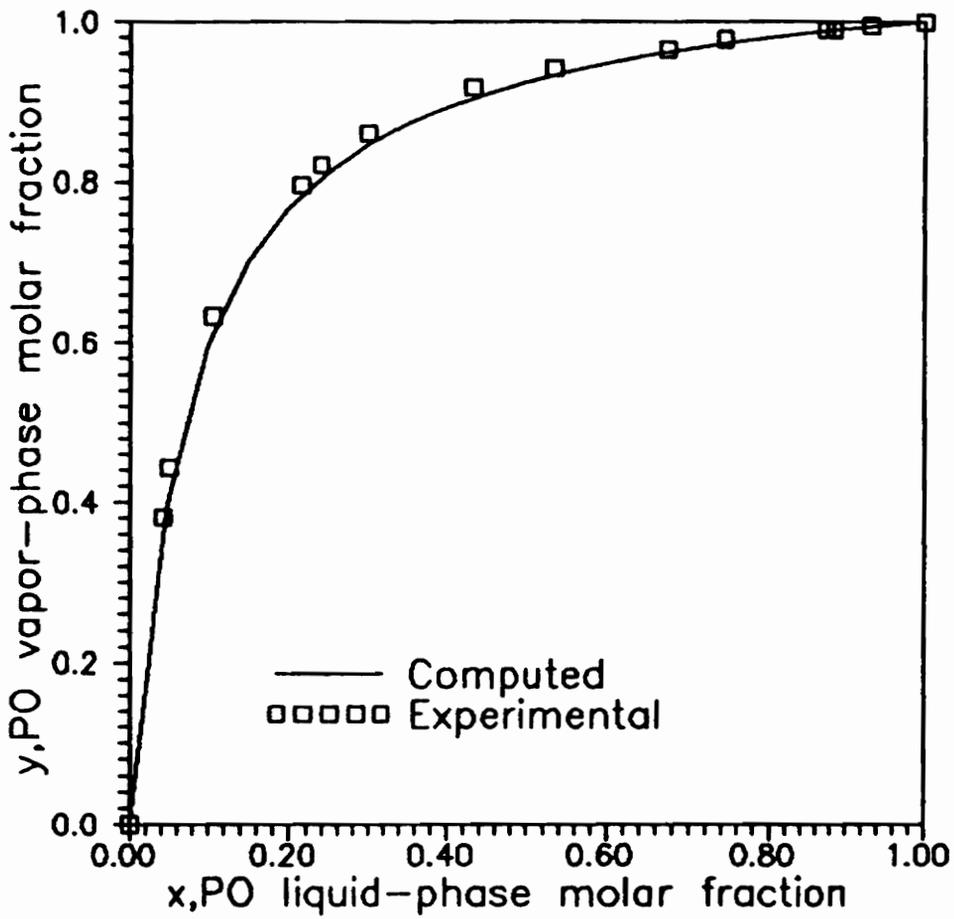


Figure 4.1 Vapor-liquid equilibrium PO-toluene,  $xy$  molar fractions.

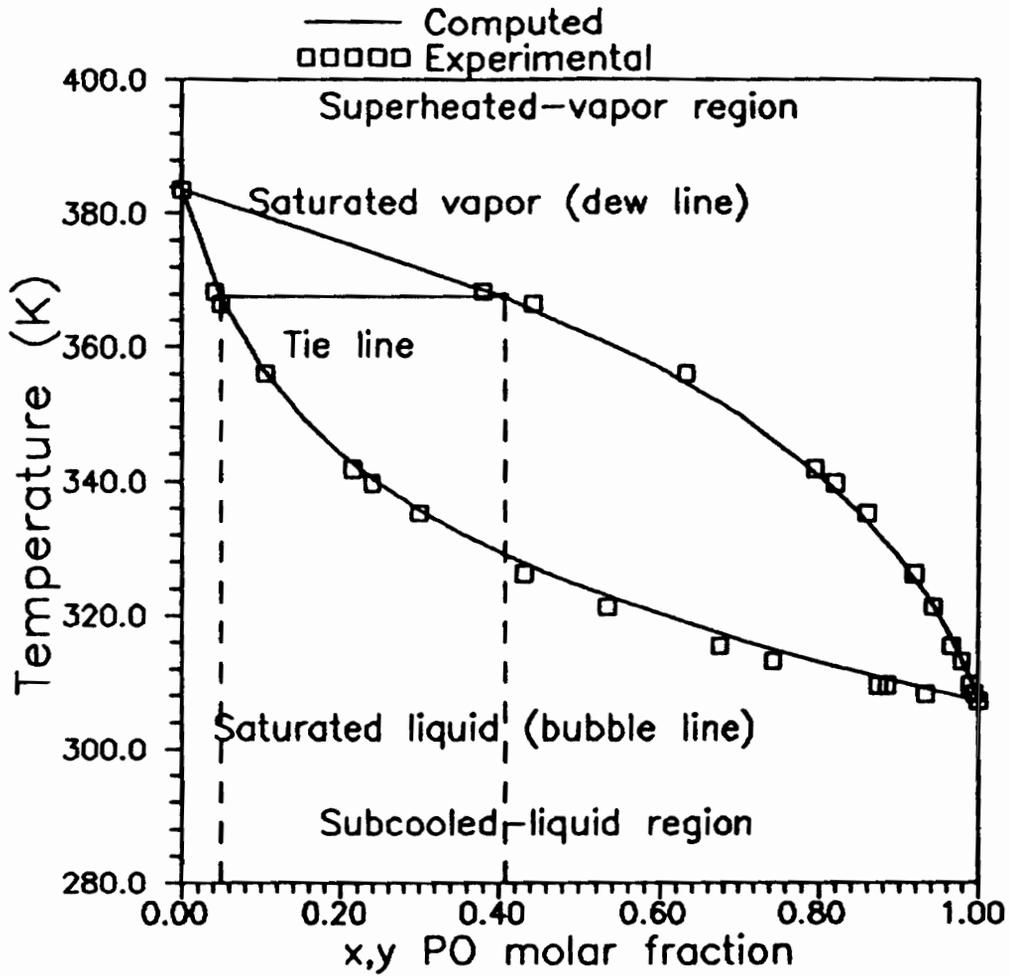


Figure 4.2 Vapor-liquid equilibrium PO-toluene, Txy diagram.

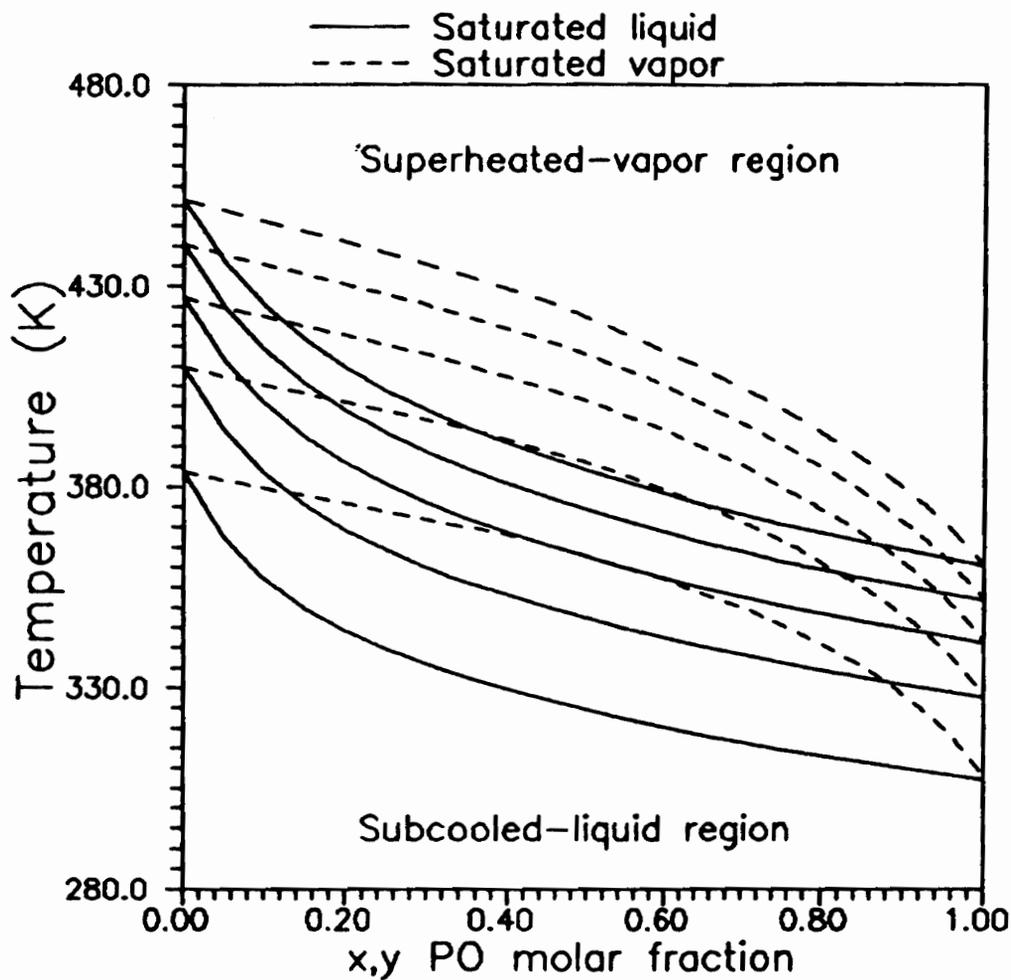


Figure 4.3 Txy diagram for five constant pressures.

molar fraction in the liquid phase and  $y$  the PO molar fraction in the vapor phase. From Figure 4.2, which is at 1 atmosphere of pressure, reading at a temperature of 95°C (368 K), the vapor-phase molar fraction of PO is 0.407 and the vapor-phase molar fraction of toluene is 0.593. In the liquid phase, at the same temperature, the molar fraction of PO is 0.05 and the molar fraction of toluene is 0.95. These are the extremes of the called tie line for 95°C. These experimental data were taken from the literature (Gmehling).

For low to moderate pressure we have the following relationships:

$$\Phi_i = \Phi ( T, P, y_1, y_2 )$$

$$\gamma_i = \gamma(T, x_1, x_2)$$

$$P_i^{sat} = P(T)$$

Given values of pressure and liquid-phase molar fraction,  $x_i$ , temperature and vapor-phase molar fraction,  $y_i$ , can be computed by bubble-temperature calculation. A Fortran program named BUBBLET, calculates the bubble temperature for the system PO-toluene. That is, given the composition in the liquid phase and the total pressure, the program calculates the composition in the vapor phase and the temperature. The calculated vapor-liquid equilibrium values are compared to the experimental data in Figures 4.1 and 4.2, for 1 atmosphere of pressure. To obtain information at higher pressures the program was run with different pressure values. The results are plotted for the five values of total pressure, from  $1.013 \cdot 10^5$  Pa (14.696 psia) to  $5.066 \cdot 10^5$  Pa (73.48 psia) in Figure 4.3. The Fortran code of the program BUBBLET is given in *Appendix C*.

The next step is to calculate the amount of PO and toluene in each phase at different conditions of pressure, temperature, and overall composition. This problem can be determined on the basis of Duhem's theorem, because two independent variables (temperature and pressure) are specified for a system made up of fixed quantities of the constituent species. The calculations are made with a Fortran program named FLASH. Since it is not known in advance whether the system is in fact a mixture of saturated liquid and saturated vapor and not entirely vapor or entirely liquid, the program makes preliminary

calculations to establish the nature of the system. The dew-point pressure and the bubble-point pressure are calculated and it is checked whether the given pressure is in between the two values. The flash calculation is only performed if the given pressure lies in between the dew-point pressure and the bubble-point pressure. The inputs to the program are pressure, temperature and  $z_i$  (the overall composition); and the outputs are  $x_i$  (the molar fraction in the liquid),  $y_i$  (the molar fraction in the vapor),  $V$  (moles of vapor over total moles), and  $L$  (moles of liquid over total moles). The Fortran code of the program FLASH is given in *Appendix D*. Table 4.4 shows the results of a flash calculation for the system PO-toluene for two sets of different overall composition. The overall compositions used in this table are  $z_1 = 0.3$  and  $z_2 = 0.7$ , corresponding to the initial charge of 400 ml of PO and 1500 ml of toluene, and  $z_1 = 0.14$  and  $z_2 = 0.86$  corresponding to an initial charge of 150 ml of PO and 1500 ml of toluene. From the values  $V$ (moles of vapor over total moles) and  $L$ (moles of liquid over total moles) the volume of vapor and liquid,  $V(\text{ml})$  and  $L(\text{ml})$ , can be calculated as it was done before for the ideal behavior. Using the density of PO and toluene we can calculate approximately the liquid volume, and subtracting the liquid volume from the total volume we can obtain the vapor volume. Note that two assumptions are made here: that the liquid density is invariable with pressure and the liquid volumes can be summed.

The liquid volume of PO is:  $L(\text{ml})\text{PO} = n x_1 L \text{Mw}_1 / \rho_1$ , and

the liquid volume of toluene is:  $L(\text{ml})\text{toluene} = n x_2 L \text{Mw}_2 / \rho_2$ . Being  $n$  the total number of moles,  $\text{Mw}_1$  the molecular weight of PO,  $\text{Mw}_2$  the molecular weight of toluene,  $\rho_1$  the PO liquid density, and  $\rho_2$  the toluene liquid density.

The total liquid volume results, then in:  $L(\text{ml}) \text{ total} = L(\text{ml})\text{PO} + L(\text{ml})\text{toluene}$ .

The total vapor volume is obtained by subtracting the liquid volume from the total reactor volume, that is:  $V(\text{ml}) \text{ total} = \text{Reactor Volume} - L(\text{ml})\text{total}$ . The liquid volume  $L(\text{ml})$  is included in the following tables. With the results from the flash calculations the PO liquid concentration can be calculated.

Table 4.4 Flash calculations for the system PO-toluene (non-ideal behavior)

| T<br>°C | P<br>psia | $z_1$ | $x_1$             | $y_1$  | L      | L<br>ml |
|---------|-----------|-------|-------------------|--------|--------|---------|
| 130     | 29        | 0.3   | Superheated vapor |        |        |         |
| 120     | 29        | 0.3   | 0.0538            | 0.3643 | 0.2059 | 429.66  |
| 110     | 29        | 0.3   | 0.1008            | 0.5346 | 0.5401 | 1106.91 |
| 100     | 29        | 0.3   | 0.1661            | 0.6713 | 0.7347 | 1468.66 |
| 90      | 29        | 0.3   | 0.2599            | 0.7782 | 0.9228 | 1777.47 |
| 80      | 29        | 0.3   | Subcooled liquid  |        |        |         |
| 140     | 43.5      | 0.3   | Superheated vapor |        |        |         |
| 130     | 43.5      | 0.3   | 0.0910            | 0.4685 | 0.4455 | 916.54  |
| 120     | 43.5      | 0.3   | 0.1495            | 0.6084 | 0.6717 | 1351.29 |
| 110     | 43.5      | 0.3   | 0.2301            | 0.7228 | 0.8581 | 1672.73 |
| 100     | 43.5      | 0.3   | Subcooled liquid  |        |        |         |
| 150     | 58        | 0.3   | 0.0590            | 0.3310 | 0.1127 | 234.56  |
| 140     | 58        | 0.3   | 0.1059            | 0.4860 | 0.4887 | 999.65  |
| 130     | 58        | 0.3   | 0.1678            | 0.6185 | 0.7052 | 1408.74 |
| 120     | 58        | 0.3   | 0.2511            | 0.7212 | 0.8969 | 1733.69 |
| 110     | 58        | 0.3   | Subcooled liquid  |        |        |         |
| 160     | 72.5      | 0.3   | 0.0641            | 0.3327 | 0.1205 | 250.45  |
| 150     | 72.5      | 0.3   | 0.1118            | 0.4807 | 0.4892 | 998.39  |
| 140     | 72.5      | 0.3   | 0.1740            | 0.6086 | 0.7088 | 1412.46 |
| 130     | 72.5      | 0.3   | 0.2563            | 0.7090 | 0.9043 | 1744.41 |
| 120     | 72.5      | 0.3   | Subcooled liquid  |        |        |         |

Table 4.4 (Continued)

| T<br>°C | P<br>psia | $z_1$ | $x_1$             | $y_1$  | L      | L<br>ml |
|---------|-----------|-------|-------------------|--------|--------|---------|
| 140     | 29        | 0.14  | Superheated vapor |        |        |         |
| 130     | 29        | 0.14  | 0.0185            | 0.1573 | 0.1145 | 196.26  |
| 120     | 29        | 0.14  | 0.0538            | 0.3657 | 0.7220 | 1221.51 |
| 110     | 29        | 0.14  | 0.1008            | 0.9094 | 0.9094 | 1511.68 |
| 100     | 29        | 0.14  | Subcooled liquid  |        |        |         |
| 150     | 43.5      | 0.14  | Superheated vapor |        |        |         |
| 140     | 43.5      | 0.14  | 0.0447            | 0.2905 | 0.6102 | 1035.84 |
| 130     | 43.5      | 0.14  | 0.0879            | 0.4609 | 0.8600 | 1436.42 |
| 120     | 43.5      | 0.14  | Subcooled liquid  |        |        |         |
| 170     | 58        | 0.14  | Superheated vapor |        |        |         |
| 160     | 58        | 0.14  | 0.0222            | 0.1500 | 0.712  | 121.82  |
| 150     | 58        | 0.14  | 0.0590            | 0.3318 | 0.7018 | 1184.94 |
| 140     | 58        | 0.14  | 0.1059            | 0.4862 | 0.9102 | 1509.94 |
| 130     | 58        | 0.14  | Subcooled liquid  |        |        |         |
| 180     | 72.5      | 0.14  | Superheated vapor |        |        |         |
| 170     | 72.5      | 0.14  | 0.0262            | 0.1621 | 0.1570 | 268.25  |
| 160     | 72.5      | 0.14  | 0.0641            | 0.3334 | 0.7170 | 1208.31 |
| 150     | 72.5      | 0.14  | 0.1118            | 0.4807 | 0.9235 | 1528.66 |
| 140     | 72.5      | 0.14  | Subcooled liquid  |        |        |         |

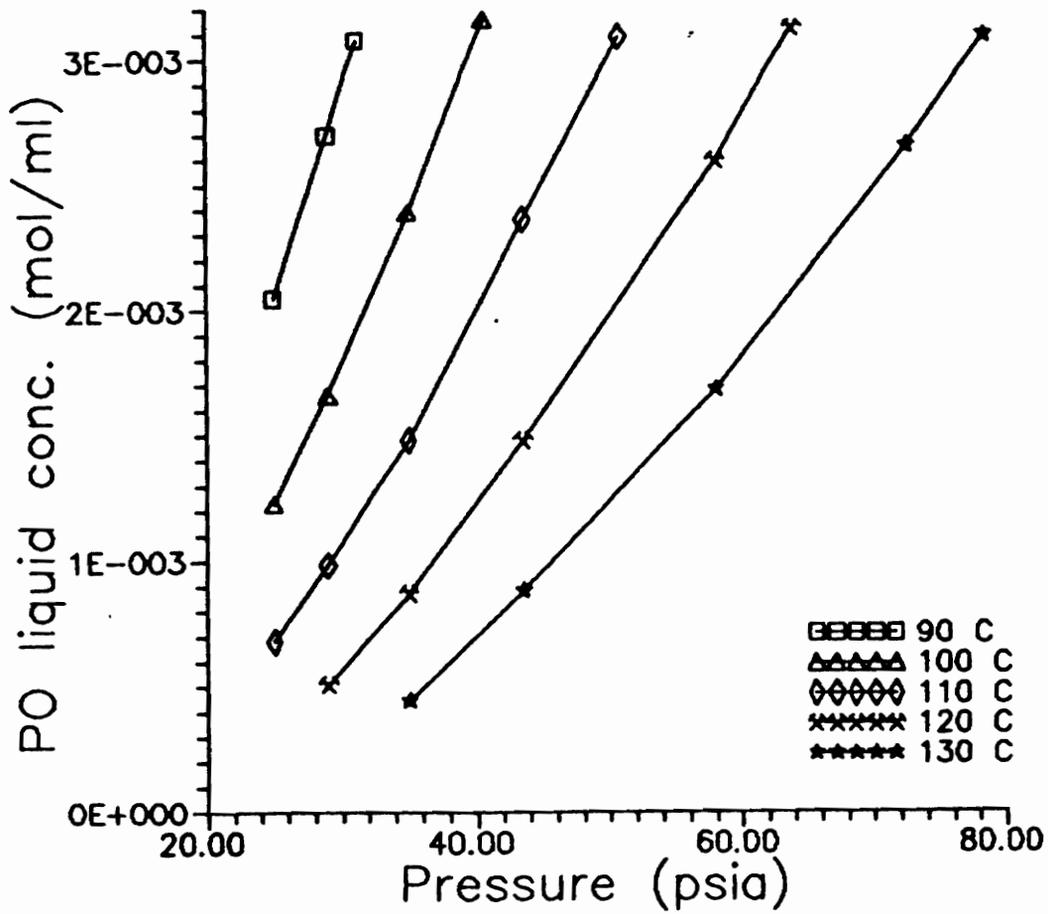


Figure 4.4 PO concentration ( $\text{kmol/m}^3$ ) in the liquid phase versus pressure (psia) and temperature ( $^{\circ}\text{C}$ ).

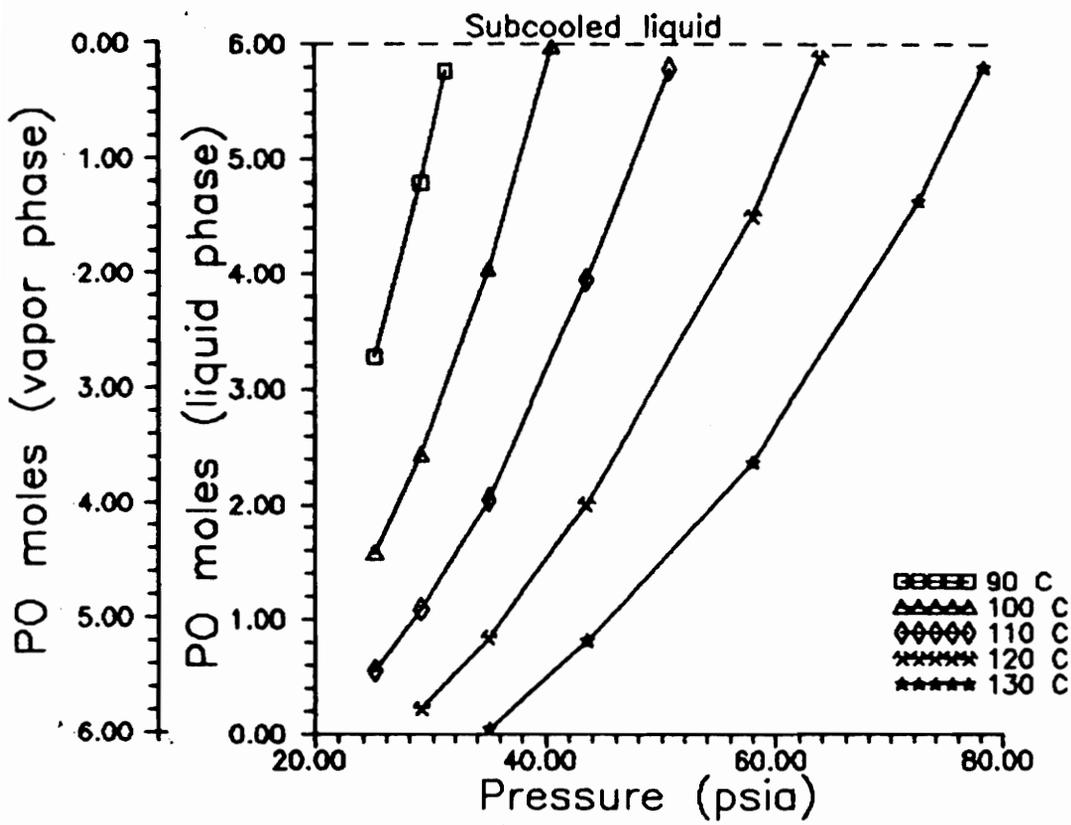


Figure 4.5 PO moles in the liquid phase and in the vapor phase versus pressure (psia) and temperature (°C).

For example, for the following initial conditions, 400 ml of PO and 1500 ml of toluene, in a 1 gallon reactor, with  $P = 2 \cdot 10^5$  Pa (43.5 psia or 29 psig), and  $T = 110^\circ\text{C}$ , from Table 4.4 we have:

$$C_{\text{PO}} = n_{x_1} L / L(\text{ml}) = 20(0.2301)(0.8581)/1672.73 = 2.360 \cdot 10^{-3} \text{ kmol/m}^3.$$

In the same way was calculated the PO liquid concentration for different sets of pressure-temperature (Figure 4.4). Having temperature and pressure we can read the PO liquid concentration from Figure 4.4. This plot is useful for choosing the best reaction conditions. The PO moles in the liquid phase and in the vapor phase as a function of pressure and temperature are given in Figure 4.5. The pressure and temperature values where all PO is in liquid phase are also shown in Figure 4.5. For the reaction conditions used experimentally, the PO concentration is approximately and  $3.0 \text{ kmol/m}^3$ .

The liquid volume is approximately 50% of the total volume, and the amount of PO in the liquid phase approximately 85%.

Finally, let's compare the ideal calculation versus the non-ideal at  $130^\circ\text{C}$ , 44.1 psia, and  $z_1 = 0.3$ .

Table 4.5 Comparison between ideal and non-ideal behavior.

| Table 4.5 Comparison between ideal and non-ideal behavior. |           |                |        |        |         |         |
|--|-----------|----------------|--------|--------|---------|---------|
| T<br>°C  | P<br>psia | Ideal behavior |        |        | L<br>ml | V<br>ml |
|  |           | $z_1$          | $x_1$  | $y_1$  |         |         |
| 130  | 44.1      | 0.3            | 0.1195 | 0.5062 | 1149    | 2636    |
| Non-ideal behavior   |           |                |        |        |         |         |
| 130  | 44.1      | 0.3            | 0.0910 | 0.4685 | 916.5   | 2868.6  |

The PO concentration in the liquid phase, considering the system as "ideal" is:

$$C_{\text{PO}} = 1.274 \text{ moles} / 1149 \text{ ml} = 1.189 \cdot 10^{-3} \text{ kmol/m}^3.$$

Considering the system as "non-ideal":

$$C_{\text{PO}} = 0.81081 \text{ moles} / 916.5 \text{ ml} = 0.8847 \cdot 10^{-3} \text{ kmol/m}^3.$$

The PO concentration in the vapor phase, considering the system as "ideal" is:

$$C_{\text{PO}} = 4.726 \text{ moles}/2636 \text{ ml} = 1.793 \cdot 10^{-3} \text{ kmol/m}^3.$$

Considering the system as "non-ideal":

$$C_{\text{PO}} = 5.196 \text{ moles}/2868.6 \text{ ml} = 1.811 \cdot 10^{-3} \text{ kmol/m}^3.$$

The PO liquid concentration calculated assuming ideal behavior is higher than that corresponding to non-ideal behavior. The liquid volume calculated using ideal behavior is approximately 25% larger than that calculated for the non-ideal system.

### 4.3 Conclusions

The vapor-liquid equilibrium solution gives the distribution of the components in the two phases. The initial PO concentration in the liquid phase after the first injection is needed in *Chapter 5* to model the semibatch polymerization process. Since the reaction takes place in the liquid phase, it is desirable to have most of the PO in the liquid phase. This can be achieved by using high pressures and low temperatures. But, if the pressure is high, the PO liquid concentration will be also high and homo-polymerization will compete successfully with copolymerization. Also if the temperature is low the reaction will be very slow. Then the best reaction conditions should result from a balance between these limits.

The experimental data given in *Chapter 6* were obtained with a constant temperature of 90°C and a pressure set at  $2.7 \cdot 10^5$  Pa (25 psig, 39.7 psia). From the vapor-liquid equilibrium analysis here presented at 90°C and 39.7 psia the system is not in vapor-liquid condition but it is present as subcooled liquid. This difference is due to:

- The presence of lignin suspended in toluene; this had not been taken into account, and can increase the non-ideality of the system.
- The presence of traces of nitrogen in the vapor phase would make the pressure readings higher than they were with PO and toluene only.

It could also be the case that the PO-toluene mixture shows a greater deviation from the ideal behavior than the one assumed on the basis of the vapor-liquid

equilibrium theory applied here. Because of the discrepancy between the vapor-liquid equilibrium results and the real readings, the liquid concentration calculated in this chapter may not be very accurate.

## Chapter 5

### MODEL EQUATIONS FOR A SEMIBATCH POLYMERIZATION PROCESS

In this chapter two process models are discussed. The first model considers a gas-liquid system with mass transport effect, operating in a semibatch mode, with constant feeding rate, constant liquid volume, and no product withdrawal. The second model is a liquid system, also operating in a semibatch mode, with constant feeding rate, no product withdrawal, and with a liquid volume gradient. The conclusions compare the two models.

#### 5.1 Model (A): Gas-Liquid System, with Mass Transport Effect:

At the temperature and pressure of work, two phases are present, and there is mass transfer from gas to liquid. The liquid volume at the beginning of the reaction is approximately 45% of the total final volume and 67% of the PO is in liquid phase. Numerous theories describe the gas-liquid mass transfer. These theories include two-film, penetration, surface renewal, and surface rejuvenation (Rase, 1977).

The oldest and simplest of all is the two-film theory. In this theory a stagnant layer is supposed to exist in both phases along the interface. In the gas phase the component that is transferred experiences a resistance to its transfer which is located in the film. At the interface itself there is no resistance, and Henry's law is satisfied. The resistance to transfer from the interface to the bulk liquid is supposed to be located entirely in the liquid film. Even though the existence of stagnant films at the interface between gas and liquid is an inaccurate description of the real phenomenon, the two-film theory gives predictions that are almost identical to the predictions of the other, more complicated theories. The two-film theory will be used to describe the mass transfer between phases.

The polymerization reaction occurs in the liquid phase, and the products

formed from these reactions are assumed to be non-volatile species. By making this assumption, it is possible to write the chemical rate equations in terms of the reagent that is diffusing from the gas, PO. The net rate of mass transfer can be expressed in terms of the overall-mass transfer coefficient,

$$\frac{1}{K_{B_{g^l}}} = \frac{1}{k_l} + \frac{1}{H_B k_g} \quad 5.0$$

where  $H_B$  is the Henry constant,  $k_l$  is the mass transfer coefficient in the liquid phase, and  $k_g$  is the mass transfer coefficient in the gas phase. These equations apply when the equilibrium function is described by Henry's law, that is the system behaves ideally. The model equations are given below for the extreme cases of either plug flow or complete backmixing of the gas. Another assumption is that the liquid volume is constant during the reaction. The reactor is a semibatch type, where the gas flows continuously and the liquid does not flow. This reactor is recommended for systems with large heat effects because of the superior heat-transfer characteristics which agitated systems provide. This reactor is also recommended for difficult-to-suspend slurries because a complete mixing can be achieved; and it is useful for slow reactions requiring high liquid hold-up (Rase, 1977). Even though the catalyst used is solid KOH, the polymerization reaction is not surface catalyzed (Steiner, 1964). Consequently, the theory of gas-liquid reaction with solid catalyst does not applied here. The following equation can be applied to both phases.

$$\left\{ \begin{array}{l} \text{Accumulation} \\ \text{of } i \end{array} \right\} = \left\{ \begin{array}{l} \text{mass rate flow of } i \\ \text{on } z \text{ direction} \end{array} \right\} + \left\{ \begin{array}{l} \text{mass rate flow of } i \\ \text{across the boundary} \end{array} \right\} + \left\{ \begin{array}{l} \text{rate of chemical} \\ \text{reaction of } i \end{array} \right\} \quad 5.1$$

Equation 5.1 is the statement of the law of conservation of mass of the  $i$ -th chemical species in a macroscopic flow system (Bird, 1986).

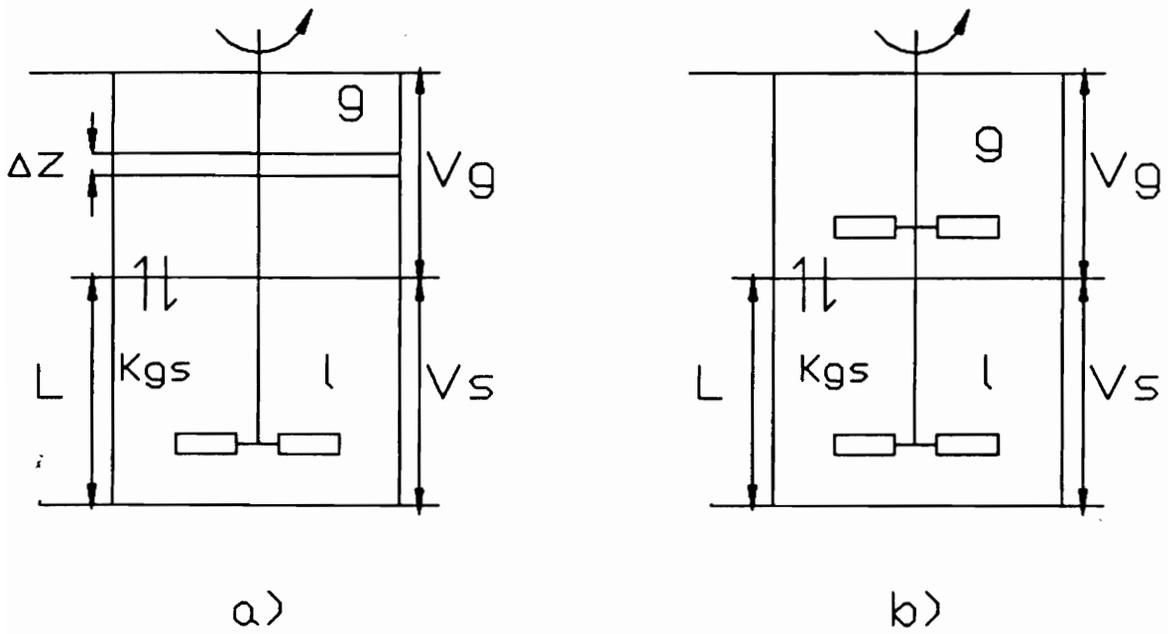
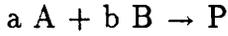


Figure 5.1 Schematic diagram of the mixing stages for a) plug flow of gas and well mixed liquid and b) well mixed gas and well mixed liquid.

The rate of chemical reaction is zero for the gas phase and non-zero for the liquid phase. The global kinetic equation, as it was given on *Chapter 3*, is:



Component A: Reacting component in the liquid phase, (lignin).

Component B: Initially in the gas phase, diffusing component, (PO).

Component P : Products, HPL and PPO.

A continuous or semibatch stirred-tank reactor is operated with the liquid phase completely mixed, and the gas phase at least partially mixed. The real behavior of the gas phase is in between a completely mixed gas and a plug flow gas. For high agitation speed the gas will approach the completely mixed model. The dispersion of the gas into the liquid can be accomplished by different ways: (a) the gas can be fed to the eye of the impeller; (b) the gas can be added through a sparge ring; and (c) the gas can be absorbed through the surface of the liquid. More turbulence, and in consequence a large interfacial area is achieved by methods (a) or (b) and using a flat-blade turbine. The gas bubbles are assumed to be either completely backmixed or in plug flow. The schematic diagrams of the mixing stages for these two cases are given in Figure 5.1. The reactor performance equations applied to an Isothermal Semibatch Polymerization Reactor were taken from Rase (1977), and Mills (1986). First, in section 5.1.a, the reactor equations are given for the gas and liquid phases, corresponding to a system with batch liquid and gas plug flow. Then, in section 5.1.b, the reactor equations for the gas and liquid phases are given, corresponding to a system with batch liquid and gas flow completely mixed. Finally, in section 5.1.c, the kinetic equation is introduced and the reactor performance equation is solved.

### 5.1.a Liquid Batch - Gas Plug Flow

#### Mass Balance of Component B (PO) in the Gas Phase

$$\epsilon_g \frac{\partial C_{B_g}}{\partial t} = - u_{lg} (1 + \epsilon_g) \frac{\partial C_{B_g}}{\partial Z} - K_{B_{gl}} a_{gl} \left( \frac{C_{B_g}}{H_B} - C_{B_l} \right) \quad 5.2$$

where:

- $\epsilon_g$  : ratio of gas volume to solvent volume, dimensionless,  $(V_g/V_l)$ ,  
 $C_{B_g}$  : concentration of B in the gas phase,  $\text{kmol m}^{-3}$ ,  
 $t$  : time, s,  
 $u_{lg}$  : superficial velocity of the gas bubbles,  $\text{m s}^{-1}$ ,  
 $z$  : reactor axial coordinate, m,  
 $K_{B_{gl}}$  : overall gas-liquid mass transfer coefficient,  $\text{m s}^{-1}$ ,  
 $a_{gl}$  : surface area of gas bubbles per unit volume of liquid,  $\text{m}^{-1}$ ,  
 $H_B$  : Henry's law constant ( $C_{B_g}^*/C_{B_l}^*$  of equilibrium),  
 $C_{B_l}$  : concentration of B in the liquid phase,  $\text{kmol m}^{-3}$ .

The first term of the right side is negative because the gradient  $\partial C_{B_g}/\partial z$  is negative in the (z) direction. The second term of the right side is negative because mass is transferred out of the system. The accumulation of the gas phase within the reactor will usually be negligible. Then

$\frac{\partial C_{B_g}}{\partial t} = 0$ , and the solution for  $C_{B_g}$  is:

$$u_{lg} (1 + \epsilon_g) \frac{\partial C_{B_g}}{\partial z} = - K_{B_{gl}} a_{gl} \left( \frac{C_{B_g}}{H_B} - C_{B_l} \right) \quad 5.3$$

The integral of this equation between  $z=0$  and  $z$  is,

$$\int_{C_{B_{gi}}}^{C_{B_g}} \frac{d C_{B_g}}{(C_{B_g}/H_B - C_{B_l})} = - \int_0^z \frac{K_{B_{gl}} a_{gl}}{\mu_{lg} (1 + \epsilon_g)} dz \quad 5.4$$

where:

$C_{B_{gi}}$ : Concentration of B in the inlet,  $\text{kmol m}^{-3}$ .

$$H_B \ln \left( \frac{C_{B_g}/H_B - C_{B_l}}{C_{B_{gi}}/H_B - C_{B_l}} \right) = - \frac{K_{B_{gl}} a_{gl} z}{\mu_{lg} (1 + \epsilon_g)} \quad 5.5$$

Rearranging,

$$\frac{C_{B_g}/H_B - C_{B_l}}{C_{B_{gi}}/H_B - C_{B_l}} = \exp \left[ - \frac{K_{B_{gl}} a_{gl} z}{H_B \mu_{lg}(1+\epsilon_g)} \right] \quad 5.6$$

$$C_{B_g}/H_B - C_{B_l} = (C_{B_{gi}}/H_B - C_{B_l}) \exp \left[ - \frac{K_{B_{gl}} a_{gl} z}{H_B \mu_{lg}(1+\epsilon_g)} \right] \quad 5.7$$

### Mass Balance of Component B (PO) in the Liquid Phase

There is one liquid phase at the on-set of the lignin propoxylation reaction. This is the solvent phase in which lignin and the polymers are soluble (or dispersed). A second, aqueous phase, formed from lignin's approximately 10% moisture content is removed prior to the reaction by azeotropic distillation.

$$\frac{d C_{B_l}}{d t} = \frac{1}{L} \int_0^L K_{B_{gl}} a_{gl} (C_{B_g}/H_B - C_{B_l}) dz + R_B \quad 5.8$$

Since the liquid phase is completely mixed, the term corresponding to mass rate flow of B in the z direction is not included. Substituting in Equation 5.7, obtained from the gas phase, we have,

$$\frac{d C_{B_l}}{d t} = \frac{1}{L} \int_0^L K_{B_{gl}} a_{gl} \left( \frac{C_{B_{gi}}}{H_B} - C_{B_l} \right) \exp \left[ - \frac{K_{B_{gl}} a_{gl} z}{\mu_{lg}(1+\epsilon_g) H_B} \right] dz + R_B \quad 5.9$$

Integrating,

$$\frac{d C_{B_l}}{d t} = \frac{1}{L} \left( \frac{C_{B_{gi}}}{H_B} - C_{B_l} \right) (-\mu_{lg}(1+\epsilon_g) H_B) \left\{ \exp \left[ - \frac{K_{B_{gl}} a_{gl} L}{\mu_{lg}(1+\epsilon_g) H_B} \right] - 1 \right\} + R_B \quad 5.10$$

$$\text{If } \frac{\mu_{lg}(1+\epsilon_g)}{L} = \frac{\mu_{gl}(V_g + V_l)}{L V_l} = \frac{Q_g}{V_l} \quad 5.11$$

where,

$Q_g$  : Volumetric flow rate of the gas phase,  $m^3 s^{-1}$  and

$V_l$  : Volume of liquid phase,  $m^3$ .

Using the Stanton Number for mass transfer,

$$\text{St} = \frac{\text{Nu}_{AB}}{\text{ReSc}} = \frac{K_{B_{gl}} a_{gl} V_l}{Q_g H_B} \quad 5.12$$

Equation 5.11 reduces to,

$$\frac{d C_{B_l}}{d t} = -(C_{B_{g,i}}/H_B - C_{B_l}) \frac{Q_g H_B}{V_l} [\exp(-St) - 1] + R_B \quad 5.13$$

$$\text{or } \frac{d C_{B_l}}{d t} = \frac{Q_g H_B}{V_l} \left( \frac{C_{B_{g,i}}}{H_B} - C_{B_l} \right) [1 - g(St)] + R_B \quad 5.14$$

where  $g(St) = \exp(-St)$ . Equation 5.14 considers the mass transfer resistance in the function  $g(St)$ .

### 5.1.b Liquid Batch - Gas Flow (completely mixed)

#### Mass Balance of Component B (PO) in the Gas Phase

$$\epsilon_g V_l \frac{d C_{B_g}}{d t} = -Q_g (C_{B_g} - C_{B_{g,i}}) - K_{B_{g,l}} a_{g,l} (C_{B_g}/H_B - C_{B_l}) V_l \quad 5.15$$

If  $\frac{d C_{B_g}}{d t}$  is negligible,

$$Q_g (C_{B_g} - C_{B_{g,i}}) = -K_{B_{g,l}} a_{g,l} (C_{B_g}/H_B - C_{B_l}) V_l \quad 5.16$$

Rearranging,

$$-Q_g C_{B_{g,i}} - K_{B_{g,l}} a_{g,l} C_{B_l} V_l = -(Q_g + K_{B_{g,l}} a_{g,l} V_l / H_B) C_{B_g} \quad 5.17$$

and,

$$\frac{C_{B_g}}{H_B} \left( 1 + \frac{K_{B_{g,l}} a_{g,l} V_l}{Q_g H_B} \right) = \frac{C_{B_{g,i}}}{H_B} + \frac{K_{B_{g,l}} a_{g,l} V_l}{H_B Q_g} C_{B_l} \quad 5.18$$

#### Mass Balance of Component B (PO) in the Liquid Phase

$$\frac{d C_{B_l}}{d t} = K_{B_{g,l}} a_{g,l} \left( \frac{C_{B_g}}{H_B} - C_{B_l} \right) + R_B \quad 5.19$$

Substituting Equation 5.18 into Equation 5.19,

$$\frac{dC_{B_l}}{dt} = K_{B_{gl}a_{gl}} \left( \left( \frac{C_{B_{gi}}}{H_B} + \frac{K_{B_{gl}a_{gl}}V_l}{H_B Q_g} C_{B_l} \right) \frac{1}{1 + \frac{K_{B_{gl}a_{gl}}V_l}{H_B Q_g}} - C_{B_l} \right) + R_B \quad 5.20$$

Using the definition of Stanton Number,  $St = \frac{Nu_{AB}}{ReSc} = \frac{K_{B_{gl}a_{gl}}V_l}{Q_g H_B}$

$$\frac{dC_{B_l}}{dt} = K_{B_{gl}a_{gl}} \left( \left( \frac{C_{B_{gi}}}{H_B} + St C_{B_l} \right) \frac{1}{1 + St} - C_{B_l} \right) + R_B \quad 5.21$$

Rearranging,

$$\frac{dC_{B_l}}{dt} = \frac{K_{B_{gl}a_{gl}}}{St} \left( \frac{C_{B_{gi}}}{H_B} - C_{B_l} \right) \frac{St}{1 + St} + R_B \quad 5.22$$

Where  $\frac{St}{1 + St} = 1 - \frac{1}{1 + St}$  and if we call  $g(St) = \frac{1}{1 + St}$

Then Equation 5.22 results,

$$\frac{dC_{B_l}}{dt} = \frac{Q_g H_B}{V_l} \left( \frac{C_{B_{gi}}}{H_B} - C_{B_l} \right) (1 - g(St)) + R_B \quad 5.23$$

This is the same as Equation 5.14,

where  $\begin{cases} g(St) = \exp(-St) & \text{for plug-flow of gas, and} \\ g(St) = \frac{1}{1 + St} & \text{for mixed-flow of gas} \end{cases}$

### 5.1.c Mass Balance for the Polymeric Species (HPL) in the Liquid Phase

$$\frac{dU_m}{dt} = R_{U_m} \quad \text{for } m = 0, 1, 2, \dots, \infty \quad 5.24$$

$U_m$  : denotes the concentration of species U whose chain length is m,  $\text{kmol m}^{-3}$ .

Equations 5.23 and 5.24 along with the following boundary condition:

$$U_m(0) = U_m^0 \quad \text{for } m = 0, 1, 2, \dots, \infty$$

are an infinite set of differential equations whose solution yields the concentration of each species  $U$  as a function of time, chain length, and physical-chemical parameters. To solve these equations a method to reduce the infinite set of equations, like the  $z$ -transform method, has to be used.

In the case of lignin propoxylation the molar substitution is one and Equation 5.24 is reduced to only one equation. The degree of substitution varies between 0.9 and 2.6 (Glasser, 1984), but it will be assumed that each hydroxypropyl group is independent of any other reaction. Since the reaction was found to be of first order in  $B$  (PO), then Equation 5.24 results in,

$$R_B = -k C_{B_i} \quad 5.25$$

The integration of Equation 5.23 produces the concentration gradient of PO as a function of time, having as parameters the Stanton number and the rate constant of the reaction,  $k$ .

$$\frac{dC_{B_i}}{dt} = \frac{Q_g H_B}{V_i} \left( \frac{C_{B_{gi}}}{H_B} - C_{B_i} \right) (1 - g(St)) - k C_{B_i} \quad 5.26$$

Rearranging,

$$\frac{dC_{B_i}}{dt} + \left( k + \frac{Q_g H_B}{V_i} (1 - g(St)) \right) C_{B_i} = \frac{Q_g C_{B_{gi}}}{V_i} (1 - g(St)) \quad 5.27$$

with the boundary condition:

$$C_B(0) = C_{B_i}^0 \quad \text{at } t = 0 \quad 5.28$$

Assuming  $H_B$  is constant, Equation 5.27 has the form,  $\frac{dy}{dt} + p y = q$  which has the solution:  $y = \frac{q}{p} + \frac{C}{\exp p t}$  where  $C = y_0 - \frac{q}{p}$ . Then

$$y = \frac{q}{p} (1 - \exp(-p t)) + y_0 \exp(-p t) \quad 5.29$$

replacing  $y$ ,  $p$  and  $q$  for its values:

$$C_{B_i} = \frac{Q_g C_{B_{g,i}}(1-g(St))}{V_l} \frac{1}{\left(k + \frac{Q_g H_B}{V_l} (1-g(St))\right)} \left\{ 1 - \exp - \left( k + \frac{Q_g H_B}{V_l} (1-g(St)) \right) t \right\} + C_{B_i}^0 \left\{ \exp - \left( k + \frac{Q_g H_B}{V_l} (1-g(St)) \right) t \right\} \quad 5.30$$

Rearranging,

$$C_{B_i} = \frac{C_{B_{g,i}}}{\left(\frac{kV_l}{Q_g}(1-g(St))\right) + H_B} \left\{ 1 - \exp - \left( k + \frac{Q_g H_B}{V_l} (1-g(St)) \right) t \right\} + C_{B_i}^0 \left\{ \exp - \left( k + \frac{Q_g H_B}{V_l} (1-g(St)) \right) t \right\} \quad 5.31$$

This equation can be used to determine the effects of transport and kinetic parameters over the hydroxypropyl lignin conversion. Two cases will be considered:

- (a)  $St \rightarrow \infty$ , negligible gas-liquid mass transfer resistance. Either for plug flow or well mixed gas flow  $g(St) \rightarrow 0$ ; and
- (b) Finite gas-liquid mass transfer resistance, or  $g(St) > 0$ .

The initial stage, where feeding and reaction take place, is described by Equation 5.31. The feeding continues until the concentration of PO reaches a limit value. In the second stage, the process is batch and there is mass transferred from the gas to the liquid phase. For the case of slow reaction, the two films and the main body act as resistances in series. For the case of a very slow reaction, the films offer no resistance and the only remaining one is the rate of reaction.

Two assumptions made in the development of these reactor performance equations are not exactly applicable to our reaction system. These assumptions are: a) the constancy of the liquid volume during the reaction, and b) the ideal

behaviour of both gas and liquid. Although PO is in both liquid and vapor phase, the lignin propoxylation reaction takes place only in the liquid phase. Then a liquid model is proposed and discussed next. This liquid model will consider the liquid volume variable. The PO concentration in the liquid phase will be obtained from the non-ideal vapor-liquid equilibrium results, *Chapter 4*.

### 5.2 Model (B): Liquid System:

Now only the liquid phase will be considered. The equation that describes the loading and reaction for a semibatch reactor is:

$$\frac{d(C_B V_t)}{dt} = C_{B_i} Q_g - r_B V_t, \quad 5.32$$

where:

$V_t$ : variable volume,  $V_t = V_i^0 + Q_g t$ ,  $m^3$

$V_i^0$ : initial volume,  $m^3$

$Q_g$ : feed rate,  $m^3/s$

$C_{B_i}$ : concentration of PO in the inlet

$r_B = k C_B$ , for an irreversible first-order reaction.

This first order equation is solved using Laplace Transform. Equation 5.32 can be written as,

$$y' + k y = g \quad 5.33$$

where  $g = C_{B_i} Q_g$  and  $y = C_B V_t$ .

Applying Laplace Transform,

$$s Y(s) + k Y(s) - y(0) = \frac{g}{s}$$

where  $y(0) = C_{B_0} V_i^0$  is the initial condition.

Solving for  $Y(s)$ ,

$$Y(s) = \left( \frac{g}{s} + y(0) \right) \frac{1}{(s+k)}. \quad 5.34$$

Using partial fractions we can write  $Y(s)$  in the form,

$$Y(s) = \frac{y(0)}{k+s} + \frac{g}{ks} - \frac{g}{k(k+s)} \quad 5.35$$

which has the anti transform,

$$y = \frac{q}{k} + C_{B_0} V_i^0 e^{-kt} - \frac{q}{k} e^{-kt}. \quad 5.36$$

Using now the values of  $q$  and  $y$ , Equation 5.36 results in

$$C_B = \frac{e^{-kt}}{(V_i^0 + Q_g t)} \left\{ C_{B_0} V_i^0 + \left[ \frac{C_{B_i} Q_g}{k} (e^{kt} - 1) \right] \right\}. \quad 5.37$$

In the initial stage PO is injected into the reactor and the reaction starts. The feeding continues until the concentration of PO reaches a limit,  $C_{B_h}$ . In the second stage, there is no feed until the concentration of PO reaches a certain lower limit,  $C_{B_l}$ . There is no product withdrawal during the reaction. For this second stage,

$$\frac{d C_B V_i}{dt} = - r_B V_i. \quad 5.38$$

For an irreversible, first-order reaction,

$$C_B = C_{B_0} \exp^{-kt}. \quad 5.39$$

Equation 5.37 of this model is equivalent to Equation 5.31 of the gas-liquid model. Next the two models are compared. Since the gas-liquid model was based in the assumption that the liquid volume is constant during the reaction, Equation 5.37 is modified to constant volume. With this assumption, Equation 5.40 results.

$$C_B = \frac{e^{-kt}}{V_i^0} \left\{ C_{B_0} V_i^0 + \left[ \frac{C_{B_i} Q_g}{k} (e^{kt} - 1) \right] \right\}. \quad 5.40$$

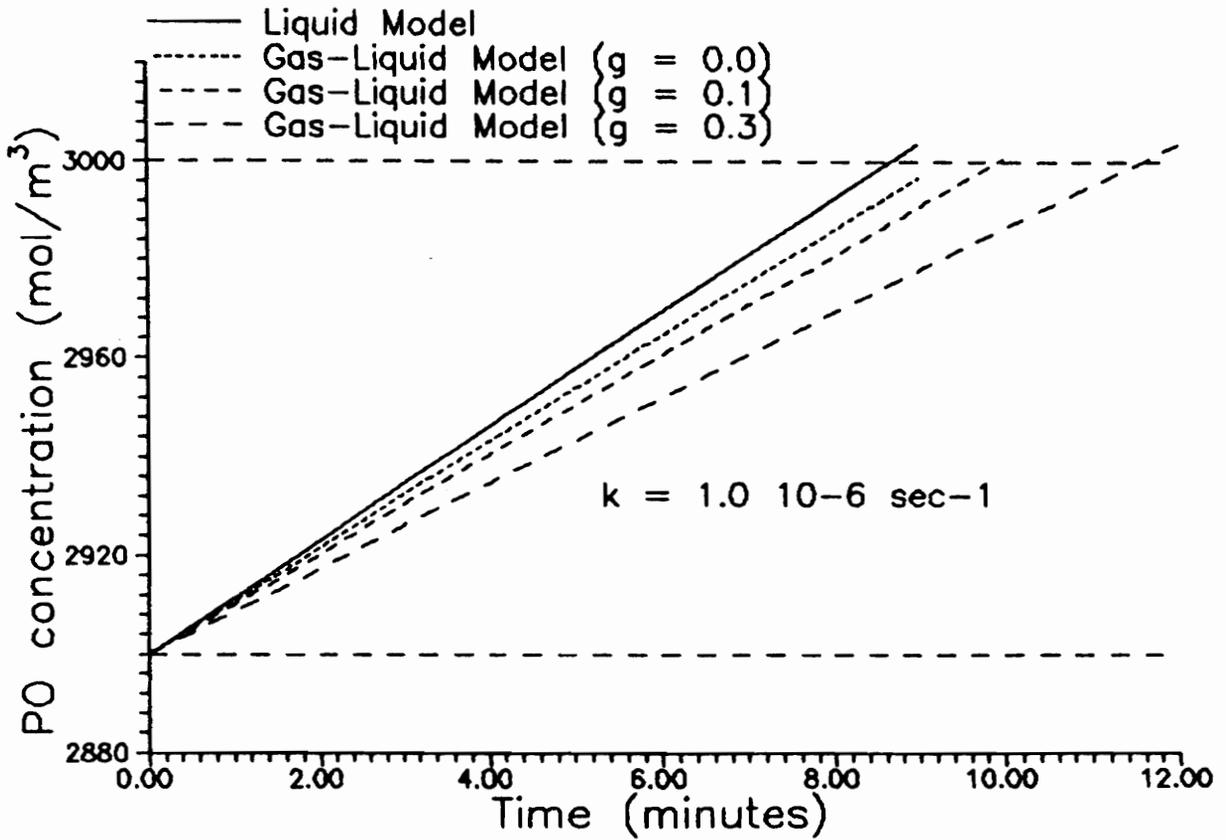


Figure 5.2 PO concentration for the liquid model compared to the gas-liquid model with finite gas-liquid mass transfer resistance.

For negligible gas-liquid mass transfer resistance, or  $g(\text{St}) \rightarrow 0$ , Equation 5.31 results,

$$C_{B_i} = \frac{C_{B_{g_i}}}{\frac{kV_l}{Q_g} + H_B} \left\{ 1 - \exp\left[-\left[k + \frac{Q_g H_B}{V_l}\right]t\right] \right\} + C_{B_i}^0 \left\{ \exp\left[-\left[k + \frac{Q_g H_B}{V_l}\right]t\right] \right\}. \quad 5.41$$

The two models are plotted in Figure 5.2, using Equation 5.40 for the liquid system, Equation 5.31 for the gas-liquid model with  $g(\text{St}) > 0$ , and Equation 5.41 for the gas-liquid with  $g(\text{St}) = 0$ . Figure 5.2 represents the initial stage of feeding and reaction. That is, the model equations are used to compute the increasing concentration between the lower limit,  $C_{B_l}$ , and the higher limit,  $C_{B_h}$ . The values of the variables used to compute Figure 5.2 are the following:

$$C_{B_h} = 3.0 \cdot 10^3 \text{ mol/m}^3,$$

$$C_{B_l} = C_{B_i}^0 = 2.9 \cdot 10^3 \text{ mol/m}^3,$$

$$C_{B_i} = C_{B_{g_i}} = 1.461 \cdot 10^4 \text{ mol/m}^3,$$

$$k = 1.0 \cdot 10^{-6} \text{ sec}^{-1},$$

$$V_l^0 = V_l = 1.5 \cdot 10^{-3} \text{ m}^3,$$

$$Q_g = 2.0 \cdot 10^{-8} \text{ m}^3/\text{sec},$$

$$\text{three values of } g(\text{St}) \left\{ \begin{array}{l} 0 \\ 0.1 \\ 0.3, \text{ and} \end{array} \right.$$

$$H_B = 0.33.$$

The value of the Henry constant was calculated at two different pressure and temperature conditions using the program FLASH, from *Chapter 4*, Vapor-Liquid Equilibrium Analysis. At  $90^\circ\text{C}$  and  $2.0 \cdot 10^5 \text{ Pa}$ ,  $H_B$  was 0.222 and at  $110^\circ\text{C}$  and  $3.0 \cdot 10^5 \text{ Pa}$   $H_B$  was 0.448. An average value of 0.33 is used here. The liquid PO concentration for the gas-liquid model is lower than the liquid PO concentration for the liquid model, as is expected. The finite resistance decreases even more the liquid PO concentration. That is, the consumption of PO by reaction is the same in both cases, but, because of the mass transfer resistance included in the gas-liquid model, the amount of PO entering the liquid phase is lower in the gas-liquid model. Then, as the function  $g(\text{St})$  increases, the two models differ more from each other.

Finally, if the concentration in the gas phase is zero, Equation 5.41 reduces to Equation 5.37. That is, if  $C_{B_g}^* = 0$  and  $H_B = C_{B_g}^*/C_{B_l}^* = 0$ , then

$$C_{B_l} = \frac{C_{B_{g_i}} Q_g}{kV_l} \{1 - \exp -kt\} + C_{B_l}^0 \{\exp -kt\}. \quad 5.42$$

Rearranging,

$$C_{B_l} = \frac{e^{-kt}}{V_l} \left\{ C_{B_l}^0 V_l + \frac{C_{B_{g_i}} Q_g}{k} (e^{kt} - 1) \right\}. \quad 5.43$$

which is the liquid model equation.

### 5.3 Conclusions

The two process models evaluated in this chapter allow the following conclusions to be drawn. 1. The system was demonstrated to be non-ideal by the vapor-liquid equilibrium analysis, and, the variation of the liquid volume is too significant to be neglected (45 to 60%). (The gas-liquid semibatch process, although it considers two phases, assumes constant liquid volume and ideal gas-liquid behaviour). The value of the gas-liquid model lies in the determination of the effects of transport and kinetic parameters over the hydroxypropyl lignin conversion. 2. The liquid semibatch process includes a liquid volume gradient and it uses the initial PO concentration calculated from a non-ideal vapor-liquid equilibrium. 3. The two models agree well with each other (Figure 5.2). 4. In one-step feeding experiments, the mass transfer resistance retards the PO concentration for reaching certain level by at most 2 minutes in each step. In 18-injection reactions, this will account for a 36-minute difference, which is insignificant compared to a 50 to 100 hour total reaction time. 5. These models describe mathematically each feeding step in the reaction process, and they are followed by a reaction step, which is mathematically described by Equation 5.39 for both models if the film resistance is negligible.

The liquid model will be used in the modelling. The next step is to model the intermittent feeding by a computer program which will include the liquid model equation here developed.

*Chapter 6*  
**PROCESS MODELLING AND CORRELATION WITH EXPERIMENTAL  
DATA**

The experimental data obtained at the laboratory are correlated with a process model in this chapter. The objective of the process model is to: a) test a global kinetic equation for the lignin propoxylation reaction, b) examine the effect of various model parameters, such as kinetic rate constants, and c) use the results for interpreting experimental data and for predicting the reaction behavior under different conditions. In the first section, a constant temperature correlation is presented. The experimental data are presented in tables and briefly analyzed. A computer program is then developed that simulates the reaction process using the liquid model. From the results a temperature gradient process is proposed which optimises the reaction in terms of rate and homopolymerization. Experimental data obtained using a temperature gradient are presented and correlated. Finally, a predictive kinetic model is presented. This provides the temperature required for a predetermined reaction rate constant.

### *6.1 Constant Temperature Correlation*

The following experimental data have been collected from strip charts which provide a pressure-time record of the reaction. All reactions were conducted in a 1-gallon reactor in the Thomas M. Brooks Forest Products Center of Virginia Polytechnic Institute & State University. A constant relationship is used to transform the pressure drop to PO consumption. This goes from 12 to 18 psia pressure drop per ml of PO consumed. The use of a constant relationship is an approximation. The volume of PO fed in each injection varies with the course of the reaction, even for the same pressure drop, since the head space of the reactor decreases. The analytic calculation of the real volume required in each injection to reach the set pressure is not direct. The specific situation of each individual injection is determined by the following

parameters:

- Temperature and pressure are known, and they may be the same for each injection.
- The total volume is constant, but the liquid volume has increased while the vapor volume has decreased. From the reaction kinetics of a semibatch reaction at variable volume, the increase in liquid volume can be estimated. But these kinetics assume constant feeding rate to the reactor. This volume can then be used as a first estimation, and then recalculated with the variation in the feeding rate until the cycle closes. The vapor volume can be calculated by subtracting the liquid volume from the total volume.
- Having the vapor volume, and by using flash calculations, the composition of the system as well as the composition of each phase can be calculated. These calculations can be programmed, but it may be difficult get them to agree with experimental observation.

Here it is assumed that the volume added in each injection is constant regardless of pressure level. That is from the experimental data  $\Delta P$  is transformed in  $\Delta \text{volume}$  using a constant relationship. The following gives a series of experimental data. These provide information of AFR (average feeding rate, or the PO consumption in each injection divided by the time between injections). Nine sets of experimental data are presented. Their main characteristics are: The temperature is constant at 90°C. Lignin (400 gr) is reacted with KOH to produce K-Lignate. Toluene is used as solvent for the reaction. K-lignate and solvent are subject to an azeotropic distillation to remove water. The liquid volume prior starting the reaction is 1,500 ml. PO (400 ml) is injected to reach the desired pressure, approximately  $2.7 \cdot 10^5$  Pa (39.7 psia or 25 psig). Then the subsequent injections are triggered by pressure dropping below a certain threshold. Complicating the reaction is the necessity of switching between several feed tanks. If one tank empties,  $N_2$  is injected automatically. The injections marked \* could be  $N_2$ . At the injections marked \*\* the pressure set-point was increased in order to accelerate the reaction. The following gives some characteristics of the data sets # 1.1 to 1.5:

Lignin from sugar cane bagasse obtained from steam exploded whole bagasse

(explosion severity of  $\log R_0$  3.9).

Extent of propoxylation: 30 M PO/kg lignin.

Average total time of reaction : 115 hours.

Maximum AFR : 7.9 ml /hr.

Average time at which the maximum AFR occurs : 79 hours after start-up.

Homopolymer content: 36 %.

The following are some characteristics of data set # 1.6:

Lignin from sugar cane bagasse obtained from steam exploded whole bagasse (explosion severity of  $\log R_0$  3.7).

Extent of propoxylation: 35 M PO/kg lignin.

Average total time of reaction : 135 hours.

Maximum AFR : 7.7 ml /hr.

Average time at which the maximum AFR occurs : 20 hours after start-up.

Homopolymer content: 9 %.

The following are some characteristics of the data sets # 1.7 to 1.9:

Lignin from steam exploded sugar cane leaf component (explosion severity  $\log R_0$  3.5).

Extent of propoxylation: 25 M PO/kg lignin.

Average total time of reaction : 39 hours.

Maximum AFR : 11.1 ml /hr.

Average time at which the maximum AFR occurs : 31.6 hours after start-up.

Homopolymer content: 22.3%.

Table 6.1 Experimental data for Series # 1.

| Injection N <sup>o</sup>     | $\Delta P$<br>psi | $\Delta vol.$<br>ml | $\Delta time$<br>hours | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | Time<br>hr |
|------------------------------|-------------------|---------------------|------------------------|-------------------------------|--------------|------------|
| Experimental data set # 1.1: |                   |                     |                        |                               |              |            |
| 1                            |                   | 400                 |                        |                               |              |            |
| 2                            | 0.06              | 0.75                | 7.5                    | 0.01                          | 0.1          | 7.5        |
| 3                            | 8.75              | 105                 | 17.5                   | 0.5                           | 6            | 25.0       |
| 4                            | 1.70              | 20.4                | 3                      | 0.57                          | 6.8          | 28.0       |

Table 6.1 (Continued) Experimental data for Series #1.

| Injection N <sup>o</sup>             | $\Delta P$<br>psi | $\Delta vol.$<br>ml | $\Delta time$<br>hours | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | time<br>hr |
|--------------------------------------|-------------------|---------------------|------------------------|-------------------------------|--------------|------------|
| Experimental data set # 1.1 (cont.): |                   |                     |                        |                               |              |            |
| 5                                    | 5.00              | 60                  | 12                     | 0.42                          | 5            | 40.0       |
| 6                                    | 3.88              | 46.5                | 5                      | 0.78                          | 9.3          | 45.0       |
| 7                                    | 3.33              | 40                  | 5                      | 0.67                          | 8            | 50.0       |
| 8                                    | 7.92              | 95                  | 10                     | 0.79                          | 9.5          | 60.0       |
| 9                                    | 1.70              | 20.4                | 3                      | 0.57                          | 6.8          | 63.0       |
| 10                                   | 5.00              | 60                  | 10                     | 0.50                          | 6            | 73.0       |
| 11                                   | 4.38              | 52.5                | 7                      | 0.63                          | 7.5          | 80.0       |
| 12                                   | 1.25              | 15                  | 6                      | 0.21                          | 2.5          | 86.0       |
|                                      |                   | 915.55              |                        |                               |              |            |
| Experimental data set # 1.2:         |                   |                     |                        |                               |              |            |
|                                      |                   | 400.00              |                        |                               |              |            |
| 1                                    | 5.22              | 62.66               | 25.4                   | 0.21                          | 2.52         | 25.4       |
| 2                                    | 3.36              | 40.32               | 11.1                   | 0.30                          | 3.6          | 36.5       |
| 3                                    | 2.24              | 26.86               | 4.5                    | 0.50                          | 6.0          | 41.0       |
| 4                                    | 2.61              | 31.33               | 5.0                    | 0.52                          | 6.24         | 46.0       |
| 5                                    | 2.61              | 31.33               | 4.2                    | 0.62                          | 7.44         | 50.2       |
| 6                                    | 3.73              | 44.76               | 6.1                    | 0.61                          | 7.32         | 56.3       |
| 7                                    | 3.36              | 40.32               | 8.7                    | 0.39                          | 4.68         | 65.0       |
| 8                                    | 1.87              | 22.38               | 8.7                    | 0.21                          | 2.52         | 73.7       |
| 9**                                  | 1.12              | 13.42               | 7.4                    | 0.15                          | 1.8          | 80.1       |
| 10**                                 | 1.87              | 11.19               | 8.7                    | 0.21                          | 2.52         | 88.8       |
| 11                                   | 4.10              | 49.24               | 11.3                   | 0.36                          | 4.32         | 100.1      |
|                                      |                   | 773.81 ml           |                        |                               |              |            |
| Experimental data set # 1.3:         |                   |                     |                        |                               |              |            |
|                                      |                   | 400.00              |                        |                               |              |            |
| 1                                    | 7.45              | 16.8                | 45.6                   | 0.16                          | 1.92         | 45.6       |
| 2                                    | 2.13              | 25.54               | 4.7                    | 0.45                          | 5.44         | 50.3       |

Table 6.1 (Continued) Experimental data for Series # 1.

| Injection N <sup>o</sup>                   | $\Delta P$<br>psi | $\Delta vol.$<br>ml | $\Delta time$<br>hours | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | time<br>hr |
|--|-------------------|---------------------|------------------------|-------------------------------|--------------|------------|
| <b>Experimental data set # 1.3 (cont):</b> |                   |                     |                        |                               |              |            |
| 3  | 1.60              | 19.15               | 4.1                    | 0.39                          | 4.67         | 54.4       |
| 4  | 1.60              | 19.15               | 4.4                    | 0.36                          | 4.36         | 58.8       |
| 5  | 1.60              | 19.15               | 4.3                    | 0.37                          | 4.47         | 63.1       |
| 6  | 1.60              | 19.15               | 5.1                    | 0.31                          | 3.72         | 68.2       |
| 7  | 1.60              | 19.15               | 3.9                    | 0.41                          | 4.92         | 72.1       |
| 8  | 2.66              | 31.92               | 4.9                    | 0.54                          | 6.48         | 77.0       |
| 9  | 2.13              | 25.54               | 4.6                    | 0.46                          | 5.52         | 81.6       |
| 10   | 2.13              | 25.54               | 5.0                    | 0.43                          | 5.16         | 86.6       |
| 11*  | 4.79              | 57.46               | 14.6                   | 0.33                          | 3.96         | 101.2      |
| 12*  | 5.32              | 62.76               | 25.9                   | 0.21                          | 2.52         | 127.1      |
| 13   | 4.26              | 51.07               | 18.9                   | 0.23                          | 2.76         | 146        |
| 14   | 4.76              | 57.46               | 15.3                   | 0.31                          | 3.72         | 161.3      |
| 15   | 1.06              | 12.77               | 3.9                    | 0.27                          | 3.26         | 165.2      |
|  |                   | 864.01              |                        |                               |              |            |
| <b>Experimental data # set 1.4:</b>        |                   |                     |                        |                               |              |            |
|  |                   | 400.00              |                        |                               |              |            |
| 1  | 6.26              | 75.07               | 54                     | 0.12                          | 1.39         | 54         |
| 2  | 3.31              | 39.74               | 14.6                   | 0.23                          | 2.72         | 68.6       |
| 3  | 4.05              | 48.58               | 12.9                   | 0.31                          | 3.72         | 81.5       |
| 4  | 4.78              | 57.4                | 16.3                   | 0.29                          | 3.48         | 97.8       |
| 5**  | 2.21              | 26.5                | 4.6                    | 0.48                          | 5.76         | 102.2      |
| 6  | 3.31              | 39.74               | 6.1                    | 0.54                          | 6.48         | 108.3      |
| 7  | 2.94              | 35.33               | 6.7                    | 0.44                          | 5.28         | 115.0      |
|  |                   | 722.36              |                        |                               |              |            |

Table 6.1 (Continued) Experimental data Series # 1.

| Injection N <sup>o</sup>             | $\Delta P$<br>psi      | $\Delta vol.$<br>ml | $\Delta time$<br>hours | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | time<br>hr |
|--------------------------------------|------------------------|---------------------|------------------------|-------------------------------|--------------|------------|
| <b>Experimental data set #1.5:</b>   |                        |                     |                        |                               |              |            |
|                                      |                        | 400.00              |                        |                               |              |            |
| 1                                    | 5.31                   | 63.67               | 33                     | 0.16                          | 1.92         | 33         |
| 2                                    | 2.27                   | 27.29               | 10.1                   | 0.23                          | 2.76         | 40.1       |
| 3                                    | 3.41                   | 40.93               | 9.9                    | 0.35                          | 4.2          | 44.3       |
| 4                                    | 3.79                   | 45.48               | 13.2                   | 0.29                          | 3.48         | 57.5       |
| 5                                    | 4.55                   | 54.58               | 19.4                   | 0.23                          | 2.76         | 76.9       |
| 6                                    | 2.27                   | 27.29               | 10.5                   | 0.22                          | 2.64         | 87.4       |
| 7                                    | 1.52                   | 18.19               | 6.7                    | 0.23                          | 2.76         | 94.1       |
| 8                                    | too short $\Delta set$ |                     |                        |                               |              |            |
| 9**                                  | 3.41                   | 40.93               | 4.4                    | 0.78                          | 9.36         | 98.5       |
| 10                                   | 4.55                   | 54.58               | 7.8                    | 0.58                          | 6.96         | 106.3      |
|                                      |                        | 772.94              |                        |                               |              |            |
| <b>Experimental data set # 1.6 :</b> |                        |                     |                        |                               |              |            |
|                                      |                        | 400.00              |                        |                               |              |            |
| 1*                                   | 7.14                   | 85.68               | 14.7                   | 0.49                          | 5.88         | 14.7       |
| 2*                                   | 1.02                   | 12.24               | 1.8                    | 0.57                          | 6.84         | 16.5       |
| 3*                                   | 1.02                   | 12.24               | 2.0                    | 0.51                          | 6.12         | 18.5       |
| 4*                                   | 1.28                   | 15.3                | 2.0                    | 0.64                          | 7.65         | 20.5       |
| 5                                    | 0.51                   | 6.12                | 7.4                    | 0.07                          | 0.84         | 27.9       |
| 6*                                   | 1.02                   | 12.24               | 2.1                    | 0.49                          | 5.88         | 30.0       |
| 7                                    | 0.51                   | 6.12                | 2.6                    | 0.20                          | 2.40         | 32.6       |
| 8                                    | 0.51                   | 6.12                | 2.3                    | 0.22                          | 2.64         | 34.9       |
| 9                                    | 0.51                   | 6.12                | 2.2                    | 0.23                          | 2.76         | 37.1       |
| 10                                   | 0.765                  | 9.18                | 2.4                    | 0.32                          | 3.84         | 39.5       |
| 11                                   | 1.02                   | 12.24               | 2.7                    | 0.38                          | 4.56         | 42.2       |
| 12                                   | 1.53                   | 18.36               | 3.5                    | 0.44                          | 5.28         | 45.7       |

Table 6.1 (Continued) Experimental data Series # 1.

| Injection N <sup>o</sup>                    | $\Delta P$<br>psi | $\Delta vol.$<br>ml | $\Delta time$<br>hours | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | time<br>hr |
|---|-------------------|---------------------|------------------------|-------------------------------|--------------|------------|
| <b>Experimental data set # 1.6 (cont.):</b> |                   |                     |                        |                               |              |            |
| 13  | 0.26              | 3.06                | 2.4                    | 0.11                          | 1.32         | 48.1       |
| 14  | 1.02              | 12.24               | 3.6                    | 0.28                          | 3.36         | 51.7       |
| 15  | 1.02              | 12.24               | 3.2                    | 0.32                          | 3.84         | 54.9       |
| 16  | 1.02              | 12.24               | 4.2                    | 0.24                          | 2.88         | 59.1       |
| 17  | 1.02              | 12.24               | 5.2                    | 0.20                          | 2.4          | 64.3       |
| 18  | 1.28              | 15.3                | 6.4                    | 0.20                          | 2.4          | 70.7       |
| 19  | 2.30              | 27.54               | 9.1                    | 0.18                          | 2.16         | 79.8       |
| 20  | 2.30              | 27.54               | 24.8                   | 0.09                          | 1.08         | 104.6      |
| 21  | 2.55              | 30.6                | 15.3                   | 0.18                          | 2.16         | 134.9      |
|   |                   | 755.14              |                        |                               |              |            |
| <b>Experimental data set # 1.7 :</b>        |                   |                     |                        |                               |              |            |
|   |                   | 400.00              |                        |                               |              |            |
| 1   | 3.18              | 38.16               | 11.3                   | 0.28                          | 3.38         | 11.3       |
| 2*  | 2.12              | 25.44               | 3.6                    | 0.59                          | 7.07         | 14.9       |
| 3*  | 2.65              | 31.8                | 2.8                    | 0.95                          | 11.36        | 17.7       |
| 4*  | 2.12              | 25.44               | 3.0                    | 0.71                          | 8.48         | 20.7       |
| 5*  | 2.12              | 25.44               | 2.5                    | 0.85                          | 10.18        | 23.2       |
| 6   | 0.53              | 6.36                | 2.8                    | 0.19                          | 2.27         | 24.0       |
| 7   | 0.53              | 6.36                | 1.8                    | 0.29                          | 3.53         | 25.8       |
| 8   | 0.53              | 6.36                | 1.6                    | 0.33                          | 3.98         | 27.4       |
| 9   | 0.53              | 6.36                | 1.6                    | 0.33                          | 3.98         | 29.0       |
| 10  | 0.53              | 6.36                | 1.3                    | 0.41                          | 4.89         | 30.3       |
| 11  | 0.53              | 6.36                | 1.7                    | 0.31                          | 3.74         | 32.0       |
|   |                   | 584.44              |                        |                               |              |            |

Table 6.1 (Continued) Experimental data Series # 1.

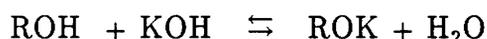
| Injection N <sup>o</sup>             | $\Delta P$<br>psi | $\Delta vol.$<br>ml | $\Delta time$<br>hours | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | time<br>hr |
|--------------------------------------|-------------------|---------------------|------------------------|-------------------------------|--------------|------------|
| <b>Experimental data set # 1.8:</b>  |                   |                     |                        |                               |              |            |
|                                      |                   | 400.00              |                        |                               |              |            |
| 1                                    | 6.36              | 76.32               | 20.2                   | 0.31                          | 3.78         | 20.2       |
| 2                                    | 2.12              | 25.44               | 4.2                    | 0.50                          | 6.0          | 24.4       |
| 3                                    | 1.59              | 19.08               | 2.7                    | 0.59                          | 7.07         | 27.1       |
| 4                                    | 1.59              | 19.08               | 2.5                    | 0.64                          | 7.63         | 29.6       |
| 5                                    | 1.33              | 15.96               | 2.0                    | 0.66                          | 7.98         | 31.6       |
| 6                                    | 1.59              | 19.08               | 2.3                    | 0.69                          | 8.29         | 33.9       |
| 7*                                   | 2.29              | 27.52               | 2.9                    | 0.79                          | 9.48         | 36.8       |
| 8*                                   | 2.82              | 33.88               | 3.3                    | 0.85                          | 10.25        | 40.1       |
| 9*                                   | 2.55              | 30.64               | 3.8                    | 0.67                          | 8.05         | 43.9       |
|                                      |                   | 667.00              |                        |                               |              |            |
| <b>Experimental data set # 1.9 :</b> |                   |                     |                        |                               |              |            |
|                                      |                   | 400.00              |                        |                               |              |            |
| 1                                    | 3.30              | 39.6                | 14.0                   | 0.24                          | 2.88         | 14.0       |
| 2*                                   | 1.30              | 15.54               | 2.3                    | 0.56                          | 6.72         | 16.3       |
| 3                                    | 1.65              | 19.8                | 2.9                    | 0.57                          | 6.83         | 19.2       |
| 4                                    | 1.65              | 19.8                | 2.6                    | 0.63                          | 7.61         | 21.8       |
| 5                                    | 1.65              | 19.8                | 2.1                    | 0.79                          | 9.43         | 23.1       |
| 6                                    | 1.65              | 19.8                | 2.4                    | 0.69                          | 8.25         | 25.5       |
| 7                                    | 1.65              | 19.8                | 2.0                    | 0.83                          | 9.9          | 27.5       |
| 8                                    | 1.65              | 19.8                | 1.9                    | 0.87                          | 10.42        | 29.4       |
| 9                                    | 1.93              | 23.26               | 2.0                    | 0.97                          | 11.58        | 31.4       |
| 10*                                  | 2.68              | 32.10               | 2.8                    | 0.96                          | 11.48        | 34.2       |
| 11*                                  | 2.95              | 35.34               | 3.9                    | 0.76                          | 9.08         | 38.1       |
| 12*                                  | 0.20              | 2.36                | 1.3                    | 0.77                          | 9.23         | 39.4       |
|                                      |                   | 667.00              |                        |                               |              |            |

According to the average feeding rate (AFR) record, the reaction can be divided in different phases. Each phase of the reaction has a different reaction constant. These reaction constants and phases follow a rather uniform pattern. This can be described as follow:

**Initiation Phase:** This is a heterogeneous phase, characterized by a very slow reaction. It may extend to 20-50 hours. The value of the reaction constant is low.

**Transition Phase:** This presumably represents the transition of lignin from the glassy to the viscous (tar) state. The reactivity increases abruptly during this phase. This lasts approximately 10-30 hours. If a mixture of KOH and lignin is used, this phase does not start until an appropriate amount of alkoxide is produced. The reaction velocity of this phase increases if K-lignate is employed instead of KOH plus lignin.

**Rapid Phase:** The reaction velocity increases rapidly in this phase. PO is incorporated into the copolymer with great efficiency. There is no homopolymer formation as long as all KOH is neutralized by phenol. It was demonstrated by Steiner (1964) that the following equilibrium is shifted to the right due to the dehydrating ability of KOH.



As phenol reacts with PO, this reaction shift to the left. If free KOH is present, this can initiate homo-polymerization as well as dehydration.

**Termination Phase :** The reaction velocity decreases again abruptly. This effect could be related to the depletion of phenolic OH groups which react faster than aliphatic OH. This may, however, also be related to concentration considerations; and it takes much more KOH to produce alkoxide than phenoxide species. If there were free KOH, homo-polymerization would occur and the reaction velocity would continue to increase (rather than decrease). In the homo-polymerization of PO with KOH, all alkoxide species add to PO at the same rate. This is not true for the present copolymerization which experiences a decrease of reaction velocity. The reaction constant decreases as the molar substitution increases.

A computer program is developed to model the reaction process as a sequence of first order reactions. Equations 5.37 and 5.39 are used in a Fortran program, named DCB, that models the reaction sequence. Program DCB is given in Appendix E. At first, the initial feeding takes place until the concentration of PO is equal to  $C_{Bh}$ . A constant feed rate,  $Q_g^0$ , is used, and the concentration of PO is calculated using Equation 5.37 (initial condition  $C_B^0 = 0$ ). Once  $C_{Bh}$  is reached, the program switches to Equation 5.39 for the calculation of  $C_B$  and the initial conditions  $C_B^0$  and  $V_l^0$  are re-calculated. This reaction stage continues until the concentration drops to the lower limit,  $C_{Bl}$ . Once again, the initial conditions are re-calculated and  $C_B$  is now calculated using Equation 5.37. From this second injection and to the end of the reaction, the constant feeding rate used is  $Q_g^1$ . The process continues until the end of the reaction time. Several reaction constants are used along the reaction time. The value of each constant and the corresponding time period are chosen to follow the experimental AFR. Since equations 5.37 and 5.39 are valid only for constant  $k$ , the value of  $k$  can not be changed during one stage. The program re-starts another cycle each time  $k$  needs to be changed. This means that the values of  $C_B^0$  and  $V_l^0$  are re-calculated when the value of  $k$  is changed. The inputs to the DCB program are the following:

- $C_{Bh}$ : Concentration of PO, higher limit
- $C_{Bl}$ : Concentration of PO, lower limit,
- $C_{Bi}$ : Concentration of PO in the inlet,
- $k_i$ : Reaction constant for the initiation phase,
- $\Delta t_i$ : Initiation phase period,
- $k_t$ : Reaction constant for the transition phase,
- $\Delta t_e$ : Transition phase period,
- $k_r$ : Reaction constant for the rapid phase,
- $\Delta t_e$ : Rapid phase period,
- $k_e$ : Reaction constant for the termination phase,
- $\Delta t_e$ : Termination phase period,
- $V_l^0$ : Initial volume,
- $Q_g^0$ : Initial feeding rate, during the loading of the reactor,
- $Q_g^1$ : Feeding rate during the course of the reaction, and

$t_{end}$  : Total time of reaction.

The following is an example of how the PO initial concentrations are calculated.  $C_{Bh}$  can be calculated using the results from the vapor-liquid analysis. Let's say the set point is 31 psia. The feed valve open at 30.0 psia, and it remains open until a pressure of 31.0 psia is reached. (The pressure will, however, continue to rise as liquid PO turns to gas). At 90°C and 31 psia, the total composition in the liquid and the vapor phase can be computed using the flash calculation given in *Chapter 4* can be obtained the composition in the liquid and in the vapor phase. The results from the program FLASH, for 90°C, 31psia, 20 moles total, and a PO overall composition of 0.3 is given below:

| T  | P    | $z_1$ | $x_1$  | $y_1$  | L      | L       |
|----|------|-------|--------|--------|--------|---------|
| C  | psia |       |        |        |        | ml      |
| 90 | 31   | 0.3   | 0.2926 | 0.7988 | 0.9855 | 1873.24 |

Then the concentration of PO in the liquid is:

$$x_1 L n_T / L(\text{ml}) = (0.2926)(0.7988)(20)/(1873.24) = 3.078 \cdot 10^{-3} \text{ mol/ml}$$

$C_{Bh}$ : 3.078 kmol/m<sup>3</sup>. Figure 4.4 gives the direct readings of concentration as a function of pressure and temperature.

$$C_{Bl}: 2.8 \text{ kmol/m}^3 \text{ (29 psia)}$$

$C_{Bi}$ : 14.61 kmol/m<sup>3</sup>, the concentration in the inlet, is calculated from  $\rho_{PO} / M_{wPO}$  considering PO is a liquid in the injection tank. The pressure in the PO supply tank is  $9.3 \cdot 10^5$  Pa (120 psig), and the pressure at the injection point is approximately  $5.8 \cdot 10^5$  Pa (70 psig). At this pressure, and at room temperature PO is liquid. Therefore, the liquid density is used.

Using the DCB program, nine different experimental data sets are modelled. Both, usual and unusual experimental results have been modelled. Table 6.2 summarises the reaction constants and the time periods for each stage of the data sets # 1.1, 1.2, 1.3, 1.7, 1.8, and 1.9. These sets show the usual sequence of phases. That is initiation, transition, rapid phase and termination phase. Most of the reactions follow this sequence of phases like sets # 1.1, 1.2, and 1.3. Sets # 1.7, 1.8, and 1.9 have the same reaction phases but they are more irregular. Table 6.3 gives the reaction constants and the time periods for

| Table 6.2 Reaction constants for sets # 1.1, 1.2, 1.3, 1.7, 1.8, and 1.9<br>They represent the usual results. $\Delta t$ (hr), $k \times 10^6$ ( $\text{sec}^{-1}$ ). |      |     |      |     |     |     |     |             |
|---|------|-----|------|-----|-----|-----|-----|-------------|
| Set #   | 1    | 2   | 3    | Av. | 7   | 8   | 9   |             |
| M PO/<br>kg lignin  | 30   | 30  | 30   |     | 25  | 25  | 25  |             |
| $k_i$   | 0.01 | 1.0 | 1.0  | 0.7 | 2.0 | 2.3 | 1.7 | Initiation  |
| $\Delta t_i$  | 10   | 24  | 44   | 26  | 12  | 20  | 14  | Phase       |
| $k_{t1}$  | 3.0  | 2.0 | 2.0  | 2.3 | —   | 3.5 | 4.5 | Transition  |
| $\Delta t_{t1}$   | 32   | 14  | 20   | 22  | —   | 17  | 14  | Phase       |
| $k_r$   | 4.8  | 3.8 | 2.5  | 3.7 | 6.0 | 5.8 | 6.0 | Rapid       |
| $\Delta t_r$  | 18   | 26  | 34   | 26  | 12  | 3   | 6   | Phase       |
| $k_{e1}$  | 3.0  | 0.9 | 0.95 | 1.6 | 1.5 | 3.0 | 5.0 | Termination |
| $\Delta t_{e1}$   | 20   | 24  | 28   | 24  | 2   | 4   | 5   | Phase       |
| $k_{e2}$  | 0.8  | 2.0 | 1.3  | 1.4 | 1.8 | —   |     |             |
| $\Delta t_{e2}$   | 20   | 12  | 34   | 22  | 7   | —   |     |             |
| Total<br>time   | 100  | 100 | 165  | 122 | 33  | 44  | 39  |             |

| Table 6.3 Reaction constants for sets # 1.4, 1.5, and 1.6.<br>Unusual sequence of phases. $\Delta t$ (hr), $k \times 10^6$ ( $\text{sec}^{-1}$ ). |      |      |         |                   |
|---|------|------|---------|-------------------|
| Set #   | 4    | 5    | Average |                   |
| M PO/<br>kg lignin  | 30   | 30   |         |                   |
| $k_i$   | 0.80 | 1.00 | 0.90    |                   |
| $\Delta t_i$  | 54   | 33   | 44      | Initiation Phase  |
| $k_{t1}$  | 1.50 | 1.70 | 1.60    |                   |
| $\Delta t_{t1}$   | 46   | 61   | 54      | Transition Phase  |
| $k_r$   | 3.00 | 3.50 | 3.25    |                   |
| $\Delta t_r$  | 20   | 16   | 18      | Rapid Phase       |
| Total<br>time   | 120  | 110  | 116     |                   |
| Set #   | 6    |      |         |                   |
| M PO/<br>kg lignin  | 30   |      |         |                   |
| $k_r$   | 3.5  |      |         |                   |
| $\Delta t_r$  | 24   |      |         | Rapid Phase       |
| $k_{e1}$  | 1.7  |      |         |                   |
| $\Delta t_{e1}$   | 31   |      |         | Termination Phase |
| $k_{e2}$  | 1.0  |      |         |                   |
| $\Delta t_{e2}$   | 21   |      |         |                   |
| $k_{e3}$  | 0.5  |      |         |                   |
| $\Delta t_{e3}$   | 24   |      |         |                   |
| $k_{e4}$  | 1.2  |      |         |                   |
| $\Delta t_{e4}$   | 35   |      |         |                   |
| Total time  | 135  |      |         |                   |

each phase for sets # 1.4, 1.5, and 1.6. Sets # 1.4 and 1.5 have the rapid phase at the end of the reaction. That is, they have very long initiation and transition phases. Free KOH initiates PO-homopolymerization, and in consequence the PO consumption increases. Then, the overall reaction rate, or the AFR, increases. This is likely to occur when higher amounts of catalyst, KOH, are used. In set # 1.6 the reaction starts with a rapid phase and then the reaction rate decreases. This is an unusual sequence of phases, and it could be that there were  $N_2$  injections at the beginning of the reaction.

Table 6.4 Parameters used in the models for sets # 1.1 to 1.9.

| Set #                                      | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
|--|------|------|------|------|------|------|------|------|------|
| $C_{Bh}$<br>(kmol/m <sup>3</sup> )         | 3.08 | 3.08 | 3.08 | 3.08 | 3.08 | 3.08 | 3.0  | 3.05 | 3.03 |
| $C_{Bl}$<br>(kmol/m <sup>3</sup> )         | 2.8  | 2.9  | 2.9  | 2.9  | 2.9  | 2.9  | 2.92 | 2.9  | 2.9  |
| $V_i^0$<br>(liters)                        | 1.5  | 1.5  | 1.5  | 1.5  | 1.5  | 1.5  | 1.5  | 1.5  | 1.5  |
| $Q_s^0 \times 10^7$<br>(m <sup>3</sup> /s) | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  |
| $Q_s^1 \times 10^8$<br>(m <sup>3</sup> /s) | 4.0  | 4.0  | 4.0  | 4.0  | 4.0  | 4.0  | 4.0  | 4.0  | 8.0  |
| Injections<br>model                        | 15   | 12   | 14   | 10   | 11   | 12   | 13   | 9    | 12   |
| Injections<br>exp.                         | 12   | 11   | 15   | 9    | 10   | 21   | 11   | 9    | 11   |
| Volume<br>injected model (ml)              | 890  | 773  | 874  | 733  | 733  | 773  | 571  | 650  | 664  |
| Volume<br>injected exp. (ml)               | 840  | 840  | 840  | 840  | 840  | 840  | 670  | 670  | 670  |

Table 6.4 gives the values of  $C_{Bh}$ ,  $C_{Bl}$ ,  $V_i^0$ ,  $Q_s^0$ ,  $Q_s^1$ , number of injections for all experimental data sets and for the computer models. Volumes injected in the model, and volumes injected in the experiment data sets # 1.1 to 1.9 are also given. Figures, 6.1 to 6.18, provide modelled PO concentration versus time followed by a plot that compares the AFR of each model with the corresponding experimental data, for data sets # 1.1 to # 1.9. The Average Feeding Rate (AFR) is the volume fed in each injection divided by the time between injections. The extent of propoxylation for the first three sets, 1.1 to 1.3, is of 30 M PO/kg lignin, and the average total time of reaction is 122 hours. For the last three sets, 1.7 to 1.9, the extent of propoxylation is only 25 M PO/kg lignin and the average total reaction time is 39 hours. It is interesting to note that the initiation phase is the longest phase, 26 hours for sets # 1.1 to 1.3 and 15 hours for the last three sets. Both spend about 27% of the total reaction time in initiation. Also, the reaction constant for the initiation phase is low; it ranges between  $1.0 \times 10^{-8}$  to  $2.3 \times 10^{-6} \text{sec}^{-1}$ . Then, for any extent of reaction, there is a long initiation phase with a low reaction constant. The increase in AFR (average feeding rate) in the last phase is due to a change in pressure set-point, and not due to an increase in the reaction rate. This can be seen in data sets # 1.2, 1.4, and 1.5.

From the results of these models and looking at the values of the reaction constants at the beginning of the reaction we decided that using a higher temperature at the beginning of the reaction would improve the reaction rate. One of the objectives of the modelling is then accomplished. The next section analyzes the use of a higher temperature during the initiation phase.

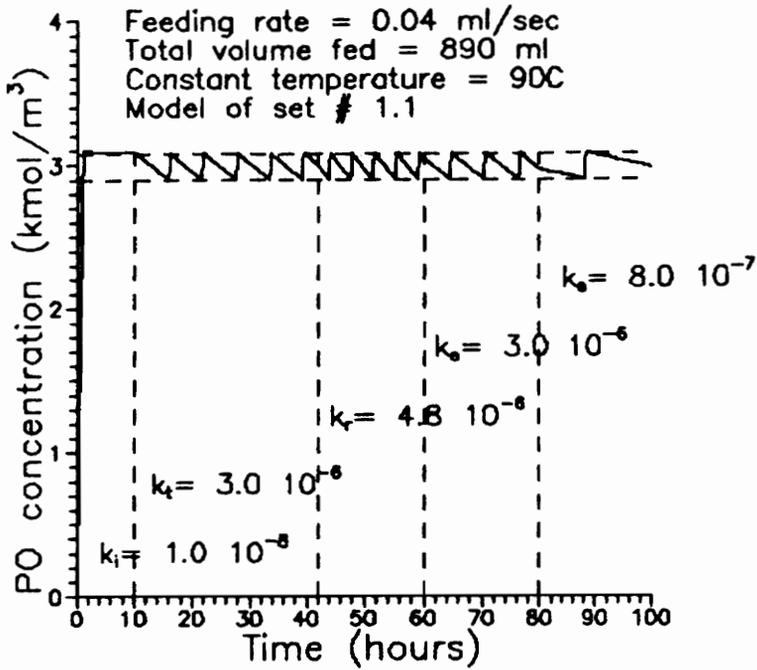


Figure 6.1 PO Concentration versus time for the liquid model for set # 1.1.

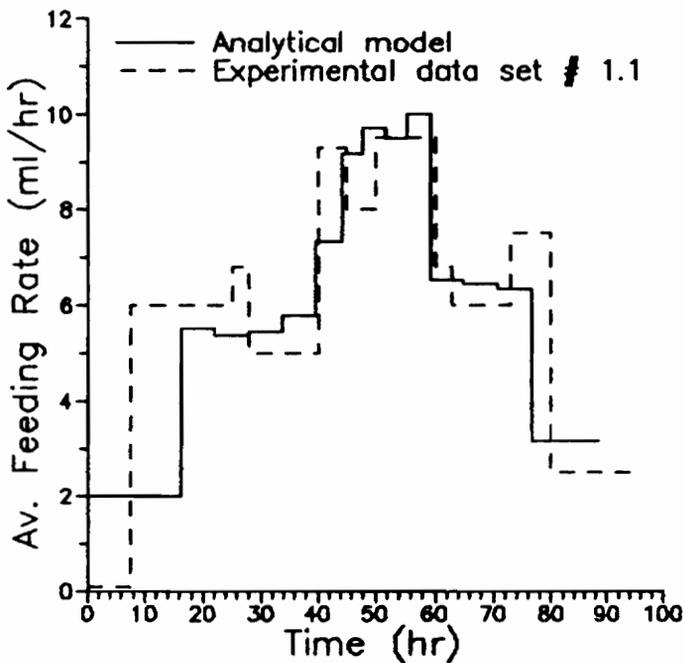


Figure 6.2 Comparison between experimental data and model for set # 1.1.

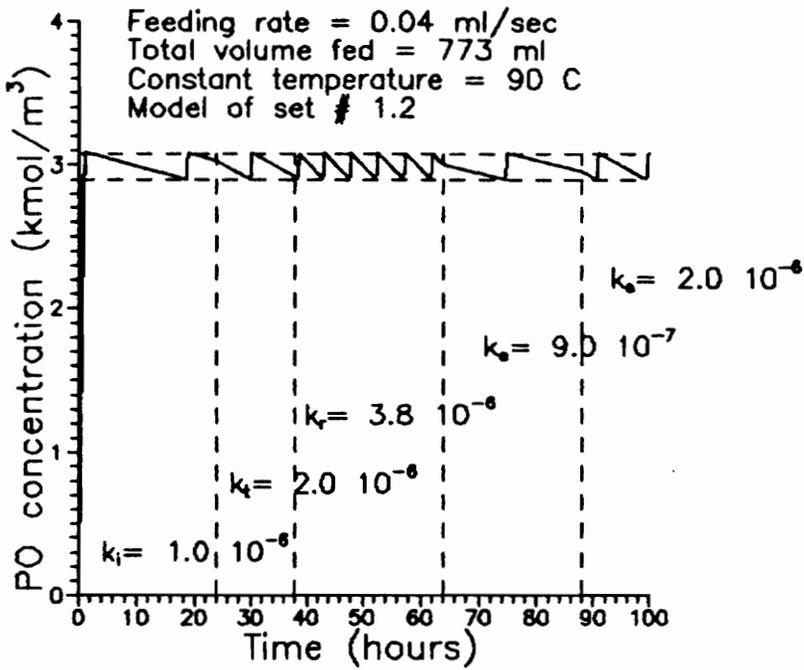


Figure 6.3 PO Concentration versus time for the liquid model for set # 1.2.

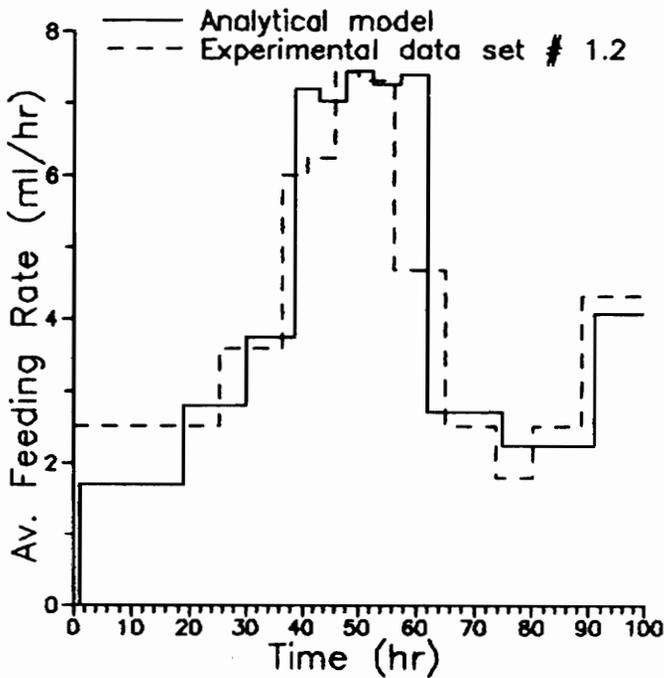


Figure 6.4 Comparison between experimental data and model for set # 1.2.

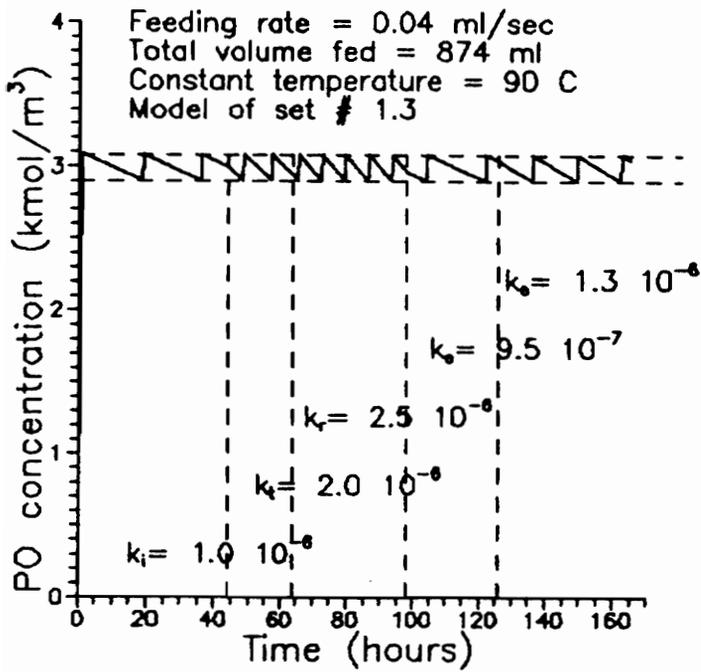


Figure 6.5 PO Concentration versus time for the liquid model for set # 1.3.

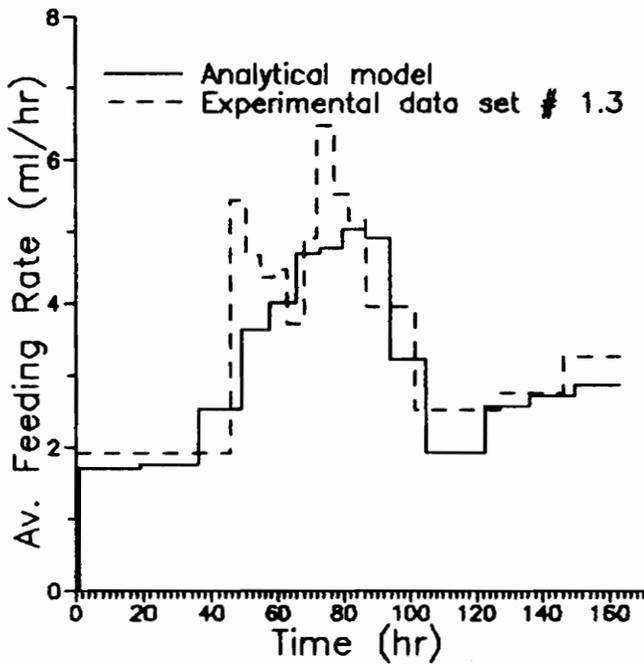


Figure 6.6 Comparison between experimental data and model for set # 1.3.

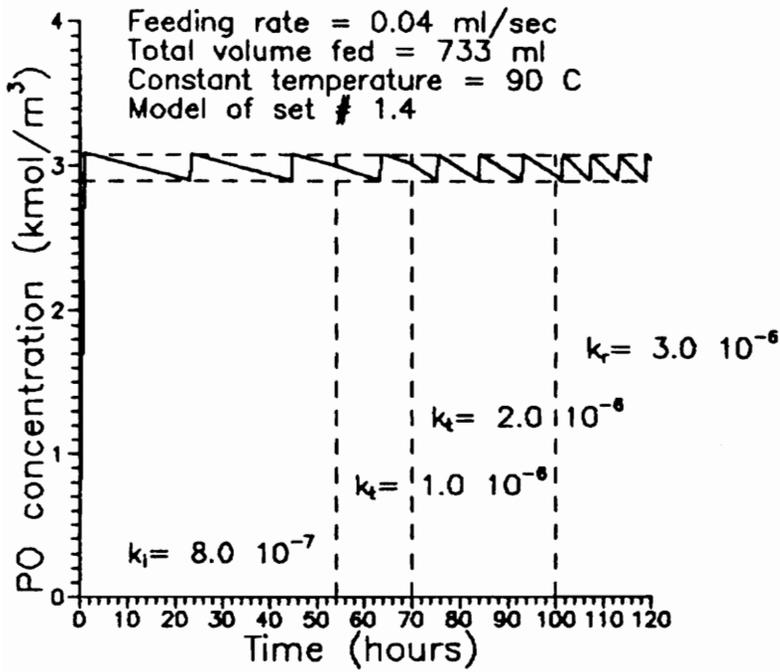


Figure 6.7 PO Concentration versus time for the liquid model for set # 1.4.

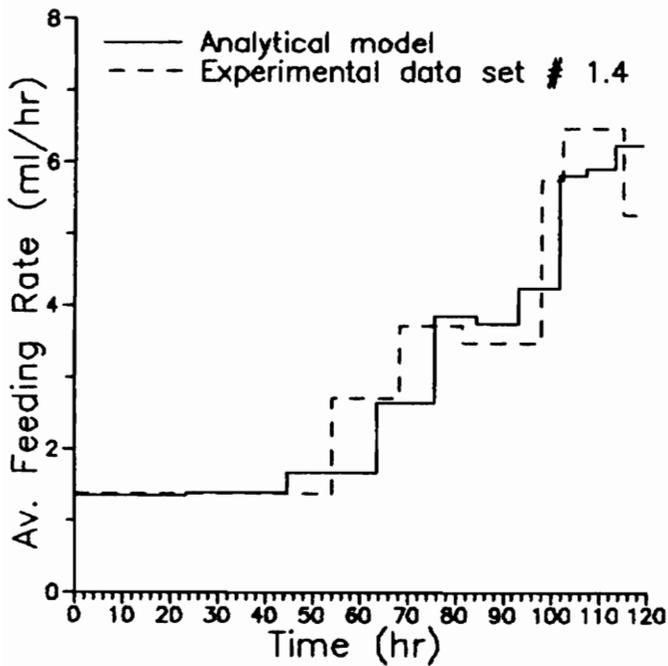


Figure 6.8 Comparison between experimental data and model for set # 1.4.

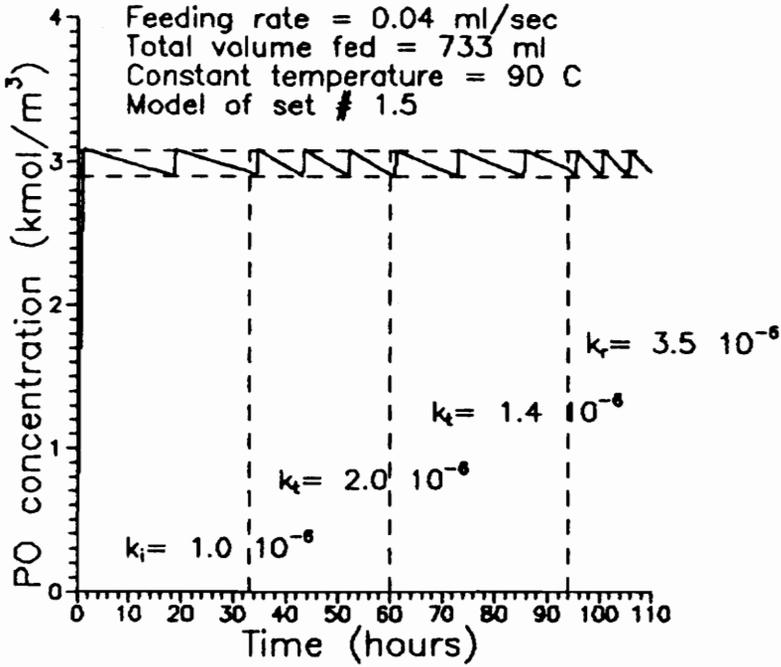


Figure 6.9 PO Concentration versus time for the liquid model for set # 1.5.

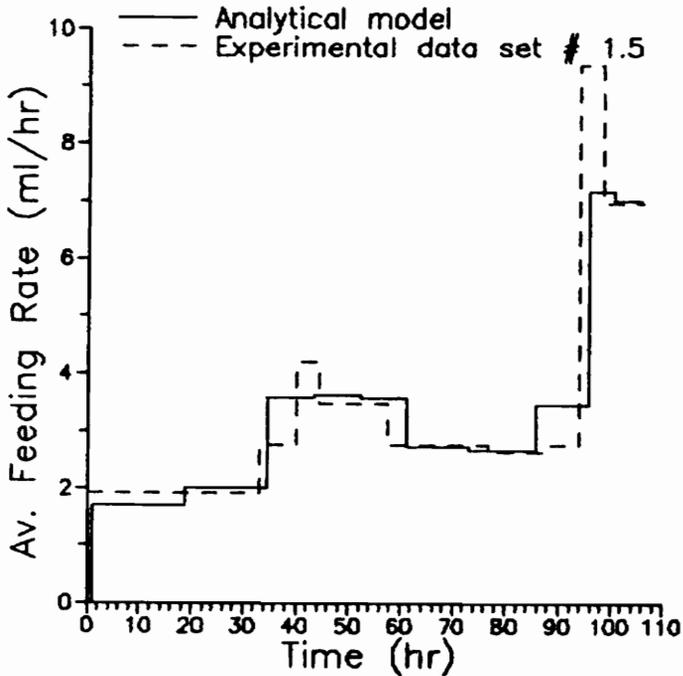


Figure 6.10 Comparison between experimental data and model for set # 1.5.

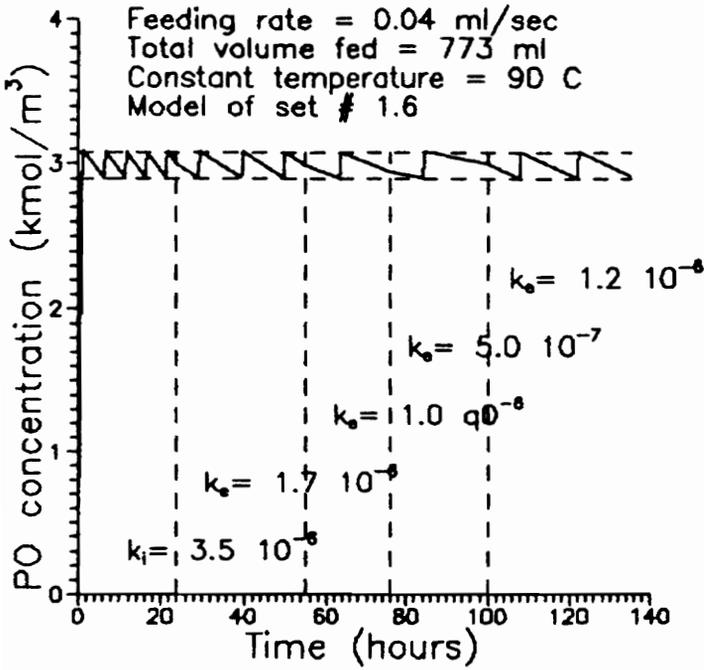


Figure 6.11 PO Concentration versus time for the liquid model for set # 1.6.

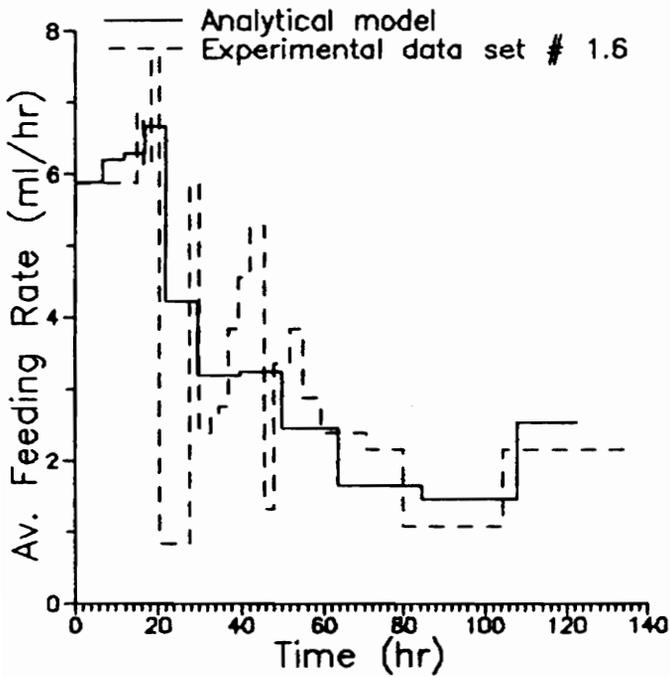


Figure 6.12 Comparison between experimental data and model for set # 1.6.

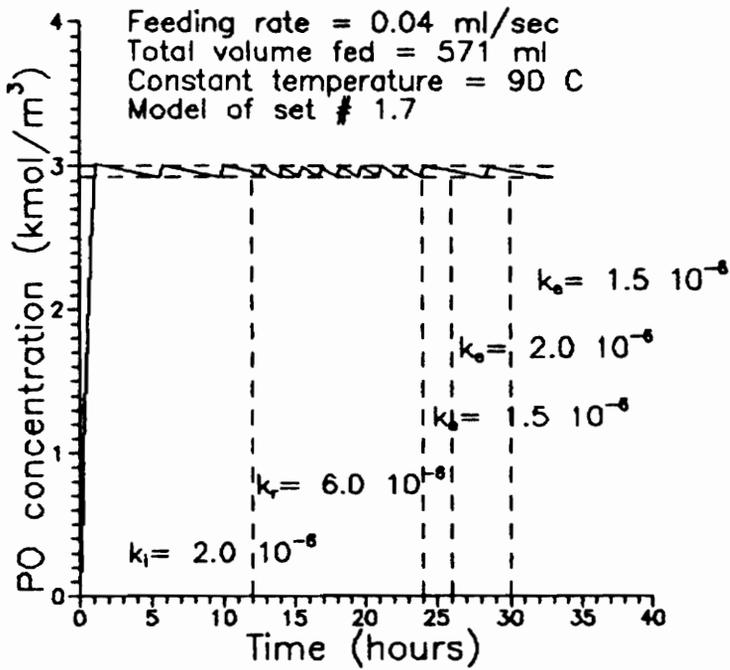


Figure 6.13 PO Concentration versus time for the liquid model for set # 1.7.

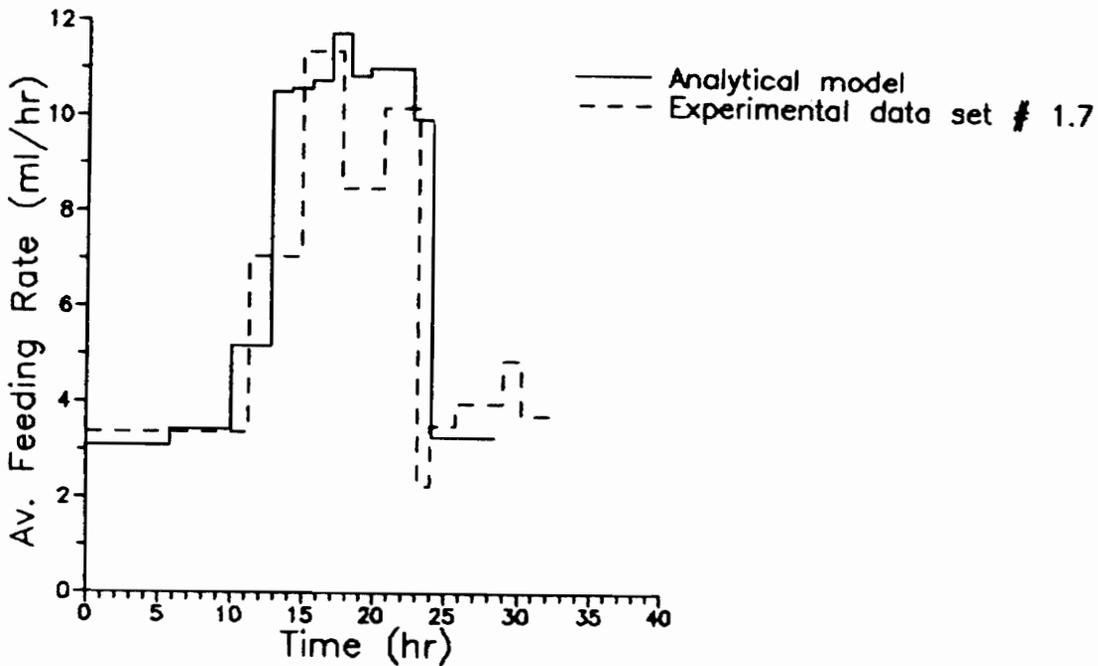


Figure 6.14 Comparison between experimental data and model for set # 1.7.

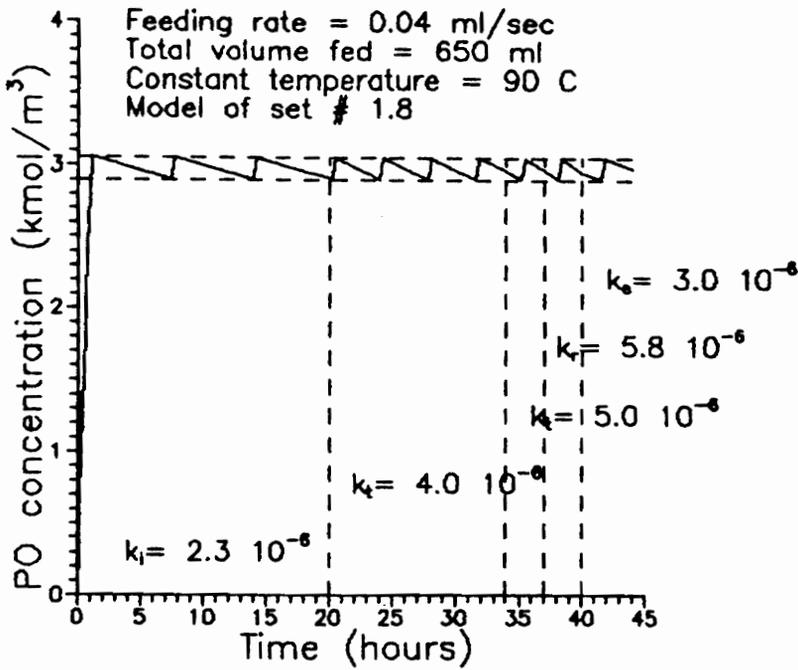


Figure 6.15 PO Concentration versus time for the liquid model for set # 1.8.

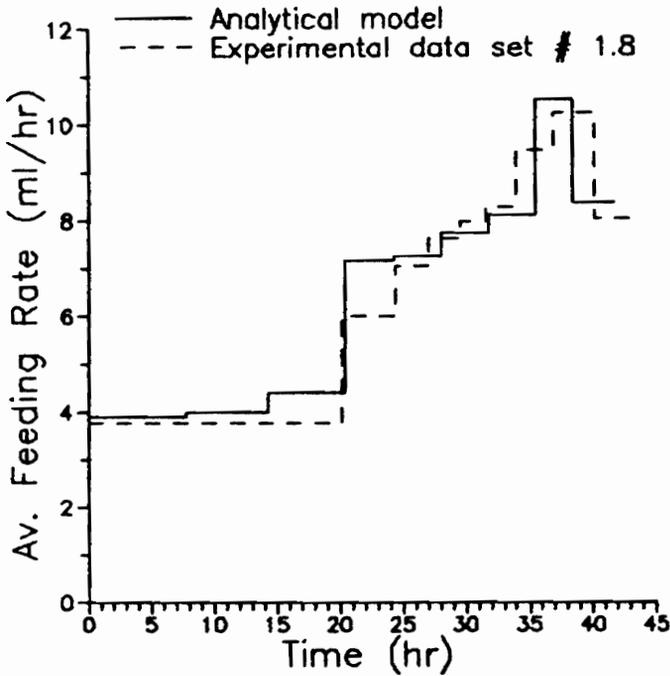


Figure 6.16 Comparison between experimental data and model for set # 1.8.

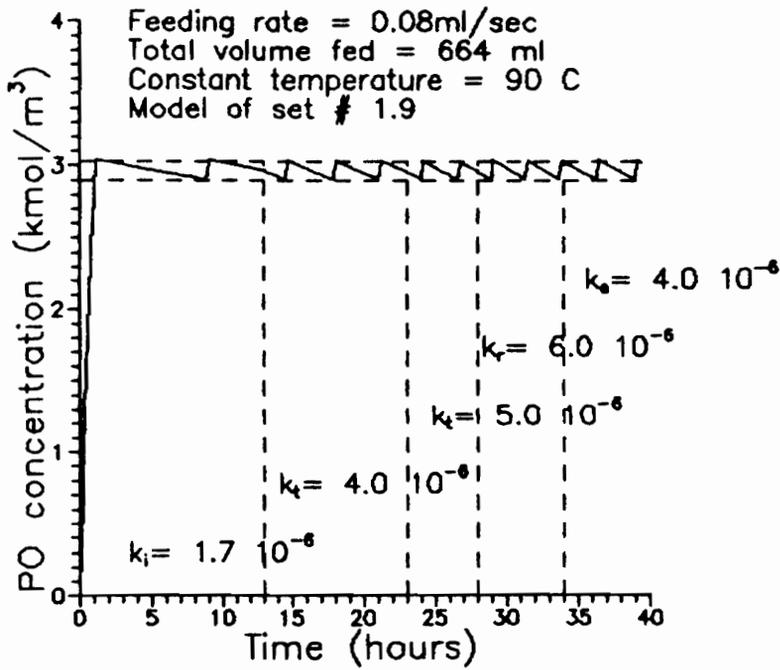


Figure 6.17 PO Concentration versus time for the liquid model for set # 1.9.

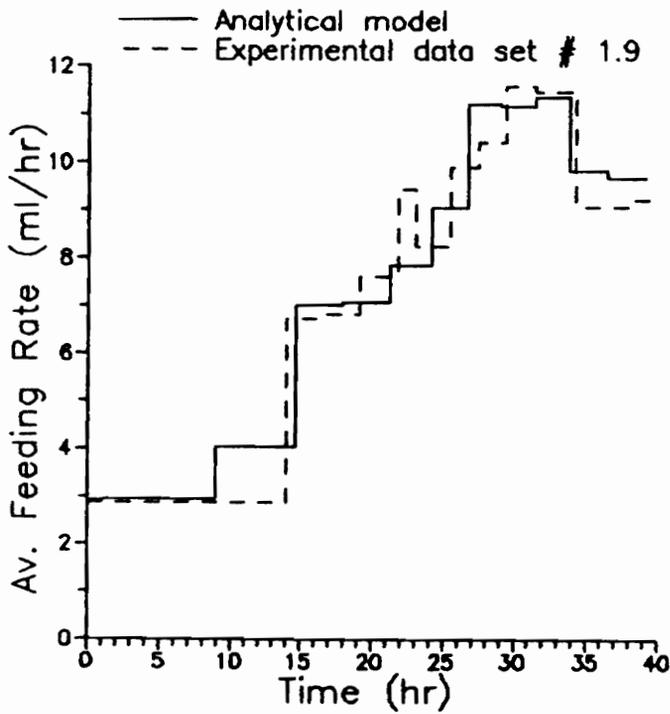


Figure 6.18 Comparison between experimental data and model for set # 1.9.

## 6.2 Variable Temperature Correlation

Phases I (Initiation) and IV-V (Termination) of the reaction are very slow. Using higher temperatures would result in an increased reaction rate in those phases. The temperature can be increased in phase I, but not in the last phases, IV and V, where an increase in temperature would favor homopolymerization. This is undesirable. The following reactions were run at 140°C at the beginning, and 110°C or 95°C after about three hours. Their main characteristics are:

PO (150 ml) is injected at the beginning of the reaction. The pressure is approximately  $2.9 \cdot 10^5$  Pa (28 psig). The temperature is set to 140°C and the pressure rises to approximately  $5.2 \cdot 10^5$  Pa (60 psig). After approximately 3 hours several injections at short succession occur. Then the temperature is lowered to 95°C; the pressure set-point drops to  $3.4 \cdot 10^5$  Pa (34 psig). Data set # 2.1 differs from the others, having a 200 ml first injection, a temperature set-point of 110°C, and a pressure set-point of  $3.4 \cdot 10^5$  Pa (35 psig). At the injections marked \*\* the pressure set-point was increased in order to accelerate the reaction. Steam explosion lignins prepared from yellow poplar using steam explosion severity of 4.1.

Extent of Propoxylation : 35 M PO/kg lignin

Average total time of reaction: 97 hours

Maximum AFR : 17.4 ml /hr

Average time at which the maximum AFR occurs: 24 hours.

Homopolymer content: 40% for data set # 2.1; and 30% for data sets # 2.2, 2.3, and 2.4.

Table 6.5 gives the the pressure variation ( $\Delta P$ ) obtained from the strip charts, the time between injections ( $\Delta t$ ), the injected volume ( $\Delta V$ ) and the average feeding rate (AFR) for sets 2.1 to 2.4.

Table 6.5 Experimental data for Series # 2.

| Injection N <sup>o</sup>            | $\Delta P$<br>psi | $\Delta vol$<br>ml | $\Delta time$<br>hours | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | Time<br>hr |
|-------------------------------------|-------------------|--------------------|------------------------|-------------------------------|--------------|------------|
| <b>Experimental data set # 2.1:</b> |                   |                    |                        |                               |              |            |
| 1                                   |                   | 200                |                        |                               |              |            |
| 2                                   | fast              |                    |                        |                               |              |            |
| 3                                   | fast              |                    |                        |                               |              |            |
| 4                                   | fast              |                    |                        |                               |              | 1.5        |
| 5                                   | 1.13              | 13.57              | .6                     | 1.88                          | 22.56        | 2.1        |
| 6                                   | 1.13              | 13.57              | 0.7                    | 1.62                          | 19.44        | 2.8        |
| 7                                   | 1.29              | 15.5               | 0.8                    | 1.62                          | 19.44        | 3.6        |
| 8                                   | 1.29              | 15.5               | 0.7                    | 1.85                          | 22.2         | 4.3        |
| 9                                   | 1.62              | 19.38              | 0.7                    | 2.31                          | 27.77        | 5.0        |
| 10                                  | 1.62              | 19.38              | 0.45                   | 3.6                           | 43.2         | 5.45       |
| 11                                  | 1.13              | 13.57              | 0.6                    | 1.88                          | 22.6         | 6.05       |
| 12                                  | 1.94              | 23.25              | 1.1                    | 1.76                          | 21.12        | 7.15       |
| 13                                  | 1.45              | 17.44              | 0.8                    | 1.82                          | 21.84        | 7.95       |
| 14                                  | 1.29              | 15.5               | 0.8                    | 1.62                          | 19.44        | 8.75       |
| 15                                  | 1.45              | 17.44              | 1.0                    | 1.45                          | 17.4         | 9.75       |
| 16                                  | 1.29              | 15.5               | 0.8                    | 1.62                          | 19.44        | 10.55      |
| 17                                  | 1.62              | 19.38              | 1.1                    | 1.47                          | 17.64        | 11.65      |
| 18                                  | 1.29              | 15.5               | 0.9                    | 1.44                          | 24.88        | 12.55      |
| 19                                  | 1.45              | 17.44              | 1.0                    | 1.45                          | 17.44        | 13.55      |
| 20                                  | 1.29              | 15.5               | 0.8                    | 1.62                          | 19.44        | 14.35      |
| 21                                  | 1.45              | 17.44              | 1.0                    | 1.45                          | 17.44        | 15.35      |
| 22                                  | 1.94              | 23.25              | .8                     | 2.42                          | 29.04        | 16.15      |
| 23                                  | 1.62              | 19.38              | 1.2                    | 1.35                          | 16.2         | 17.35      |
| 24                                  | 1.62              | 19.38              | 1.4                    | 1.15                          | 13.8         | 18.75      |
| 25                                  | 1.62              | 19.38              | 1.6                    | 1.01                          | 12.12        | 20.35      |
| 26                                  | 1.62              | 19.38              | 1.8                    | 0.90                          | 10.8         | 21.15      |
| 27                                  | 1.62              | 19.38              | 1.8                    | 0.90                          | 10.8         | 22.95      |

Table 6.5 (continued) Experimental data Series # 2.

| Injection N <sup>o</sup>                 | $\Delta P$<br>psi | $\Delta vol$<br>ml | $\Delta time$<br>hours | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | Time<br>hr |
|--|-------------------|--------------------|------------------------|-------------------------------|--------------|------------|
| <b>Experimental data set 2.1 (cont):</b> |                   |                    |                        |                               |              |            |
| 28                                       | 1.62              | 19.38              | 2.2                    | 0.73                          | 8.76         | 25.15      |
| 29                                       | 1.62              | 19.38              | 2.2                    | 0.73                          | 8.76         | 27.35      |
| 30                                       | 1.62              | 19.38              | 2.6                    | 0.62                          | 7.44         | 29.95      |
| 31                                       | 1.62              | 19.38              | 3.4                    | 0.48                          | 5.76         | 33.35      |
| 32                                       | 1.78              | 21.32              | 4.1                    | 0.43                          | 5.16         | 37.45      |
| 33**                                     | 1.94              | 23.26              | 3.5                    | 0.55                          | 6.6          | 40.95      |
| 34                                       | 1.78              | 21.32              | 2.9                    | 0.61                          | 7.32         | 43.85      |
| 35                                       | 1.78              | 21.32              | 3.5                    | 0.51                          | 6.12         | 47.35      |
| 36                                       | 1.62              | 19.38              | 4.2                    | 0.39                          | 4.68         | 51.55      |
| 37                                       | 1.78              | 21.32              | 5.0                    | 0.32                          | 3.84         | 56.55      |
| 38                                       | 1.94              | 23.26              | 11.3                   | 0.17                          | 2.04         | 67.85      |
| 39                                       | 1.78              | 21.32              | 14.2                   | 0.13                          | 1.56         | 82.05      |
| 40                                       | 1.94              | 23.26              | 14.7                   | 0.13                          | 1.56         | 96.75      |
| 41**                                     | 0.32              | 3.88               | 2.0                    | 0.16                          | 1.92         | 98.75      |
|  |                   | 882.17             |                        |                               |              |            |

**Experimental data set # 2.2 :**

|   |      |     |      |       |       |      |
|---|------|-----|------|-------|-------|------|
| 1 |      | 6.3 | 150  |       |       | 6.3  |
| 2 | 3.15 | 0.2 | 50.4 | 15.75 | 252.0 | 6.5  |
| 3 | 2.80 | 0.2 | 44.8 | 14.0  | 224.0 | 6.7  |
| 4 | 2.45 | 0.2 | 39.2 | 12.25 | 196.0 | 6.9  |
| 5 | 2.45 | 4.0 | 39.2 | 0.61  | 9.8   | 10.9 |
| 6 | 2.80 | 4.0 | 44.8 | 0.70  | 11.2  | 14.9 |
| 7 | 2.45 | 5.5 | 39.2 | 0.45  | 7.1   | 20.4 |

Table 6.5 (continued) Experimental data Series # 2.

| Injection N <sup>o</sup>             | $\Delta P$<br>psi | $\Delta$ time<br>hours | $\Delta$ vol.<br>ml | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | Time<br>hr |
|--------------------------------------|-------------------|------------------------|---------------------|-------------------------------|--------------|------------|
| Experimental data set # 2.2 (cont) : |                   |                        |                     |                               |              |            |
| 8                                    | 2.80              | 4.9                    | 44.8                | 0.57                          | 9.1          | 25.3       |
| 9                                    | 2.45              | 4.6                    | 39.2                | 0.53                          | 8.5          | 29.9       |
| 10                                   | 2.45              | 4.7                    | 39.2                | 0.52                          | 8.3          | 34.6       |
| 11                                   | 2.80              | 4.8                    | 44.8                | 0.58                          | 9.3          | 39.4       |
| 12                                   | 2.45              | 5.0                    | 39.2                | 0.49                          | 7.8          | 44.4       |
| 13                                   | 2.80              | 6.0                    | 44.8                | 0.47                          | 7.5          | 50.4       |
| 14                                   | 3.50              | 7.7                    | 56.0                | 0.45                          | 7.3          | 58.1       |
| 15                                   | 3.50              | 11.0                   | 56.0                | 0.32                          | 5.1          | 69.1       |
| 16**                                 | 3.50              | 7.6                    | 56.0                | 0.46                          | 7.4          | 76.7       |
| 17                                   | 4.90              | 8.4                    | 78.4                | 0.58                          | 9.3          | 85.1       |
| 18                                   | 3.50              | 1.6                    | 56.0                | 2.19                          | 35.0         | 86.7       |
|                                      |                   |                        | 962.0               |                               |              |            |
| Experimental data set # 2.3 :        |                   |                        |                     |                               |              |            |
| 1                                    | 58.9              | 3.3                    | 150                 |                               |              | 3.3        |
| 2                                    | 2.5               | 0.25                   | 42.5                | 10                            | 170.0        | 3.55       |
| 3                                    | 3.6               | 0.35                   | 61.2                | 14.4                          | 174.9        | 3.90       |
| 4                                    | 2.5               | 1.7                    | 42.5                | 1.47                          | 25.0         | 5.6        |
| 5                                    | 2.9               | 6.0                    | 49.3                | 0.48                          | 8.2          | 11.6       |
| 6                                    | 2.5               | 5.3                    | 42.5                | 0.47                          | 8.0          | 16.9       |
| 7                                    | 2.5               | 5.0                    | 42.5                | 0.5                           | 8.5          | 21.9       |
| 8                                    | 2.5               | 3.6                    | 42.5                | 0.69                          | 11.8         | 25.5       |
| 9                                    | 2.7               | 4.2                    | 45.9                | 0.64                          | 10.9         | 29.7       |
| 10                                   | 2.5               | 4.7                    | 42.5                | 0.53                          | 9.0          | 34.4       |
| 11                                   | 2.7               | 4.7                    | 45.9                | 0.57                          | 9.8          | 39.1       |
| 12                                   | 3.0               | 4.6                    | 51.0                | 0.65                          | 11.1         | 43.7       |
| 13                                   | 3.5               | 5.5                    | 59.5                | 0.64                          | 10.8         | 49.2       |

Table 6.5 (continued) Experimental data Series # 2.

| Injection N <sup>o</sup>              | $\Delta P$<br>psi | $\Delta$ time<br>hours | $\Delta$ vol.<br>ml | $\Delta P/\Delta t$<br>psi/hr | AFR<br>ml/hr | Time<br>hr |
|---------------------------------------|-------------------|------------------------|---------------------|-------------------------------|--------------|------------|
| Experimental data set # 2.3 (cont.) : |                   |                        |                     |                               |              |            |
| 14                                    | 3.0               | 7.6                    | 51.0                | 0.4                           | 6.7          | 56.8       |
| 15                                    | 2.15              | 9.3                    | 36.6                | 0.23                          | 3.9          | 66.1       |
| 16**                                  | 2.15              | 11.5                   | 36.6                | 0.19                          | 3.2          | 77.6       |
| 17                                    | 3.0               | 13.4                   | 51.0                | 0.22                          | 3.8          | 91         |
| 18                                    | 3.0               | 1.3                    | 51.0                | 2.3                           | 39.2         | 92.3       |
|                                       |                   |                        | 944.0               |                               |              |            |
| Experimental data set # 2.4:          |                   |                        |                     |                               |              |            |
| 1                                     | 29                | 2.0                    | 150                 |                               |              | 2.0        |
| 2                                     | 2.3               | 0.2                    | 27.6                | 11.5                          | 138.0        | 2          |
| 3                                     | 2.3               | 4.0                    | 27.6                | 0.56                          | 6.72         | 4.2        |
| 4**                                   | 3.6               | 12.0                   | 43.0                | 0.30                          | 3.6          | 16.2       |
| 5                                     | 1.4               | 0.2                    | 16.8                | 7.0                           | 84           | 16.4       |
| 6                                     | 5.4               | 7.0                    | 64.4                | 0.77                          | 9.2          | 23.4       |
| 7                                     | 2.5               | 5.1                    | 30.0                | 0.49                          | 5.9          | 28.5       |
| 8                                     | 2.5               | 5.5                    | 30.0                | 0.45                          | 5.45         | 34.0       |
| 9                                     | 2.9               | 5.0                    | 34.8                | 0.58                          | 7.0          | 39.0       |
| 10                                    | 3.22              | 5.3                    | 38.6                | 0.61                          | 7.3          | 44.3       |
| 11                                    | 3.2               | 5.2                    | 38.6                | 0.62                          | 7.4          | 49.5       |
| 12                                    | 2.9               | 3.2                    | 34.8                | 0.90                          | 10.9         | 52.7       |
| 13                                    | 3.2               | 5.2                    | 38.6                | 0.62                          | 7.4          | 57.9       |
| 14                                    | 3.2               | 4.7                    | 38.6                | 0.68                          | 8.2          | 62.6       |
| 15                                    | 3.2               | 6.7                    | 38.6                | 0.48                          | 5.73         | 69.3       |
| 16                                    | 3.2               | 6.8                    | 38.6                | 0.47                          | 5.6          | 76.1       |
| 17                                    | 3.2               | 7.5                    | 38.6                | 0.43                          | 5.2          | 88.6       |
| 18**                                  | 3.2               | 8.5                    | 38.6                | 0.38                          | 4.5          | 92.1       |
| 19                                    | 6.1               | 15.0                   | 73.2                | 0.41                          | 4.9          | 107.1      |
| 20**                                  | 5.4               | 2.5                    | 64.4                | 2.16                          | 25.9         | 109.6      |
|                                       |                   |                        | 905.4               |                               |              |            |

In order to compare the difference between the average feeding rate for the reactions at constant temperature and that for the temperature gradient experiments, the AFR for two sets of experimental data, 1.2 and 2.1, are plotted in Figure 5.19. When a temperature gradient is applied the maximum AFR is higher and it occurs earlier in the reaction time. This is convenient for accelerating the reaction. Also, the total reaction time for the experiments using a temperature gradient is shorter. The use of a temperature gradient is therefore found to accelerate the lignin propoxylation reaction. If the quality of the reaction product is not affected by these new operation conditions, the temperature gradient produces an improved propoxylation process.

Each set of experimental data, 2.1 to 2.4, is correlated with modelled reaction. The reaction constants for each phase are given in Table 6.6. Table 6.7 compiles the values for  $C_{Bh}$ ,  $C_{Bl}$ ,  $V_i^0$ ,  $Q_s^0$ ,  $Q_s^1$ , number of injections in the model, number of injections in the experiment, total volume injected in the model, and total volume injected in the experimental data sets # 2.1 to 2.4. The PO concentration versus time diagrams of the models for sets # 2.1 to 2.4 are given in Figures 6.20, 6.22, 6.24, and 6.26. To compare the model with the experimental data, the program calculates the Average Feeding Rate (AFR). The AFR's for the first three injections are very high, approximately 170 ml/hr. The reason for this initial cycling is that a few nitrogen injections occur during the change from the first feeding tank to the second one. The slow initiation phase has disappeared. The reaction constant for the initiation phase is similar or even higher than the reaction constant for the rapid phase. The total reaction time has been reduced.

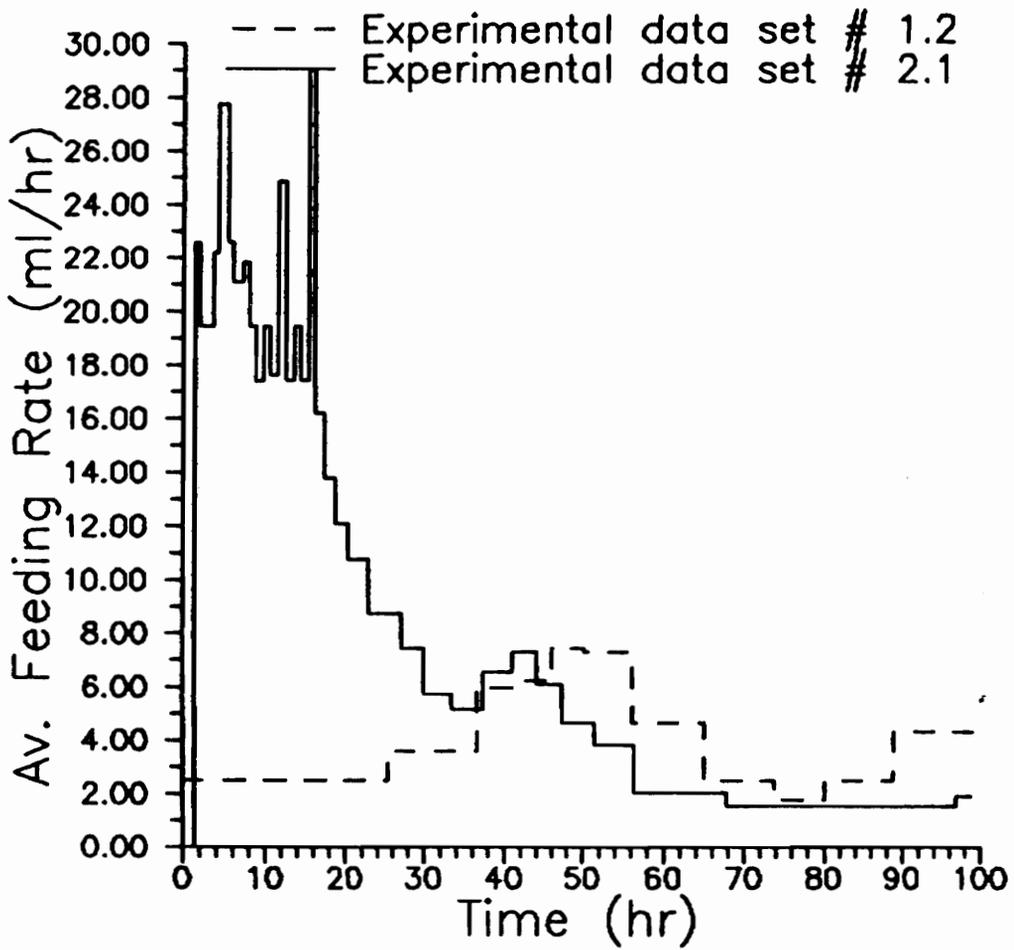


Figure 6.19 Average feeding rate versus time using constant temperature and using a temperature gradient.

| Table 6.6 Reaction constants for sets # 2.1, 2.2, 2.3, and 2.4.<br>$\Delta t$ (hr), $k \times 10^6$ ( $\text{sec}^{-1}$ ). |     |     |     |     |                     |
|--|-----|-----|-----|-----|---------------------|
| Set #  | 1   | 2   | 3   | 4   |                     |
| M PO/kg lignin   | 35  | 35  | 35  | 35  |                     |
| $k_i$  | 9.5 | 5.5 | 5.5 | 1.5 | Initiation Phase or |
| $\Delta t_i$   | 20  | 15  | 6   | 17  | First rapid Phase   |
| $k_t$  | 3.5 | 3.2 | 4.0 | 3.5 | Transition          |
| $\Delta t_t$   | 17  | 5   | 19  | 19  | Phase               |
| $k_r$  | 0.7 | 4.2 | 5.0 | 3.8 | Second Rapid        |
| $\Delta t_r$   | 4   | 38  | 30  | 28  | Phase               |
| $k_{e1}$   | 1.5 | 2.7 | 1.8 | 2   | Termination         |
| $\Delta t_{e1}$  | 25  | 12  | 38  | 44  | Phase               |
| $k_{e2}$   | 0.5 | 3.8 | 3.8 | 2.5 |                     |
| $\Delta t_{e2}$  | 34  | 17  | 1   | 2   |                     |
| Total time   | 100 | 87  | 94  | 110 |                     |

| Table 6.7 Parameters used in the models for sets # 2.1 to 2.4. |      |      |      |      |  |
|--|------|------|------|------|--|
| Set #  | 1    | 2    | 3    | 4    |  |
| $C_{Bh}$ ( $\text{kmol}/\text{m}^3$ )                          | 3.0  | 3.0  | 3.0  | 3.0  |  |
| $C_{Bl}$ ( $\text{kmol}/\text{m}^3$ )                          | 2.95 | 2.85 | 2.85 | 2.90 |  |
| $V_i^0$ (liters)   | 1.5  | 1.5  | 1.5  | 1.5  |  |
| $Q_s^0 \times 10^7$ ( $\text{m}^3/\text{s}$ )                  | 1.0  | 1.0  | 1.0  | 1.0  |  |
| $Q_s^1 \times 10^8$ ( $\text{m}^3/\text{s}$ )                  | 2.0  | 3.0  | 3.0  | 4.0  |  |
| $N^{\circ}$ injections model                                   | 25   | 22   | 17   | 23   |  |
| $N^{\circ}$ injections exp.                                    | 41   | 18   | 18   | 20   |  |
| Volume model   | 1000 | 1100 | 1048 | 1083 |  |
| Volume exp.  | 970  | 970  | 970  | 970  |  |

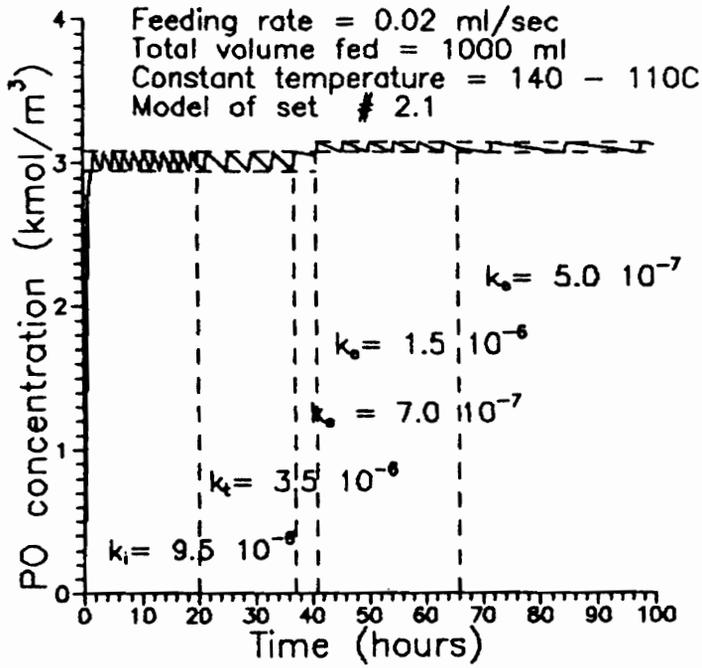


Figure 6.20 PO Concentration versus time for the liquid model for set # 2.1.

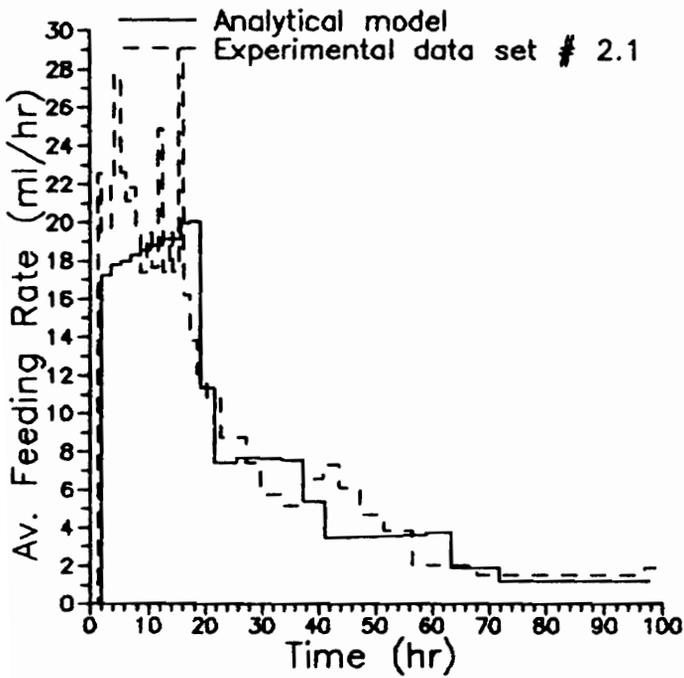


Figure 6.21 Comparison between experimental and model for data set # 2.1.

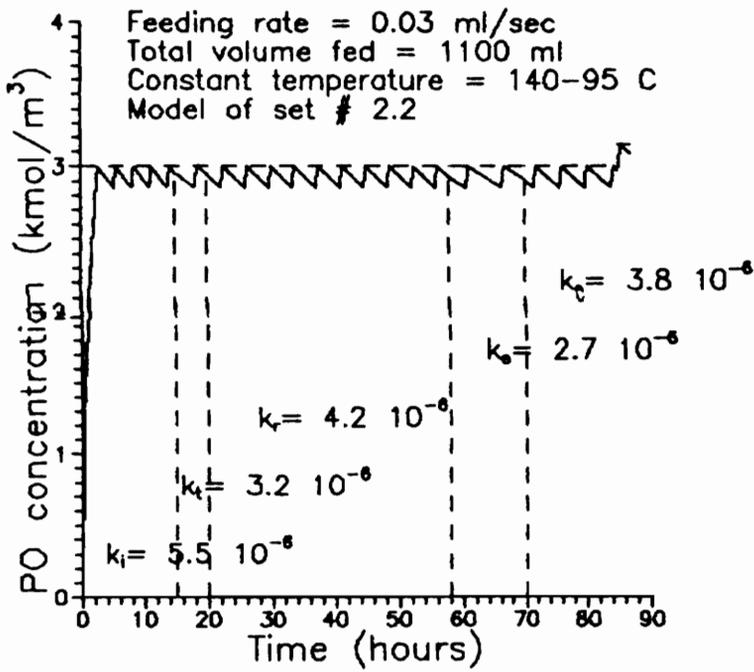


Figure 6.22 PO Concentration versus time for the liquid model for set # 2.2.

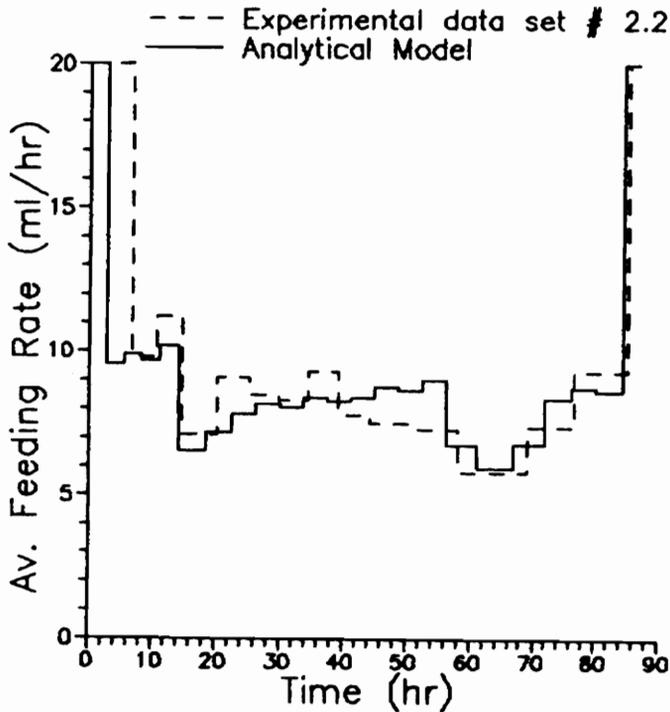


Figure 6.23 Comparison between experimental data and model for set # 2.2.

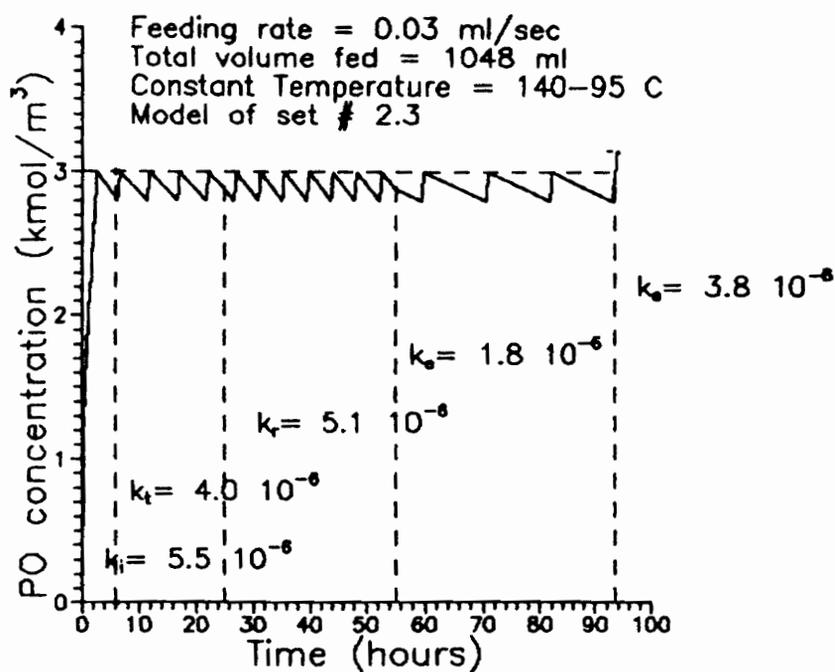


Figure 6.24 PO Concentration versus time for the liquid model for set # 2.3.

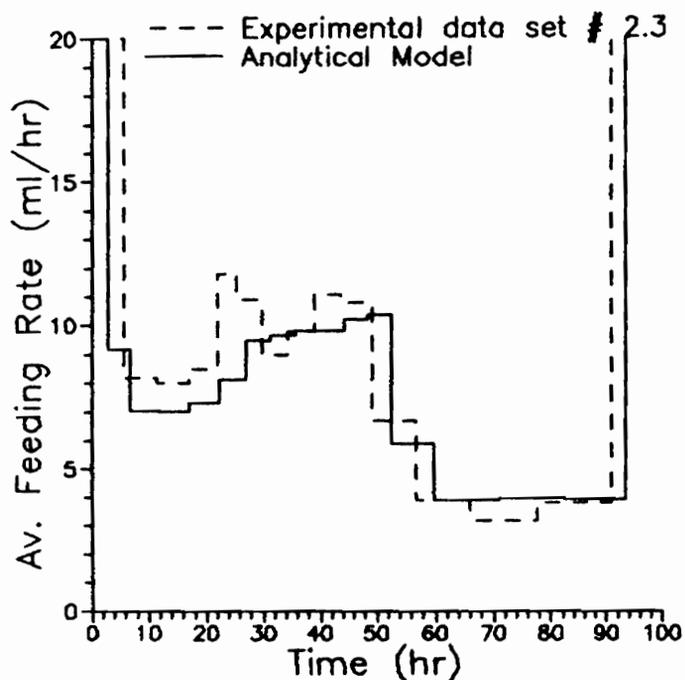


Figure 6.25 Comparison between experimental data and model for set # 2.3.

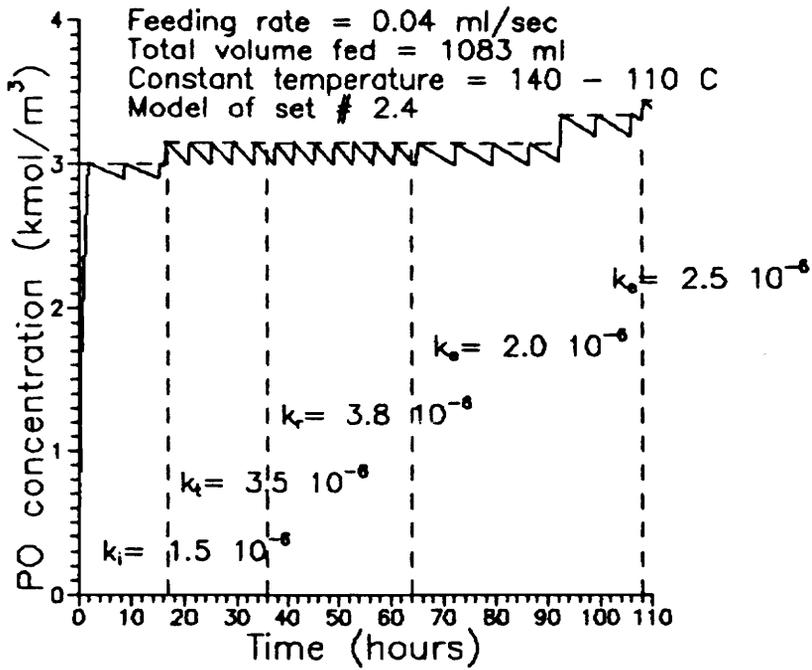


Figure 6.26 PO Concentration versus time for the liquid model for set # 2.4.

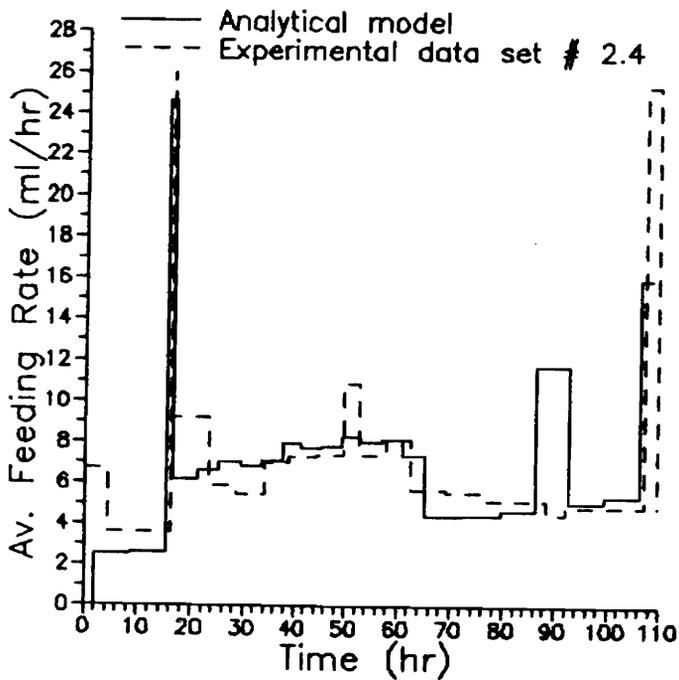


Figure 6.27 Comparison between experimental data and model for set # 2.4.

### 6.3 Predictive Kinetic Model

In the previous section a temperature gradient was used to accelerate the reaction rate in the initiation phase. In this section the temperature required for increasing the reaction constants to a certain limit is predicted analytically. If  $k'$  is the desired rate constant, using the Arrhenius equation we can calculate the value of  $T'$  necessary to reach  $k'$ . That is, from Equation 6.0

$$k = k' \exp \left[ \frac{E_a}{R} \left( \frac{1}{T'} - \frac{1}{T} \right) \right] \quad 6.0$$

we calculate  $T'$ , the temperature in each phase to have the desired reaction constant,

$$\frac{1}{T'} = \frac{1}{T} + \frac{R}{E_a} \ln \frac{k}{k'} \quad 6.1$$

Zhang and Glasser(1987) have measured an activation energy of  $10.2 \pm 10\%$  kcal/mol for the lignin propoxylation reaction. Equation 6.0 is plotted in Figure 6.28 using an activation energy of 10.2 kcal/mol,  $T = 90^\circ\text{C}$ , and two values for  $k'$ ,  $1.0 \cdot 10^{-5}\text{sec}^{-1}$  and  $5.0 \cdot 10^{-6}\text{sec}^{-1}$ . In Figure 6.28, with the known  $k$  value moving toward the corresponding  $k'$  line the temperature  $T'$  can be read in the x-axis.

For the model of the data set # 1.2, the values of  $T'$  are calculated using Equation 6.1:

Phase I:  $k_i = 1.0 \cdot 10^{-6}\text{sec}^{-1}$  ( $90^\circ\text{C}$ ),  $T' = 160^\circ\text{C}$ ,  $k' = 1.0 \cdot 10^{-5} \text{sec}^{-1}$

Phase II:  $k_t = 2.0 \cdot 10^{-6}\text{sec}^{-1}$  ( $90^\circ\text{C}$ ),  $T' = 137^\circ\text{C}$ ,  $k' = 1.0 \cdot 10^{-5} \text{sec}^{-1}$

Phase III:  $k_r = 3.8 \cdot 10^{-6}\text{sec}^{-1}$  ( $90^\circ\text{C}$ ),  $T' = 115^\circ\text{C}$ ,  $k' = 1.0 \cdot 10^{-5} \text{sec}^{-1}$

Phase IV:  $k_e = 9.0 \cdot 10^{-7}\text{sec}^{-1}$  ( $90^\circ\text{C}$ ),  $T' = 167^\circ\text{C}$ ,  $k' = 1.0 \cdot 10^{-5} \text{sec}^{-1}$

Phase V:  $k_e = 2.0 \cdot 10^{-6}\text{sec}^{-1}$  ( $90^\circ\text{C}$ ),  $T' = 137^\circ\text{C}$ ,  $k' = 1.0 \cdot 10^{-5} \text{sec}^{-1}$

The temperature can be increased only in the initiation phase to avoid homopolymerization. Then an acceptable temperature gradient could be  $160^\circ\text{C}$ ,  $137^\circ\text{C}$ , and  $115^\circ\text{C}$ . Another factor needs to be considered in the selection of the temperature gradient. The temperature has to be lower than the lignin glass

transition temperature. In the last section an initiation temperature 140°C was selected, which is 10-20°C below the glass transition temperature. An initiation temperature of 160°C is too high, because is close to the glass transition temperature value for most lignin samples. A temperature gradient of 140-95°C will be used to calculate the rate constants for set 1.2. Following the values for  $k'$  are calculated using Equation 6.0.

Phase I:  $k_i = 1.0 \cdot 10^{-6} \text{sec}^{-1}$  (90°C),  $T' = 140^\circ\text{C}$ ,  $k' = 5.6 \cdot 10^{-5} \text{sec}^{-1}$

Phase II:  $k_t = 2.0 \cdot 10^{-6} \text{sec}^{-1}$  (90°C),  $T' = 95^\circ\text{C}$ ,  $k' = 2.5 \cdot 10^{-6} \text{sec}^{-1}$

Phase III:  $k_r = 3.8 \cdot 10^{-6} \text{sec}^{-1}$  (90°C),  $T' = 95^\circ\text{C}$ ,  $k' = 4.6 \cdot 10^{-6} \text{sec}^{-1}$

Phase IV:  $k_e = 9.0 \cdot 10^{-7} \text{sec}^{-1}$  (90°C),  $T' = 95^\circ\text{C}$ ,  $k' = 1.1 \cdot 10^{-6} \text{sec}^{-1}$

Phase V:  $k_e = 2.0 \cdot 10^{-6} \text{sec}^{-1}$  (90°C),  $T' = 95^\circ\text{C}$ ,  $k' = 2.5 \cdot 10^{-6} \text{sec}^{-1}$

Finally lets compare the values of  $k'$  obtained using a temperature gradient of 140-95°C for set # 1.2 with the rate constants of set # 2.2, in which already was used a temperature gradient of 140-95°C.

#### Set # 2.2

from model of experimental results

Phase I:  $k_i = 5.5 \cdot 10^{-6} \text{sec}^{-1}$  (140°C)

Phase II:  $k_t = 3.2 \cdot 10^{-6} \text{sec}^{-1}$  (95°C)

Phase III:  $k_r = 4.2 \cdot 10^{-6} \text{sec}^{-1}$  (95°C)

Phase IV:  $k_e = 2.7 \cdot 10^{-6} \text{sec}^{-1}$  (95°C)

Phase V:  $k_e = 3.8 \cdot 10^{-6} \text{sec}^{-1}$  (95°C)

#### Set # 1.2

predicted values

$5.6 \cdot 10^{-6} \text{sec}^{-1}$  (140 °C)

$2.5 \cdot 10^{-6} \text{sec}^{-1}$  (95°C)

$4.6 \cdot 10^{-6} \text{sec}^{-1}$  (95°C)

$1.1 \cdot 10^{-6} \text{sec}^{-1}$  (95°C)

$2.5 \cdot 10^{-6} \text{sec}^{-1}$  (95°C)

The two sets of values are very similar. Then it could be say that if reaction set # 1.2 were done with a temperature gradient of 140-95°C the reaction rate of set # 1.2 will be similar to the reaction rate of set # 2.1.

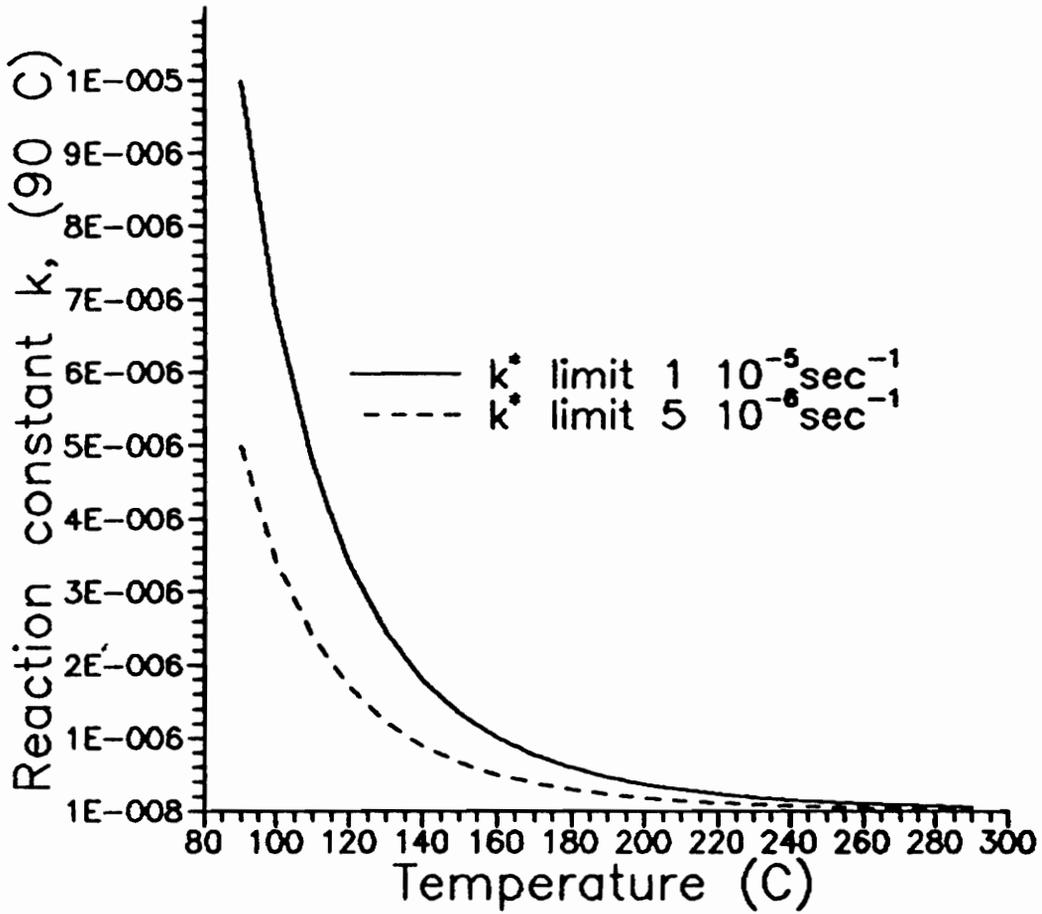


Figure 6.28 Temperature prediction for a given reaction constant.

### 6.4 Conclusions

From the laboratory data, using a constant reaction temperature, the reaction process can be divided in several phases. Each phase is associated with a different reaction constant. An initial slow reaction, is followed by a transition stage, which is succeeded by a rapid reaction phase, and this is finally succeeded by a slow reaction rate or termination phase. These phases are explained by both physical changes, the transition of lignin from glassy particles to a viscous tar, and by differences in the chemical reactivity of different functional groups.

Under the present conditions the reaction is quite slow. In this chapter the experimental data are correlated with a process model. First, a constant temperature correlation is applied to nine sets of experimental data. A variable called AFR, average feeding rate, is calculated during the reaction, and this is used to compare the analytical model with the experimental data. The liquid model, with variable volume, follows very closely the experimental data. It is possible to conclude that the first order kinetic equation for the lignin propoxylation reaction agrees quite well with the experimental data.

The reaction rate constants were obtained by comparison of the model predictions with the experimental data. Having these reaction constants we can compare now the reaction rate with the mass transfer rate. A gas-liquid model was presented in *Chapter 5* where the gas to liquid mass transfer resistance was considered. For the mass transfer rate, the product  $a_{gl} H_B K_{B_{gl}}$  has a value of  $0.1 \text{ sec}^{-1}$  approximately for our system. For the reaction rate, the  $k$  values range from  $1 \cdot 10^{-8}$  to  $9 \cdot 10^{-6} \text{ sec}^{-1}$ . Then, the controlling step is the reaction over the mass transfer. This is the case of very slow reaction, where the mass transfer is negligible, and the rate is determined by chemical kinetics alone.

From the analysis of the results, and from the correlation of experimental and modelled data, it is concluded that the use of a temperature gradient could accelerate the reaction. Some experimental results are presented and modelled using a higher temperature at the beginning of the reaction. The reaction rate is in fact improved without increasing the amount of homo-polymerization. Furthermore, the Arrhenius equation is used to predict the temperature

necessary to reach a desired reaction rate. Then, the model is used for predicting the reaction behavior at different reaction conditions. It is concluded that the use of a temperature gradient is the best way to get better reaction rates.

## *Chapter 7*

### *PILOT PLANT PROCESS DESIGN*

*Chapter 7* is concerned with the design of a pilot plant to produce larger quantities of HPL needed for mechanical testing. The size of some available equipment limit the capacity of the pilot plant. The design of this pilot plant will be approached like a design of a full-scale plant. This chapter gives the description of the raw materials, products, and HPL production process for the lignin propoxylation pilot plant. The HPL production process is illustrated in the process flow diagram. Related to this flow diagram is the material balance, which gives a quantitative description of the process. The flow diagram is the source of specifications used in equipment designation and design, which is given in *Section 7.6*. The flow sheet is also the framework for the cost estimation, which is given in *Appendix A*.

#### *7.1 Description of the Process*

The following "best procedure" has emerged after years of research at laboratory scale (Glasser, 1991) and it will be applied at the pilot plant scale. Isolated lignin is slurred in toluene and KOH is added as an aqueous 50% solution. The mixture is stirred and water is removed by azeotropic distillation. Other alternative is to stirr isolated lignin with aqueous KOH followed by spray drying. Following pressure testing, the lignin-solvent-catalyst batchwise phase is contacted with an initial load of PO, 150-200 ml. Stirring begins at 300 to 400 rpm and the reactor is heated. The reaction occurs in the liquid phase and the products are assumed not to be volatile. After the initial injection, PO is added intermittently in approximately 20 ml injections. These injections are controlled by an electronically controlled solenoid valve triggered by a lower and upper pressure threshold. The PO addition continues until the desired level of propoxylation is reached. Then ethylene oxide injections occur, which produce capping. The products of the reaction are a copolymer of lignin and PO (HPL), and a homopolymer of PO (PPO). After the polymerization reaction is

completed the catalyst needs to be removed. Two methods for the catalyst removal are discussed. In the first one the catalyst is removed by ion-exchange. This process, called Process 1, includes the following steps: reaction, solvent evaporation, dissolution of the reaction product in ethanol, and ion-exchange through a column packed with an acid cation-exchange resin. An economic analysis of this process is given in *Appendix A*. The cost of HPL produced by this process is relatively high for intended use. As a consequence, a new process for the removal of KOH was developed. In this process, called Process 2, the catalyst is removed by precipitation. Sulfuric acid is added to the product of the polymerization reaction, and the potassium sulfate formed is removed by filtration. Also CO<sub>2</sub> can be used to neutralize the KOH. Then the solvent of the reaction is evaporated. The economic analysis of this process is given in *Appendix A*. The advantages of each alternative for catalyst removal are discussed in *Chapter 8*. Hydrochloric acid is used to regenerate the ion exchange resin. The process of lignin propoxylation includes the following main process areas:

- Area 100 : Propoxylation Reaction.
- Area 200 : Solvent Evaporation.
- Area 300 : Catalyst Removal.

## 7.2 Raw Materials

The raw material description and its physical and chemical properties are given next.

### 1. LIGNIN

The characteristics of isolated lignins depend upon its source and the type of isolation process applied. The principal types of lignins obtained by biomass-to-chemicals conversion processes are: Milled Wood Lignin (MWL), Kraft Lignin (KL), Organosolv Lignin (OSL), Steam Explosion Lignin (SEL), and Acid Hydrolysis Lignin (AHL) (Glasser, 1983). The glass transition temperature of all these lignins ranges between 95 and 160°C. The difference between them are related mainly to the phenolic hydroxyl content, the interunit linkages, and the molecular parameters (Mw and Tg). The factors that determine the value of

lignin for polymer utilization are viscoelasticity and phenolic functionality. Viscoelasticity is related to molecular weight, glass transition temperature, solubility, viscosity, chemical functionality, and interunit linkages. Lignin preparations with high alkyl-aryl ether content can impart greater flexibility and less rigidity to materials derived from them than lignins with high C-C bonding content. AHLs are exposed to severe condensation reactions. OSL and SEL have regularly narrow molecular weight distribution, with degree of polymerization between 4 and 5, and the highest alkyl-aryl ether linkage. Propoxylation of AHL lignins produced an undissolved polyol (Glasser, 1991). On this basis, SEL and OSL are more attractive for the manufacture of polymeric products (Glasser, 1983). SELs are obtained by extracting steamexploded biomass samples with aqueous ethanol or aqueous alkali. Resulting in a brown powder. The lignin content of SEL is approximately 90%. OSLs are obtained by pulping at 160°C to 175°C in aqueous ethanol containing sodium bisulfate or ammonium sulfide followed by washing and drying. SELs with lowest molecular weight and lowest glass transition temperature produce polyols having lowest viscosity.

Lignins may either be prepared for the propoxylation reaction by a) mixing isolated lignin with KOH pellets or a KOH solution, or b) spray drying an aqueous potassium lignate solutions of pH 7.5-11.2. These potassium lignate solutions may be obtained by dissolving isolated lignin in aqueous alkali or by extracting lignin from steam exploded pulp using alkali followed by pH adjustment with CO<sub>2</sub> (Glasser, 1991). The characteristics of the lignin used in this work are:

Steam Explosion Lignin (SEL): brown powder with approximately 10 % moisture.

Density: 0.58 kg/l.

Cost: 0.55 \$ /kg (0.25 \$ /lb)

Source: Wood Fractionation Pilot Plant, Bio-Regional Energy Associates Ltd. (BREAL).

Amount per batch, from *Section 7.5*: 6.25 kg (13.75 lb).

## 2. PROPYLENE OXIDE

Lignin is reacted with aliphatic ethers to give a product with lower modulus. 1,2 alkene sulfide and 1,2 alkene carbonate have been used. Most of the reactions studied employ PO (Wu, 1984). The characteristics of PO used in this work are:

Mw: 58.08 kg/kmol.

Formula:  $\text{H}_2\text{COCHCH}_3$

Feed Relation: 15 mol PO/ kg lignin.

Specific Gravity: 0.859.

Normal Boiling Point: 34.3°C.

Sources: Hydrochlorination of propylene (Dow); peroxidation of propylene (Arco); or as a coproduct (Oxirane).

Cost: 1.04\$/kg (0.47 \$ /lb) as of May 1988.

Amount per batch, from *Section 7.5*: 5.45 kg (15 mol/kg lignin)

7.26 kg (20 mol/kg lignin)

9.08 kg (25 mol/kg lignin)

10.89 kg (30 mol/kg lignin)

## 3. KOH

Potassium hydroxide is used as base catalyst. The anionic polymerization of 1,2-epoxides occurs under basic conditions. Initial studies concluded that LiOH and NaOH were ineffective catalysts while KOH, RbOH, and CsOH were effective (Steiner, 1964). These results are in conflict with later studies which showed a series of Na alkoxides to be effective catalysts in the presence of various solvents and initiators (Yeates, 1984, and Teo, 1982). The catalyst addition can take place in different ways: a) KOH pellets added to powderous lignin in toluene, b) KOH in a 50% aqueous solution added to lignin in toluene, c) slurring isolated lignin in aqueous KOH followed by spray drying, and d) employing the aqueous alkaline extract of steam exploded pulp, following pH adjustment and spray drying. The use of pellets is not recommended; solid KOH remained after azeotropic distillation (Glasser, 1991). The extracted steam exploded pulp retains organic componets that affect the propoxylation reaction. Then, the best

procedures are either b) or c) (Glasser, 1991). The characteristics of KOH used in this work are:

Mw: 56.1 kg/kmol.

Form: Pellets.

Cost: 2.9 \$/kg (1.32 \$/lb) as May 1988, pellets.

Amount per batch, from *Section 7.5*:

7%, 0.44 kg (0.96 lb), 1.25 mol/kg lignin

16.8%, 1.05 kg (2.3 lb), 3 mol/kg lignin

At catalyst contents of 5% on lignin no reaction occurred. A KOH content of 7% on lignin is the minimum acceptable catalyst level. High catalyst content is undesirable because it increases homopolymerization and ash content. A catalyst content of 7% on lignin will be used in this process design.

#### 4. TOLUENE

The product of the polymerization reaction is soluble in toluene, and toluene is inert to this reaction. Toluene is a good solvent to perform the azeotropic distillation of the lignin-catalyst solution, but other solvents are also as good as toluene, or even better for the reaction. Isopropanol is a superior solvent for HPL, specially for low levels of substitution. However, using isopropanol there is more homopolymer formation at high levels of substitution (Glasser, 1991). The characteristics of toluene used in this work are:

Mw: 92.13 kg/kmol.

Formula:  $C_6H_5CH_3$

Function: solvent.

Specific Gravity: 0.866.

Normal Boiling Point: 110.6°C. Azeotrope with water: T min 84.10°C.

Cost: 0.80 - 0.88 \$/ gal as of May 1988

Amount per batch, from *Section 7.5*: 20 l (5.28 gal).

#### 5. ETHANOL

The product of the polymerization reaction free of toluene is dissolved in a

60% aqueous solution of ethanol to produce a 20 % solution. This solution will be exchanged in an anionic column to remove the catalyst, KOH. If bleaching of the product is required this solution is treated with hydrogen peroxide. The characteristics of ethanol used in this work are:

Mw: 44.5 kg/kmol.

Formula:  $\text{CH}_3\text{CH}_2\text{OH}$

Function: Solvent for Process 1.

Normal Boiling Point: 78.4°C.

Specific Gravity: 0.789.

Cost: 1.06 - 1.28 \$/ gal as of May 1988.

Amount per batch, from *Section 7.5*: 43 l (11 gal) for process and 172 l (45 gal) for wash.

## 6. SULFURIC ACID

HPL is mixed with sulfuric acid which precipitates KOH as potassium sulfate. Carbon dioxide could be also used to precipitate the catalyst, giving potassium carbonate as precipitate. The disadvantage of using carbon dioxide is that more deposit is formed with the consequence of additional loss of product.

Mw: 98.08 kg/kmol.

Formula:  $\text{H}_2\text{SO}_4$

Function: used to precipitate the catalyst, Process 2.

Specific Gravity: 1.841 (96 - 98%).

Normal Boiling Point: 330°C (100 %).

Cost: 0.15 \$/ kg.

Amount used, from *Section 7.5*: 0.92 kg if 3 mol KOH /kg lignin or 0.38 kg if 1.25 mol KOH/kg of lignin.

## 7. ETHYLENE OXIDE

The characteristics of ethylene oxide used in this work are:

Mw: 44.05 kg/kmol.

Formula:  $\text{H}_2\text{COCH}_2$

Function: R-OH groups are capped with ethylene oxide to produce more reactive primary terminal OH-groups.

Normal Boiling Point: 13.5°C.

Specific Gravity: 0.887.

Cost: 0.77 - 1.02 \$/kg (0.35 - 0.46 \$/lb) as of May 1988.

Amount used, from *Section 7.5*: 1.4 kg, 5 mol EO/kg lignin.

## 8. HCl

The characteristics of HCl used in this work are:

Mw: 36.48 kg/kmol.

Function: Used to regenerate the ion exchange column for Process 1.

Normal Boiling Point: 110°C.

Specific Gravity: 1.187.

Cost: 20 Be, 55 - 70 \$/ ton as of May 1988.

Amount per Batch, from *Section 7.5*: 265 l (70 gal) (110 % eq).

## 7.3 Products

The modification of lignin with propylene oxide (PO) gives hydroxypropyl lignin (HPL) and PO homopolymer (PPO). A schematic structure of HPL was given in Figure 3.2. This chemical modification and derivatization, involving the combination of a high modulus polyaromatic component with a low modulus substituent such as an aliphatic ether, has been suggested as a promising route to tailoring viscoelastic properties of polymeric lignin derivatives for specific end uses. The product of the propoxylation reaction is analyzed with regard to homopolymer and ash content, viscosity, and hydroxyl number. HPL in mixture with PO homopolymer (PPO) constitutes a polyol with useful properties for the preparation of rigid polyurethane foams (Muller, 1983). HPLs can also be reacted with PO to produce chain extended hydroxypropyl lignin (CEHPL), a schematic structure of CEHPL was given in Figure 3.3. The CEHPLs were incorporated into lignin polyurethane networks (LPUs) (Muller, 1983). Other modified lignins are: epoxy-functional, cross-linkable lignin derivatives, acrylate-functional lignin

derivatives, and star-like block copolymers.

The product of the polymerization reaction (HPL and PPO) is a viscous tar, with glass transition temperature below room temperature (at a lignin content between 40 and 60 %). The viscosity of HPL tars depends on the lignin type and molecular weight, the PO content, and several other factors. The viscosity properties of HPLs are of interest since they constitute polymeric building blocks for the preparation of thermosetting resins (i.e., resins that solidify out of a fluid state).

Viscosity studies of hydroxypropyl derivatives of methanol organosolv (OS) lignin and hardwood Kraft (K) lignin have been reported (Bradley, 1987). HPL derivatives have higher viscosity in propylene glycol as compared to parent lignins. This is due to the better solubility of the HPL derivatives in glycol than the parent lignins. The HPL molecules assume a more relaxed conformation than the parent lignins. HPL solutions in propylene glycol and PPO homopolymer have relatively low viscosity, and it is dependent of the temperature and concentration of the solutions. For example OS-HPL has a viscosity of 0.032 Pa sec (32 cp) at 0 % concentration; this increases to 0.2 Pa sec (200 cp) at 25%, and to 3.16 Pa sec (3,160 cp) at 50% concentration of OS-HPL. The viscosity of K-HPL increases from 0.032 Pa sec (32 cp) at 0% concentration to 0.632 Pa sec (632 cp) at 25% Concentration. Organosolv HPL forms have the lowest viscosity among other HPLs made from other types of lignins (like Kraft HPL). It was found that the viscosities of HPL, and of lignin solutions in homopolymer and of chain extended HPL copolymers can be predicted on the basis of UV absorptivity coefficient determinations (Bradley, 1987).

The viscosity of HPL has also been measured directly, without dissolution. Steam-explosion lignin, extracted from water-washed wood by aqueous alkali, was reacted with PO using K-lignate as a catalyst. The viscosity of the products range between 45 Pa sec (45,000 cp) to 160 Pa sec (100,000 cp) at 25°C.

#### 7.4 Process Flow Diagram

Two methods for the catalyst removal will be discussed. The two processes will be analysed in parallel and the selection will be made the economic analysis. Two main flow diagrams for the Lignin Propoxylation pilot plant are presented in this section, called Process 1 and Process 2. The flow diagram of Process 1 is given in Figure 7.1. The process areas are: Reaction, Solvent Evaporation, and Catalyst Removal. Isolated lignin is slurried in toluene and KOH is added. The mixture is stirred and then allowed to reflux to remove water. Following pressure testing, an initial load of PO is added to the sealed reactor. The reactor is heated and PO injections start. This PO addition continues until the desired level of propoxylation has been reached. This can be followed by capping with ethylene oxide. After cooling the reaction, the product flows to a blow tank. Then, toluene is recovered by evaporation under reduced pressure in a rotary evaporator. The polyol is transferred to a dissolver where it is dissolved in 60 % aqueous ethanol. Finally, the catalyst is separated by ion-exchange and ethanol is recovered by evaporation.

The flow diagram of Process 2 is given in Figure 7.2. The process areas for Process 2 are: Reaction, Catalyst Removal, and Solvent Evaporation. K-lignate is prepared by slurrying lignin in aqueous KOH of known concentration followed by spray drying. K-lignate is charged to the reactor and the reaction process continues as in Process 1. Then, the polyol-toluene solution is saturated with sulfuric acid to neutralize KOH. Next, the catalyst is removed by filtration and toluene is recovered by evaporation under reduced pressure.

The material balances refer to these flow diagrams giving the flow and characteristics of each stream. The equipment is described in *Section 7.6*. Temperature and pressure in each step of the process is not given in the process flow diagram, but in the design of each equipment. The flow sheets and the equipment numbering are drafted following the specifications given by G.D. Ulrich, 1984. The identification numbers of the main equipment are shown in the process flow diagram. The mechanical and utility flow diagrams need to be prepared after the approval of the present step.

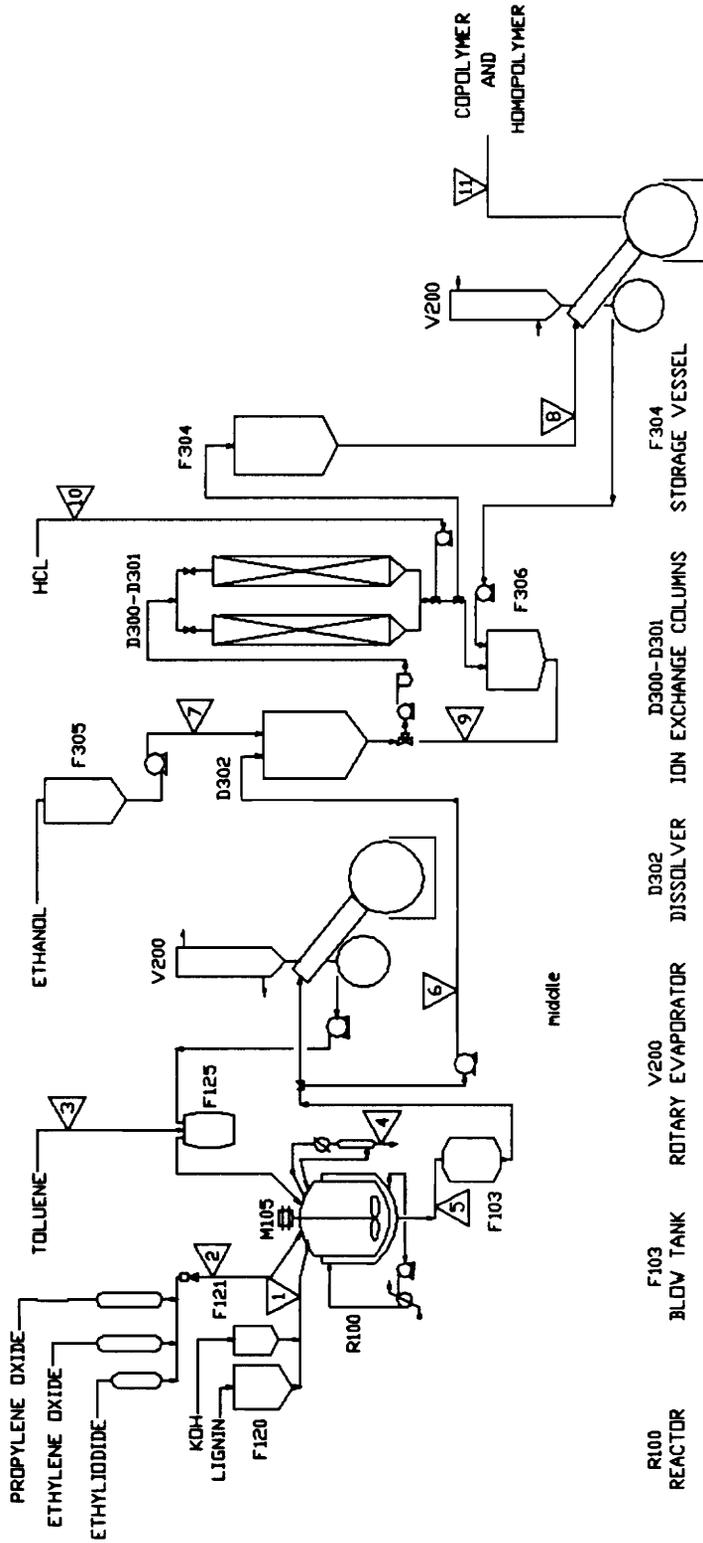


Figure 7.1 Pilot-plant process flow diagram - Process 1.



### 7.5 Pilot Plant Material Balance

Mass balances for the two processes described in *Section 7.4* are presented here. These material balances are constructed on the basis of a fixed reactor size. The amount of raw materials is calculated on this basis. Since this is a batch process the streams are given in units of mass instead of units of flow, as it should be in a continuous process. The time that it takes for each batch to be completed is not fixed since the pilot plant will be used to test the reaction and the product for different process conditions. The reaction is completed in approximately two to three days. The following material balances do not include the optional substances to produce capping, blocking, or epoxy terminated macromers. The material balance for Process 1 is given in Table 7.1. The amount of each component is given on kg or/and liters. This table includes the solvents used. The amount of material fits one batch of the reactor. Since the reaction is carried out in semibatch condition, the amount of PO given in the table is the total amount required. The material balance for Process 2 is given in Table 7.2. The numbers of the process streams refer to those given in the respective flow diagrams of *Section 7.4*. The principle of mass conservation applied to the process streams gives the following balances:

#### For Process 1:

| Streams(Composition) kg |             | Streams(Composition) kg |             |
|-------------------------|-------------|-------------------------|-------------|
| 1 (Lignin and KOH)      | 6.69        | 6 (HPL)                 | 11.64       |
| 2 (PO)                  | <u>5.45</u> | 4 (H <sub>2</sub> O )   | <u>0.50</u> |
|                         | 12.14       |                         | 12.14       |
| 13 (Copolymer)          | 8.29        | 1                       | 6.69        |
| 14 (Homopolymer)        | <u>2.91</u> | 2                       | 5.45        |
|                         | minus       | KOH                     | 0.44        |
|                         | minus       | H <sub>2</sub> O        | <u>0.55</u> |
|                         | 11.20       |                         | 11.20       |

For Process 2:

| Streams(Composition) |             | Streams(composition) |             |
|----------------------|-------------|----------------------|-------------|
| 1 (lignin )          | 6.25        | 9 (polym.)           | 10.76       |
| 2 (PO)               | <u>5.45</u> | 4 (H <sub>2</sub> O) | 0.50        |
|                      |             | loss                 | <u>0.44</u> |
|                      | 11.70       |                      | 11.70       |

In Table 7.3 is given a molar balance. The following molecular weights were used: for lignin 905 kg/kmol, for HPL 1200 kg/kmol, and for PPO 600 kg/kmol. It is also given a molar balance taking a C<sub>9</sub> unit as basis.

For the design of a full-scale production plant it is not recommended to use an over-design factor because conservative allowances are built into most of the design data and equations. On the contrary, a pilot plant should be over-designed to provide flexibility. Approximately 50 percent excess capacity is a reasonable allowance. The capacity of the lignin propoxylation pilot plant is limited by the size of the polymerization reactor. The capacity calculated here is the maximum capacity. The design capacity is a 50 percent of the maximum capacity, or a production of approximately 5.5 kg (12 lb) of product per batch.

It is important to make a comment respect to the size of this pilot plant, wich was fixed to the size of the reactor. As a reference, typical scale-up ratios for a system consisting of liquid-liquid reactants and solid or viscous products (polymerizations, agricultural chemicals manufacturing, etc.) are the following: for laboratory scale 10 gr/hour, for a prepilot plant scale 0.2 kg/hour, for pilot plant 1-10 kg/hour an for commercial scale 1-100 ton/hour (Ohsol, 1972). According to this typical values the size of the process being here designed correspond to a prepilot plant. In consecuense, a new pilot plant should be designed and constructed before any full scale project be approached.

| Table 7.1 Material Balance - Process 1. |                             |       |           |           |          |          |
|---|-----------------------------|-------|-----------|-----------|----------|----------|
| Process Streams [liters] kg             |                             |       |           |           |          |          |
|   |                             | 1     | 2         | 3         | 4        | 5        |
| Components                              |                             |       |           |           |          |          |
| 1                                       | lignin                      | 6.25  |           |           |          |          |
| 1                                       | KOH [1]                     | 0.44  |           |           |          |          |
| 2                                       | PO [2]                      |       | [6.3]5.45 |           |          |          |
| 3                                       | toluene                     |       |           | [20]17.32 |          |          |
| 4                                       | water removed               |       |           |           | 0.5      |          |
| 5                                       | polyol + toluene            |       |           |           |          | 28.96    |
| Process Streams [liters] kg             |                             |       |           |           |          |          |
|   |                             | 6     | 7         | 8         | 9        | 10       |
| Components                              |                             |       |           |           |          |          |
| 6                                       | Polyol + KOH                | 11.64 |           |           |          |          |
| 7                                       | Polyol + ethanol [3]        |       | 69.84     |           |          |          |
| 8                                       | Sol. KOH free               |       |           | 69.4      |          |          |
| 9                                       | Ethanol wash                |       |           |           | [284]245 |          |
| 10                                      | HCL [4]                     |       |           |           |          | [265]315 |
| Process Streams [liters] kg             |                             |       |           |           |          |          |
|   |                             | 11    |           |           |          |          |
| Components                              |                             |       |           |           |          |          |
| 11                                      | Polyol                      | 11.20 |           |           |          |          |
|   | Copolymer (74%)             | 8.29  |           |           |          |          |
|   | Homopolymer (26%)           | 2.91  |           |           |          |          |
| [1]                                     | 1.25 mol KOH/kg lignin (7%) |       |           |           |          |          |
| [2]                                     | 15 mol PO/kg lignin         |       |           |           |          |          |
| [3]                                     | Resulting in a 20% solution |       |           |           |          |          |
| [4]                                     | 110% of required            |       |           |           |          |          |

Table 7.2 Material Balance - Process 2.

|            |                             | Process Streams [liters] kg |           |           |       |       |
|------------|-----------------------------|-----------------------------|-----------|-----------|-------|-------|
|            |                             | 1                           | 2         | 3         | 4     | 5     |
| Components |                             |                             |           |           |       |       |
| 1          | lignin                      | 6.25                        |           |           |       |       |
| 1          | KOH [1]                     | 0.44                        |           |           |       |       |
| 2          | PO [2]                      |                             | [6.3]5.45 |           |       |       |
| 3          | toluene                     |                             |           | [20]17.32 |       |       |
| 4          | water removed               |                             |           |           | 0.5   |       |
| 5          | polyol + toluene            |                             |           |           |       | 28.96 |
|            |                             | Process Streams [liters] kg |           |           |       |       |
|            |                             | 6                           | 7         | 8         | 9     | 10    |
| Components |                             |                             |           |           |       |       |
| 6          | Sulfuric acid               | 0.38                        |           |           |       |       |
| 7          | Polyol + KOH                |                             | 11.64     |           |       |       |
| 8          | Filter cake                 |                             |           | 1.26      |       |       |
| 9          | Polyol                      |                             |           |           | 10.76 |       |
|            | Copolymer (74%)             |                             |           |           | 7.96  |       |
|            | Homopolymer (26%)           |                             |           |           | 2.8   |       |
| [1]        | 1.25 mol KOH/kg lignin (7%) |                             |           |           |       |       |
| [2]        | 15 mol PO/kg lignin         |                             |           |           |       |       |

| Table 7.3 Molar Balance. |   | Streams moles (C <sub>9</sub> basis) |      |           |         |         |
|--------------------------|---|--------------------------------------|------|-----------|---------|---------|
|                          |   | 1                                    | 2    | 12        | 13      | 14      |
|                          | <b>Components</b>   |                                      |      |           |         |         |
| 1                        | lignin (C <sub>9</sub> )  | 6.9(34)                              |      |           |         |         |
| 1                        | KOH [1]   | 7.8                                  |      |           |         |         |
| 2                        | PO [2]  |                                      | 93.8 |           |         |         |
| 12                       | Polyol  |                                      |      | 11.8(128) |         |         |
| 13                       | Copolymer (74%)   |                                      |      |           | 6.9(95) |         |
| 14                       | Homopolymer (26%)   |                                      |      |           |         | 4.9(33) |
| [1]                      | 7.8 mol KOH = 1.25 mol KOH/kg lignin (7%)<br>15.6 molKOH =2.5 mol KOH/kg lignin (14%)                       |                                      |      |           |         |         |
| [2]                      | HPL-5 31.3 mol PO<br>HPL-10 62.7 mol PO<br>HPL-15 93.8 mol PO<br>HPL-25 156.3 mol PO<br>HPL-30 187.7 mol PO |                                      |      |           |         |         |

### 7.6 Specifications and Design of Pilot Plant Equipment

Once the pilot plant process flow diagram has been prepared the next logical step is to specify equipment that appears on it.

#### 7.6.a List of Equipment - Process 1

| Eq. Identification | Description              | Capacity                                 |
|--------------------|--------------------------|--|
| AREA 100           |                          |  |
| R 100              | Reactor                  | 38 l (10 gal)                            |
| E 101              | Condenser                | 7 m <sup>2</sup> (75 feet <sup>2</sup> ) |
| F 102              | Receiver                 | 19 l (5 gal)                             |
| F 103              | Blow Tank                | 38 l (10 gal)                            |
| E 104              | Oil Heater               |  |
| M 105              | Agitator                 |  |
| L 110              | Gas Injector             |  |
| L 111              | Toluene Charge Hand Pump |  |
| L 112              | Toluene Recycle Pump     |  |
| L 113              | Oil Pump                 |  |
| F 120              | Lignin Storage Bin       | 76 l (20 gal)                            |
| F 121              | KOH Storage Bin          | 38 l (10 gal)                            |
| F 122              | Propylene Oxide Storage  | 76 l (20 gal)                            |
| F 123              | Ethylene Oxide Storage   | 38 l (10 gal)                            |
| F 124              | Ethyl iodide Storage     | 19 l (5 gal)                             |
| F 125              | Toluene Storage          | 189 l (50 gal)                           |
| AREA 200           |                          |  |
| V 200              | Rotary Evaporator        | Ev. Flask 10 l<br>Receiv. Flask 5 l      |
| L 210              | Toluene Recycle Pump     |  |
| L 211              | HPL Pump                 |  |
| AREA 300           |                          |  |
| D 300              | Ion Exchange Column      |  |

|       |                                 |                 |
|-------|---------------------------------|-----------------|
| D 301 | Ion Exchange Column             |                 |
| D 302 | Dissolver                       | 95 l (25 gal)   |
| H 303 | Cartridge Filter                |                 |
| F 304 | Storage Vessel                  | 95 l (25 gal)   |
| F 305 | Ethanol Storage                 | 189 l (50 gal)  |
| F 306 | Ethanol Washing Process Storage | 378 l (100 gal) |
| L 310 | Ethanol Pump                    |                 |
| L 311 | Peristaltic Pump                |                 |
| L 312 | HCl Pump                        |                 |

#### 7.6.b List of Equipment - Process 2

| Eq. Identification | Description               | Capacity                                |
|--------------------|---------------------------|---|
| AREA 100           |                           |   |
| R 100              | Reactor                   | 38 l (10 gal)                           |
| E 101              | Condenser                 | 7 m <sup>2</sup> (75feet <sup>2</sup> ) |
| F 102              | Receiver                  | 19 l (5 gal)                            |
| F 103              | Blow Tank                 | 38 l (10 gal)                           |
| E 104              | Oil Heater                |   |
| M 105              | Agitator                  |   |
| L 110              | Gas Injector              |   |
| L 111              | Toluene Charge Hand Pump  |   |
| L 112              | Toluene Recycle Pump      |   |
| L 113              | Oil Pump                  |   |
| F 120              | Lignin Storage Bin        | 76 l (20 gal)                           |
| F 121              | KOH Storage Bin           | 38 l (10 gal)                           |
| F 122              | Propylene Oxide Storage   | 76 l (20 gal)                           |
| F 123              | Ethylene Oxide Storage    | 38 l (10 gal)                           |
| F 124              | Ethyl iodide Storage      | 19 l (5 gal)                            |
| F 125              | Toluene Storage           | 189 l (50 gal)                          |
| F 126              | Potassium lignate Storage | 38 l (10 gal)                           |
| B 130              | Spray Dryer               | 3 l/h                                   |

|          |                      |                                     |
|----------|----------------------|-------------------------------------|
| H 131    | Cyclon               |                                     |
| D 132    | Dissolver            | 19 l (5 gal)                        |
| AREA 200 |                      |                                     |
| V 200    | Rotary Evaporator    | Ev. Flask 10 l<br>Receiv. Flask 5 l |
| L 210    | Toluene Recycle Pump |                                     |
| L 211    | HPL Pump             |                                     |
| AREA 300 |                      |                                     |
| H 300    | Filter Press         |                                     |
| F 304    | Storage Vessel       | 95 l (25 gal)                       |

### *7.6.c Design of Equipment Process 1*

In this section the specifications, characteristics, and selection of the equipment are given.

#### AREA 100: PROPOXYLATION REACTION REACTOR

Identification: R - 100

Function: Propoxylation reaction.

Operation: Semibatch.

Temperature of operation: 90 - 140°C.

Pressure: 25 - 60 psig.

Capacity: 37.85 l (10 gal).

Material of construction: Stainless Steel.

Utilities: Feeder

Oil Heater E - 104

Oil Pump L - 113

Gas Injector L - 110

Toluene Pump L - 111 (hand pump)

Toluene Recycle Pump L - 112

Temperature Controller

Pressure Controller

Agitator E - 105.

Cost: 2,500 \$ paid for this used equipment. The actual cost is 35,000 \$ (Ulrich, 1984).

#### CONDENSER

Identification: E - 101

Function: Total condensation of toluene-water mixture.

Operation: 2 hours.

Temperature of operation: 110°C.

Capacity: Exchange area: 7 m<sup>2</sup> (75 feet<sup>2</sup>).

Material of construction: Stainless Steel.

Cost: Included in reactor cost.

#### RECEIVER

Identification: F - 102

Function: Receive the condensate and allow the separation of water from toluene.

Temperature of operation:

Capacity: 19 l (5 gal).

Material of construction: Stainless Steel.

Cost: Included in reactor cost.

#### BLOW TANK

Identification: F - 103

Function: Hold the products of the reaction at 50 - 60°C .

Temperature of operation: 50 - 60°C.

Capacity: 38 l (10 gal) (DI: 15 in L:14 in) .

Materials handled: HPL in solution.

Material of construction: Stainless Steel (plastics or fiberglass).

Insulation: Yes.

Discharge Mechanism: Blower.

Utilities: External heater.

Cost: 1000.0 \$ APC ALLOY PRODUCTS CORP. Model 75-10

## AREA 200: SOLVENT EVAPORATION

### ROTARY EVAPORATOR

Identification: V - 200

Function: Toluene recovering.

Type: Yamato Product Model RE - 71.

Capacity: Evaporating Flask 10 l and Receiving Flask 5 l.

Cost: 6,600 \$ YAMATO Model RE-71

### TOLUENE RECYCLE PUMP

Identification: L - 210

Type: Air motor to use in conjunction with existing centrifugal pump head.  
(Cole Palmer pg. 587).

Cost: 367.00 \$

### HPL PUMP

Identification: L - 211

Type: Gear pump ( Cole Palmer pg. 617).

Cost: 233.00 \$

## AREA 300: ION EXCHANGE

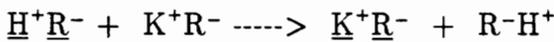
Ion exchange offers the possibility of removing one or more ionic species from one liquid phase and transferring them to another liquid phase via an intermediate solid. Potassium ions can be removed from hydroxypropyl lignin by ion exchange using strong acid cation-exchange resins.

Characteristics of the resin: The resin contains styrene-divinylbenzene (DVB) as base polymer and a sulfonic acid as a functional group.

Crosslinked : 8 %.

Dry weight Capacity: 4.3 meq/gr.  
 Wet weight Capacity: 1.9 meq/mL.  
 Interstitial Volume (mean): 38 %.  
 Effective operating pH range: 0-14.  
 Density (bulk wet) : 0.8 - 0.93 kg/ l.  
 Commercial brand: DOWEX 50 8X100.

Ionic Equilibria: The following reaction takes place:



where  $\underline{\text{R}}$  represents the resin,  $\text{K}^+$  is the potassium ion,  $\text{H}^+$  is the hydrogen ion, and  $\text{R}$  is the compound from which the potassium ion needs to be removed. All the components of the inside phase ( resin phase) are underlined. The hydrogen leaving the inside phase reacts with the hydroxypropyl lignin in the exterior phase. The reaction continues until there are no potassium ions left outside. The molar-selectivity coefficient  $K$  is defined by:

$$K = \frac{\underline{\text{K}^+\text{K}^+}}{\underline{\text{H}^+\text{H}^+}} = 2.9 / 1.3 = 2.2$$

If  $K$  is greater than 1, exchange is favorable. In general the ion exchange front attains and maintains a constant shape as it pass down the column. The sharpness of the breakthrough curve increases with such factors as decreasing linear flow rate; decreasing ratio of solution concentration to resin concentration; smaller resin particle size; and increasing exchange rates.

#### Design

Volume of resin = 18.75 eq KOH / 1.9 eq/L = 9.87 L.

Flow (0.5 - 2.0 ) = 1.25 mL/cm<sup>2</sup>min.

a) Glass Design

ID : 17cm

Area : 227 cm<sup>2</sup>

h : 43.5 cm

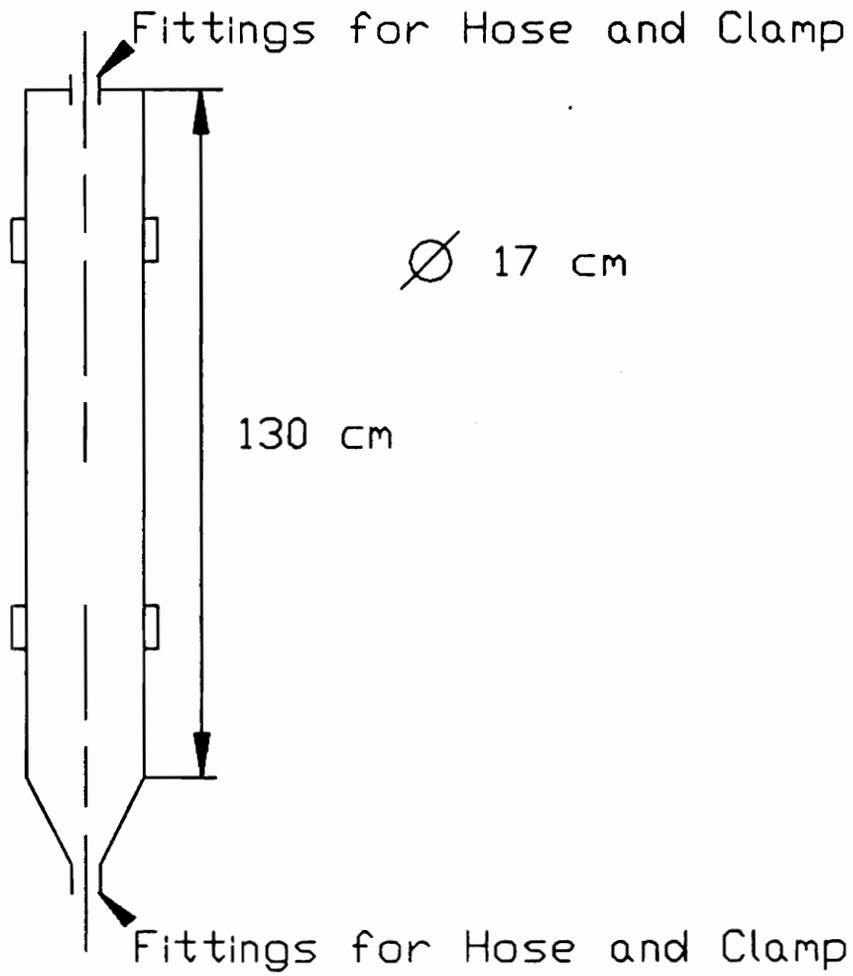


Figure 7.3 Ion-exchange column, glass design.

For complete absorption the capacity of the column should, as a rough guide, be about three times the required amount. Then,  $h : 130 \text{ cm}(4.3 \text{ ft})$ .

To reduce the time of the operation two identical columns will be constructed. A drawing of this design is given in Figure 8.5.

Total cost: 1,200 \$

b) Stainless Steel Design

ID : 21.45 cm (8.58 in)

Wall thickness: 5.37 mm (.2148 in)

$h : 113 \text{ cm}(3.7 \text{ ft})$

To reduce the time of the operation two identical columns will be constructed.

Identification: D-300 and D-301

Cost: 49.20 \$ per foot 304 Stainless Steel

Total cost of material : 364 \$

Cost of auxiliars and labor: 600 \$

Total cost: 1000 \$

## DISSOLVER

Identification: D - 302

Function: Dissolution in ethanol, 20% concentration.

Temperature of operation: Room temperature.

Capacity: 95 l (25 gal).

Materials handled: HPL in ethanol 60%.

Material of construction: Stainless Steel.

Utilities: Agitator.

Cost: 1,300 \$ APC ALLOY PRODUCTS CORP. Model 77-25.

## FILTER

Identification: H - 303

Type: In line, Effective filtration area 35 mm, Aluminium.

Cost: 180.00 \$ ( Thomas Scientific page 780).

**STORAGE VESSEL**

Identification: F - 304

Function: Storage the solution of HPL free of KOH.

Temperature of operation: Room temperature.

Capacity: 95 l (25 gal).

Materials handled: HPL in ethanol 60%.

Material of construction: Stainless Steel.

Cost: 1,010 \$

**ETHANOL WASHING PROCESS STORAGE**

Identification: F - 306

Function: Storage of ethanol used for washing the resin.

Temperature of operation: Room temperature.

Capacity: 378 l (100 gal).

Materials handled: 60% ethanol.

Material of construction: Stainless Steel.

Cost: 1,350 \$

**PERISTALTIC PUMP**

Identification: L - 311

Capacity: 75 to 4500 mliter/min.

Cost: 990.00 \$ (Thomas Scientific page 1294).

**7.6.d Design of Equipment - Process 2****AREA 300: CATALYST REMOVAL****FILTER**

Identification: H - 300

Type: In line, effective filtration area 35 mm, Aluminium.

Cost: 180.00 \$ ( Thomas Scientific page 780).

Alternative: Filter Press.

Cost: 800.00 \$

**STORAGE VESSEL**

Identification: F - 304

Function: Storage the solution of HPL free of KOH.

Temperature of operation: Room temperature.

Capacity: 95 l (25 gal).

Materials handled: HPL in 60% ethanol.

Material of construction: Stainless Steel.

Cost: 1,010 \$

Some observations need to be made about the equipment selected. The rotation evaporator is not an equipment item which can be easily scaled up, since the evaporators used industrially have not the same characteristics. For example, an industrial evaporator could be a forced-circulation, vertical-film evaporator which could produce the required evaporations in the process.

With respect to the ion exchange process, two observations need to be made: (a) Extensive use of oxidants increase moisture uptake, and as a result the resin becomes soft and deformable. Severe oxidants are chromic acid, hydrogen peroxide, and hot concentrated nitric acid. If bleaching with hydrogen peroxide is done before ion exchange, the resin may degrade rapidly; and (b) for complete absorption, the capacity of the column was taken as three times the required amount.

*Chapter 8*  
**PROCESS SELECTION**

Process 1 differs from Process 2 in the area of catalyst removal. The two processes will be compared with respect to their mass balance, capital cost, and raw material cost. Comparing the mass balances, Process 2 has the disadvantage of loss of polymer and the problem of disposal of filter cake. Usually a loss of polymer in the same amount as that of catalyst is encountered. This means 0.44 kg (0.97 lb) of HPL or \$ 0.58 per batch.

If the equipment cost required in each process is compared, the benefits of Process 2 are revealed. If we account for the cost of equipment used for the catalyst removal we find that Process 1 is more expensive.

Catalyst removal, Process 1

| Equipment             | Cost     |
|-----------------------|----------|
| Ion exchange columns  | 1,000.00 |
| Dissolver             | 1,300.00 |
| Filter                | 180.00   |
| Storage vessel        | 1,010.00 |
| Ethanol wash storage  | 1,350.00 |
| Ethanol recovery pump | 300.00   |
| Peristaltic pump      | 990.00   |
| Ion Exchange resin    | 3,775.00 |
|                       | -----    |
| Total                 | 9,905.00 |

Catalyst removal, Process 2

| Equipment      | Cost     |
|----------------|----------|
| Filter press   | 800.00   |
| Pump           | 233.00   |
| Storage vessel | 1,010.00 |
|                | -----    |
| Total          | 2,043.00 |

Process 2 significantly simplifies the catalyst removal by eliminating ion  
130

exchange and solvent exchange. Finally by comparing the raw material cost and the manufacturing cost, Process 2 gives a lower total cost. For Process 1 the raw material cost is 1.20 \$/kg HPL (0.55 \$/lb HPL) and the manufacturing cost 1.55 \$/kg HPL (0.71 \$/lb HPL), while for Process 2 the raw materials cost is 1.02 \$/kg HPL (0.46 \$ /lb HPL) and the manufacturing cost 1.33 \$/kg HPL (0.60 \$/lb HPL), at 15 mol PO and 1 mol KOH per kg of lignin. The difference represent 15% reduction in cost. Also, Process 1 requires more operating labor than Process 2.

*Chapter 9*  
**CONCLUSIONS, CONTRIBUTIONS, AND RECOMMENDATIONS**

**9.1 Conclusions**

The reaction of lignin with PO giving HPL and PPO can be considered a pseudo-first order reaction under the present conditions. The existing process is semibatch with lignin, the catalyst, and the solvent processed batchwise; and with PO and eventually EO injected intermittently throughout the reaction time. The temperature needs to be kept as low as possible, in a compromise value that results from a balance between reaction rate and PPO formation. Depending upon pressure and temperature, PO and toluene are distributed in the two phases, vapor and liquid. The lignin propoxylation reaction occurs in the liquid phase only.

The concentration distribution of the reactants must be determined in order to model the process. The vapor-liquid equilibrium solution gives the distribution of the components in the two phases. The liquid PO concentration after the first injection can then be calculated. Differences between pressure and temperature readings and the results from the vapor-liquid equilibrium calculation were found. The reasons were explained in *Chapter 4*, and these can be summarized as being due to a non-ideal behavior of the system plus the presence of nitrogen gas in the reactor. Since the reaction takes place in the liquid phase it is desirable to have most of the PO in the liquid phase. This can be achieved by using high pressures and low temperatures. But if the pressure is too high, homo-polymerization will compete successfully with copolymerization. Also, if the temperature is too low, the reaction will be very slow. Therefore, the best reaction conditions should result from a balance between these limits.

Two process models were discussed: a gas-liquid semibatch process, with constant liquid volume and ideal gas-liquid behaviour; and a liquid semibatch process, with variable liquid volume and an initial PO concentration calculated from a non-ideal vapor-liquid equilibrium. These two models are very close as it was shown in Figure 5.2. They are the basis for a mathematical description of

each feeding step in the reaction process. The liquid model is used in the modelling because: most of PO is in the liquid phase; the liquid considers a variable liquid volume; and the liquid-model equation can be easily incorporated into the model program.

From the laboratory data, using a constant temperature, the reaction time is divided into several phases, with a different reaction constant associated with each phase. An initial slow reaction, a transition phase, a rapid reaction phase, and finally a slow termination phase are distinguished. These phases are explained by both physical changes and chemical reactivity variations of different functional groups. The experimental data are correlated with a process model. First, a constant temperature correlation is applied to nine sets of experimental data. A variable called AFR, average feeding rate, is calculated during the reaction to compare the liquid model and the experimental data. The liquid model, with variable volume, follows very closely the experimental data. It is possible to conclude that the first order kinetic equation for the lignin propoxylation reaction fits well the experimental data. From the analysis of the results from the correlation is concluded that the use of a temperature gradient could accelerate the reaction. Some experimental results are presented and modelled using a higher temperature at the beginning of the reaction. Furthermore, an equation is used to predict the temperature necessary to reach the desired reaction rate. Then, the model is used for predicting the reaction behavior at different reaction conditions. It is concluded that a temperature gradient is the best approach to get better reaction rates without increasing the amount of homo-polymerization.

Two alternative process are analyzed at a pilot plant scale. Process 1 includes the following areas of processes: reaction, evaporation of solvent, dissolution in a solvent appropriate for the ion-exchange, ion-exchange to remove the catalyst, and evaporation. Process 2 differs from Process 1 in the removal of catalyst, which is done by neutralization followed by filtration. The process design given in *Chapter 7* describes the raw materials and products, presents two process flow diagrams with its respective mass balances, and a description of the equipment selected. An economic analysis of both processes developed in

*Appendix A*, and the capital cost estimations as well as the manufacturing costs are calculated. Process 2 gives a 30% lower capital cost and a 15% lower manufacturing cost than Process 1. Process 2 is selected in base a discussion given in *Chapter 8*. A preliminary design of a full scale plant is presented in *Appendix B*. The polyol cost is compared with the cost of different polyols used in the manufacture of rigid polyurethane foams:

| HPL + PPO                       | Raw materials cost | Selling price        |
|---------------------------------|--------------------|----------------------|
|                                 | \$/kg (\$/lb)      | \$/kg (\$/lb)        |
| Process 1                       | 1.20 (0.55)        |                      |
| Process 2                       | 1.02 (0.46)        |                      |
| Ethylene glycol                 |                    | 0.88 (0.40)          |
| Polyether and Polyester polyols |                    | 1.28 (0.58)          |
| Polyhydric alcohols             |                    | 0.88–1.76(0.40–0.80) |

In this comparison the price of HPL is higher than the price of other polyols, since we are comparing raw materials cost of HPL with selling prices of other polyols. This situation conduces to a further studies before the process of design continues. If the preliminary design gets its approval the next step is the building of the pilot plant, from which the necessary information can be obtained to proceed with the definitive design of the industrial process.

With the information from the pilot plant this process design can be highly improved, and the final full scale design can be recalculated. In *Appendix B* is given a list of the most important information that needs to be obtained from the pilot process.

## 9.2 Contributions

A semibatch process is used at Thomas M. Brooks Forest Products Laboratory to produce HPL by lignin propoxylation. HPL is then used to produce polyurethane foams to be tested for mechanical properties. *Chapters 3 to 6* of this thesis are concerned with the analysis and modelling of lignin

propoxylation. *Chapter 7* describes the design of a pilot plant to produce larger quantities of HPL needed for mechanical testing. This thesis complements the experimental work reported by Glasser (1991), that consisted of the actual production of HPL by the lignin propoxylation process. This thesis has produced the following contributions to the lignin propoxylation process:

- After the economic analysis was completed, a new more convenient lignin propoxylation process was developed. Using the information from this thesis, the catalyst removal process was changed from ion-exchange to neutralization (Process 2 in this thesis) with significant cost reductions.
- One of the main problems of the lignin propoxylation process is the very slow reaction rate, mainly in the initiation phase. The reaction was modelled in *Chapter 6* and the reaction rate constants were obtained by comparison of the model predictions with the experimental data from the actual runs of the process. From observation of the reaction rate constants it was concluded that using a temperature gradient the reaction rate will be increased without diminishing the product quality. The computer model predicted a faster process using higher reaction constants and helped to select a temperature gradient which was used in the laboratory. Good correlation was found between the model and the experimental data.
- A first order kinetics describes adequately the lignin propoxylation reaction in a laboratory-scale batch process. The first order kinetics was used here to model a semibatch process for the first time. The analytical model follows very closely the experimental data. Therefore, from this work it can be said that a global first order kinetics describes very well the propoxylation reaction under the present conditions.
- Two models were used in this thesis, a liquid and a gas-liquid model. The results obtained reveals that the effect of the gas phase is very small. Therefore the liquid model is the most appropriate for the reaction conditions used in this study.

- The PO-toluene vapor-liquid equilibrium calculations developed in this thesis constitute a useful tool to predict the phase distribution of PO at different pressure and temperature conditions.
- The study of the characteristics of the lignin propoxylation reaction and of the process of production of HPL done in this thesis contributes to the technology of *Engineering Plastics from Lignin* with new information, assessment of the profitability of its production as well as introduces new areas of work and investigation in the area of production and commercialization lignin-containing polymers.

### 9.3 Recommendations

Finally, some recommendations are proposed:

- All nitrogen injections should be minimized to have reliable temperature and pressure readings. Then, the results from the vapor-liquid equilibrium computations would give the exact initial concentration of PO.
- An exhaustive collection of laboratory scale information will permit a more precise modelling of the reaction. For example, exact readings of the initial and final liquid volume, recording of any change in the pressure set points will improve the correlation between the model and the experimental data. Also, it is important to make changes of one variable at the time to identify the effects of each one independently.
- Attempt a product analysis of each of the reactions individually. This information is important to select the best reactions conditions.
- All the recommendations above apply for either laboratory or pilot plant work. However, for a pilot plant it is also important to collect some more information that will be used later in the full-scale plant design. For example, (a) obtain the overall properties of the reactor mixture, that is, heat capacity,

density, and viscosity; (b) select the best reaction temperature gradient at the pilot plant scale; (c) select the best design pressure or pressure gradient; (d) obtain the heat of reaction to calculate the required area of heat exchange; (e) calculate the percentage of recycle of solvents to produce an exact mass balance; and (f) obtain the yield loss of HPL to by-products in the reactor, regardless of conversion, to adjust the net production.

*Chapter 10*  
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*Appendix A*  
**PILOT PLANT ECONOMIC ANALYSIS**

The following pilot-plant economic analysis will be developed following the traditional economic analysis for a full scale plant.

**A.1 Capital Cost Estimation**

After the flow sheet and the design of the process equipment have been completed, the next step in a plant design is to determine the price of the plant. First, the *Fixed Capital*, the capital invested in real equipment, is calculated. The process flow diagram is the basis for the capital cost estimate. The cost of an equipment is composed of the purchase price plus the installation cost. The installation cost involves direct materials and labor, indirect expenses, contingency and fee allowances, and capital for auxiliary facilities. Thus the installed cost is usually several times greater than the purchase price. One approach to calculate the fixed capital is to add purchase prices of all equipment on the flow sheet and multiply this sum by a factor, called *Lang factor*, usually between 3 and 5. Peters & Timmerhaus, 1980, suggest a factor of 4.1 for a plant that processes solids and fluids. Using this approach the installed cost for each process will be:

Process 1: Purchase price \* 4.1 = 22,467 \* 4.1 = \$ 92,115 and for

Process 2: Purchase price \* 4.1 = 14,372 \* 4.1 = \$ 58,925.

Another approach proposed by Guthrie, 1969, utilizes the so called *module factors*. This method is an efficient method for calculation of Lang factors specific to processes under consideration. Using this approach the Capital Cost Estimation for Process 1 is given in Table A.1 and the Capital Cost Estimation for Process 2 is given in Table A.2. Some of the equipment listed in *Section 7.6* was not included in the capital cost estimation because there were available, and will be shared with the Wood

Table A.1 Capital Cost Estimation of Process 1, using Module Factors.

| Eq. Identification              | Number | Purchased<br>Eq. Cost | Capacity | B.B. Module<br>Factor | B.B. Module<br>Factor |
|---------------------------------|--------|-----------------------|----------|-----------------------|-----------------------|
| Reactor                         | R 100  | 2,500.0               | 10 gal   | 4.4                   | 11,000.0              |
| Blow tank                       | F 103  | 1000.0                | 10 gal   | 2.2                   | 2,200.0               |
| Feeder                          |        | 40.7                  |          | 1.2                   | 48.8                  |
| Gas injector                    | L 110  | 1,800.0               |          | 3.2                   | 5,760.0               |
| Toluene hand pump               | L 111  | 21.4                  |          | 1.00                  | 21.4                  |
| Rotary evaporator               | V 200  | 6,600.0               |          | 4.5                   | 29,700.0              |
| Toluene rec. pump               | L 210  | 367.0                 |          | 3.2                   | 1,174.0               |
| HPL pump                        | L 211  | 233.0                 |          | 3.2                   | 745.6                 |
| Ion exch. column                | D 300  | 500.0                 |          | 4.0                   | 2,000.0               |
| Ion exch. column                | D 301  | 500.0                 |          | 4.0                   | 2,000.0               |
| Dissolver                       | D 302  | 1,300.0               | 25 gal   | 2.2                   | 2,860.0               |
| Filter                          | H 303  | 180.0                 |          | 2.0                   | 360.0                 |
| Storage vessel                  | F 304  | 1,010.0               | 25 gal   | 2.2                   | 2,222.0               |
| Eth. wash storage               | F 306  | 1,350.0               | 100 gal  | 2.2                   | 2,970.0               |
| Eth rec. pump                   | L 310  | 300.0                 |          | 3.2                   | 960.0                 |
| Peristaltic pump                | L 311  | 990.0                 |          | 3.2                   | 3,168.0               |
| Ion Exchange resin              |        | 3,775.0               |          |                       | 3,775.0               |
| Total purchase price            |        | 22,467.1              |          |                       |                       |
| TOTAL BARE MODULE               |        |                       |          |                       | 70,965.2              |
| Contingency and fee (0.18 CTBM) |        |                       |          |                       | 12,773.7              |
| TOTAL MODULE CAPITAL            |        |                       |          |                       | 83,739.0              |
| Auxiliary facilities (0.3 CTBM) |        |                       |          |                       | 21,289.6              |
| TOTAL FIXED CAPITAL             |        |                       |          |                       | 105,028.6             |

| Table A.2 Capital Cost Estimation of Process 2, using Module Factors. |        |                       |          |                       |                       |
|---|--------|-----------------------|----------|-----------------------|-----------------------|
| Eq. Identification  | Number | Purchased<br>Eq. Cost | Capacity | B.B. Module<br>Factor | B.B. Module<br>Factor |
| Reactor   | R 100  | 2,500.0               | 10 gal   | 4.4                   | 11,000.0              |
| Blow tank   | F 103  | 1,000.0               | 10 gal   | 2.2                   | 2,200.0               |
| Feeder  |        | 40.7                  |          | 1.2                   | 48.8                  |
| Gas injector  | L 110  | 1,800.0               |          | 3.2                   | 5,760.0               |
| Toluene hand pump   | L 111  | 21.4                  |          | 1.00                  | 21.4                  |
| Rotary evaporator   | V 200  | 6,600.0               |          | 4.5                   | 29,700.0              |
| Toluene rec. pump   | L 210  | 367.0                 |          | 3.2                   | 1,174.4               |
| HPL pump  | L 211  | 233.0                 |          | 3.2                   | 745.6                 |
| Filter  | H 300  | 800.0                 |          | 1.4                   | 1,120.0               |
| Storage vessel  | F 304  | 1,010.0               | 25 gal   | 2.2                   | 2,222.0               |
| Total purchase price  |        | 14,373.1              |          |                       |                       |
| TOTAL BARE MODULE   |        |                       |          |                       | 53,992.2              |
| Contingency and fee (1.18 CTBM)                                       |        |                       |          |                       | 9,718.6               |
| TOTAL MODULE CAPITAL  |        |                       |          |                       | 63,710.8              |
| Auxiliary facilities (0.3 CTBM)                                       |        |                       |          |                       | 16,197.7              |
| TOTAL FIXED CAPITAL   |        |                       |          |                       | 79,908.5              |

Fractionation Plant. The purchased price for the reactor is the price paid for an used equipment . From Table A.1 the total fixed capital for Process 1: \$ 105,030 or Purchase price \* 4.7. From Table A.2 the total fixed capital for Process 2: \$ 79,909 or Purchase price \* 5.6. By comparison the Lang factors from the Guthrie's approach are considerably higher than the standard 4.1 proposed by Peters and Timmerhaus. If the cost of installation is split in its components the resulting capital costs for process 1 and 2 are the ones given in Tables A.3 and A.4 respectively.

| Table A.3 Capital Cost Estimation of Process 1,<br>specifying Installation Costs. |        |                       |                        |                      |                  |
|---|--------|-----------------------|------------------------|----------------------|------------------|
| Eq. Identification  | Number | Purchased<br>Eq. Cost | Installation<br>Factor | Installation<br>Cost | B.Module<br>Cost |
| Reactor   | R 100  | 2,500.0               | 40%                    | 1,000.0              | 3,500.0          |
| Blow tank   | F 103  | 1000.0                | 40%                    | 400.0                | 1,400.0          |
| Feeder  |        | 40.7                  | 25%                    | 10.2                 | 50.8             |
| Gas injector  | L 110  | 1,800.0               | 25%                    | 450.0                | 2,250.0          |
| Toluene hand pump   | L 111  | 21.4                  |                        |                      | 21.4             |
| Rotary evaporator   | V 200  | 6,600.0               | 25%                    | 1,650.0              | 8,250.0          |
| Toluene rec. pump   | L 210  | 367.0                 | 20%                    | 73.40                | 440.4            |
| HPL pump  | L 211  | 233.0                 | 20%                    | 46.6                 | 279.6            |
| Ion exch. column  | D 300  | 500.0                 | 30%                    | 150.0                | 650.0            |
| Ion exch. column  | D 301  | 500.0                 | 30%                    | 150.0                | 650.0            |
| Dissolver   | D 302  | 1,300.0               | 20%                    | 260.0                | 1,560.0          |
| Filter  | H 303  | 180.0                 | 80%                    | 144.0                | 324.0            |
| Storage vessel  | F 304  | 1,010.0               | 20%                    | 202.0                | 1,212.0          |
| Eth. wash storage   | F 306  | 1,350.0               | 20%                    | 270.0                | 1,620.0          |
| Eth rec. pump   | L 310  | 300.0                 | 20%                    | 60.0                 | 360.0            |
| Peristaltic pump  | L 311  | 990.0                 |                        |                      | 990.0            |
| <b>DIRECT PROJECT EXPENSES</b>  |        |                       |                        |                      |                  |
| Ion Exchange resin  |        | 3,775.0               |                        |                      | 3,775.0          |
| Total Eq. Cost (Cp)   |        | 22,467.1              |                        |                      |                  |
| Materials for Inst. (Cm)  |        |                       |                        | 4,866.2              |                  |
| Instrumentation (0.13 Cp)   |        |                       |                        |                      | 2,920.7          |
| Direct labor for Inst.  |        |                       |                        |                      | 20,000.0         |
| Total Direct Expenses   |        |                       |                        |                      | 50,253.9         |
| <b>INDIRECT PROJECT EXPENSES</b>  |        |                       |                        |                      |                  |
| Contractor Eng. Exp. (0.15 (Cp+Cm))   |        |                       |                        |                      | 4,100.0          |
| <b>BARE MODULE CAPITAL (CBM)</b>  |        |                       |                        |                      | <b>54,353.9</b>  |

| Table A.3 (Continued) Capital Cost Estimation of Process 1,<br>specifying Installation Costs. |                  |
|---|------------------|
|   | Cost             |
| Start Up Expenses (0.08 CBM)  | 4,348.3          |
| Freight, insurance, taxes (0.08 (Cp+Cm))  | 2,186.7          |
| Construction overhead (0.44 Cp)   | 9,885.5          |
| Contingency and fee (0.18 CBM)  | 9,783.7          |
| Site development (0.19 Cp)  | 4,268.7          |
| Auxiliary buildings (0.15 Cp)   | 3,370.1          |
| Offsite facilities (0.79 Cp)  | 17,749.0         |
| <b>FIXED CAPITAL INVESTMENT</b>   | <b>105,945.8</b> |

| Table A.4 Capital Cost Estimation of Process 2,<br>specifying Installation Costs. |        |                       |                        |                      |                  |
|---|--------|-----------------------|------------------------|----------------------|------------------|
| Eq. Identification  | Number | Purchased<br>Eq. Cost | Installation<br>Factor | Installation<br>Cost | B.Module<br>Cost |
| Reactor   | R 100  | 2,500.0               | 40%                    | 1,000.0              | 3,500.0          |
| Blow tank   | F 103  | 1000.0                | 40%                    | 400.0                | 1,400.0          |
| Feeder  |        | 40.7                  | 25%                    | 10.2                 | 50.9             |
| Gas injector  | L 110  | 1,800.0               | 25%                    | 450.0                | 2,250.0          |
| Toluene hand pump   | L 111  | 21.4                  |                        |                      | 21.4             |
| Rotary evaporator   | V 200  | 6,600.0               | 25%                    | 1,650.0              | 8,250.0          |
| Toluene rec. pump   | L 210  | 367.0                 | 20%                    | 73.4                 | 440.4            |
| HPL pump  | L 211  | 233.0                 | 20%                    | 46.6                 | 279.6            |
| Filter  | H 300  | 800.0                 | 80%                    | 640.0                | 1,440.0          |
| Storage vessel  | F 304  | 1,010.0               | 20%                    | 202.0                | 1,212.0          |

| Table A.4 (Continued) Capital Cost Estimation of Process 2,<br>specifying Installation Costs. |        |           |              |              |                 |
|---|--------|-----------|--------------|--------------|-----------------|
| Eq. Identification  | Number | Purchased | Installation | Installation | B.Module        |
|   |        | Eq. Cost  | Factor       | Cost         | Cost            |
| <b>DIRECT PROJECT EXPENSES</b>  |        |           |              |              |                 |
| Total Eq. Cost (Cp)   |        | 14,372.1  |              |              |                 |
| Materials for Inst. (Cm)  |        |           |              | 4,472.2      |                 |
| Instrumentation (0.13 Cp)   |        |           |              |              | 1,868.4         |
| Direct labor for Inst.  |        |           |              |              | 20,000.0        |
| Total Direct Expenses   |        |           |              |              | 40,712.6        |
| <b>INDIRECT PROJECT EXPENSES</b>  |        |           |              |              |                 |
| Contractor Eng. Exp. (0.15 (Cp+Cm))   |        |           |              |              | 2,826.6         |
| <b>BARE MODULE CAPITAL (CBM)</b>  |        |           |              |              |                 |
| Stat Up Expenses (0.08 CBM)   |        |           |              |              | 43,539.3        |
| Stat Up Expenses (0.08 CBM)   |        |           |              |              | 3,483.1         |
| Freight, insurance, taxes (0.08 (Cp+Cm))  |        |           |              |              | 1,507.5         |
| Construction overhead (0.44 Cp)   |        |           |              |              | 6,323.7         |
| Contingency and fee (0.18 CBM)  |        |           |              |              | 7,837.1         |
| Site development (0.19 Cp)  |        |           |              |              | 2,730.7         |
| Auxiliary buildings (0.15 Cp)   |        |           |              |              | 2,155.8         |
| Offsite facilities (0.79 Cp)  |        |           |              |              | 11,354.0        |
| <b>FIXED CAPITAL INVESTMENT</b>   |        |           |              |              | <b>78,931.2</b> |

### A.2 Manufacturing Cost Estimation

The manufacturing cost includes the direct manufacturing expenses, the indirect manufacturing expenses, and the general expenses. Costs in the direct manufacturing category are comprised of those due to materials or labor that

either are physically in the product or have come in tangible contact with it during its evolution, for example, raw materials, by-product credits, operating labor, utilities, etc. The so called indirect manufacturing expenses include taxes, insurance, overhead expenses, etc. Finally, the general expenses are composed of the administrative costs, distribution costs, and research and development. The manufacturing cost amounts about 20% of the raw material cost. For example, the manufacturing cost of motor alkylate is about 1.3 of the raw material cost, but it may be 4 times the raw material cost, depending of the kind of product. Since this study deals with the development of a pilot plant whose objective is more the testing of a product than the generation of profits, the calculation of the manufacturing costs will not be as precise as it will be for a processing plant where all items that form part of the total cost can be estimated. Then, the raw material cost is calculated for Process 1 and 2 in Tables A.3 and A.4, respectively, and the manufacturing cost of HPL is estimated as 1.3 and 4 times the raw material cost. Resulting:

#### Manufacturing Cost

Process 1 . . . . . 1.20 (1.3) = 1.56 \$ per kg HPL (0.71 \$ per lb HPL)

Process 1 . . . . . 1.20 (4) = 4.80 \$ per kg HPL (0.71 \$ per lb HPL)

Process 2 . . . . . 1.02 (1.3) = 1.33 \$ per kg HPL (0.60 \$ per lb HPL)

Process 2 . . . . . 1.02 (4) = 4.08 \$ per kg HPL (0.60 \$ per lb HPL).

These manufacturing cost values are a preliminary estimation. They are calculated to compare them with the actual prices of polyols used in the manufacture of rigid polyurethane foams.

| Table A.5 Raw Material Cost - Process 1. |                                    |                |                       |
|--|------------------------------------|----------------|-----------------------|
| Raw Materials                            | Amount per \$ per kg<br>Batch (kg) | Recycling<br>% | Total per Batch<br>\$ |
| Lignin                                   | 6.25                               | 0.55           | 3.44                  |
| KOH                                      | 0.44                               | 2.91           | 1.28                  |
| PO                                       | 5.45                               | 1.2            | 5.72                  |
| Toluene                                  | 17.32                              | 0.26           | 90.0                  |
| Ethanol                                  | 15.67 l                            | 0.31           | 90.0                  |
| Ethanol wash                             | 63.00 l                            | 0.31           | 90.0                  |
| CLH                                      | 0.25                               | 0.24           | <u>0.06</u>           |
| Cost of raw materials without optionals  |                                    |                | 13.39                 |
| Cost of Polyol/kg                        |                                    |                | 1.20                  |
| Cost of Polyol / lb                      |                                    |                | 0.55                  |

| Table A.6 Raw Material Cost - Process 2. |                                    |                |                       |
|--|------------------------------------|----------------|-----------------------|
| Raw Materials                            | Amount per \$ per kg<br>Batch (kg) | Recycling<br>% | Total per Batch<br>\$ |
| Lignin                                   | 6.25                               | 0.55           | 3.44                  |
| KOH                                      | 0.44                               | 2.91           | 1.28                  |
| PO                                       | 5.45                               | 1.2            | 5.72                  |
| Toluene                                  | 17.32                              | 0.26           | 90.0                  |
| Sulfuric Acid                            | 0.38                               | 0.15           | <u>0.06</u>           |
| Cost of raw materials without optionals  |                                    |                | 10.95                 |
| Cost of Polyol/kg                        |                                    |                | 1.02                  |
| Cost of Polyol / lb                      |                                    |                | 0.46                  |

## Appendix B

### SCALE-UP TO INDUSTRIAL PRODUCTION

The pilot plant is scaled-up to an industrial level to utilize the lignin produced by a fractionation plant that processes 10 tons of green wood per hour. This correspond to 6 tons of dry wood of which 70 %, or 4.2 tons, are fibers and the rest are water-soluble wood components. The fibers consist of 60 % cellulose and 40 % lignin, that is 2 tons of lignin per hour.

The plant will process 2 tons of lignin per hour or 32 tons of lignin per day (for a working day of 16 hours), or approximately 10,000 tons of lignin per year. Considering that lignin is available at factories producing pulp for papermaking in quantities in excess of 16 million tons per year, this plant will process ca. 0.0625 % of the total lignin potentially available.

The following analysis is performed to determine the most convenient HPL production process. The polymerization reactor is the center of the process. If a continuous reactor is chosen, the process is continuous and if the reactor operates batchwise, the process is batch. The batch reactor is the best kind of reactor for small production levels since it provides great flexibility, and the capital cost is often less than for a corresponding continuous reactor. Also, since the reaction kinetics are usually studied in the laboratory under batch conditions, the scale-up is easily done for a batch reactor. The selection of a pilot plant batch reactor is therefore an appropriate one. Continuous reactors are adopted in almost all large-scale chemical industries because the labor cost for a continuous process is lower than for a batch process. In addition the automatic controls are more easily applied to a continuous process. Another advantage of the continuous process is the constancy in the reactions conditions and hence in the product quality, which is very important for an industrial production. The kinetic results obtained from the laboratory can be applied to a continuous process since the molecular changes are the same, but both processes have different flow patterns, an this is the cause of the differences in the yield and characteristics of the product from each one. In the continuous reactor, not all

molecules passing through the flow system will have the same residence time, nor they will have the same history of temperature and concentration changes. The yield of a reaction performed in a batch reactor will differ from the yield of the same reaction in a continuous reactor, and this is more accentuated when competing reactions take place, like in the present case. But an important consideration needs to be addressed, and this is related to the characteristics of the raw material, lignin used in the process. Lignin can be isolated from different sources and by different methods of isolation. The properties of the lignin will depend directly on the origin and type of method of isolation. In a continuous process it is required constancy of the characteristics of the feed to allow the process work. Then this is a drawback for a continuous process. A continuous process can be the process of choice if constant properties lignin is used. But a continuous process will not be the best choice if the plant process lignin produced for different firms and according to its price or tendency of the market. In this second case a batch process will be more convenient.

Besides the selection of a batch or continuous process, the choice of the reactor type is also important. Each type of reactor gives a different molecular weight distribution of the polymer produced (Denbigh, 1984). Tubular reactors are used for gaseous polymerizations, but not for liquid phase or emulsion polymerizations with high liquid viscosity, where agitation is important. Due to the high viscosity, the velocity profile in a tubular reactor produces a broad residence time distribution, and the polymerization rate will vary from the center to the wall of the tube. For HPL production, the tubular reactor is not a good choice. The stirred tank reactor (S.T.R.) either continuous or batch is the best choice for HPL production. First we analyze a continuous stirred tank reactor (C.S.T.R.). Since the reaction is very slow several vessels in series will be needed. Two important points related to the C.S.T.R. are as follows: (a) The residence time of all molecules is different and this will cause a broad molecular weight distribution of PPO and also production of some molecules of chain extended HPL (CEHPL see Figure 3.3). (b) The concentration history remains constant in each vessel. The monomer concentration is stationary, and, in general, is a at

lower average level than it would be, for the same feed conditions, if the reaction were carried out batchwise. This factor is favorable to the lignin copolymerization reaction since this requires that the concentration of PO remains low at all times.

In Table B.1 is given the material balance for a continuous process performed in a series of C.S.T.R. reactors.

| Table B.1 Preliminary Material Balance                 |                                  |
|--|----------------------------------|
| Material   | Flow, tons/h (m <sup>3</sup> /h) |
| Lignin   | 2.0                              |
| Propylene Oxide  | 1.74                             |
| Toluene  | (6.4)                            |
| KOH  | 0.14/0.28 *                      |
| H <sub>2</sub> SO <sub>4</sub>                         | 0.12/0.24 *                      |
| Copolymer  | 2.7                              |
| Homopolymer  | 0.7                              |
| Total Product  | 3.4                              |
| * 1.25 mol KOH per kg lignin/2.5 mol KOH per kg lignin |                                  |

A block diagram for the continuous synthesis of HPL is given in Figure B.1 and a preliminary flow diagram is given in Figure B.2. A preliminary capital cost estimation is presented in Table B.1 and the raw material cost for the continuous process is given in Table B.2. In discussing economic attractiveness of a process decision makers usually speak in terms of *rate of return*, i. This is the net annual profit after taxes; and it is calculated for this project on Table B.3. The simple after taxes rate

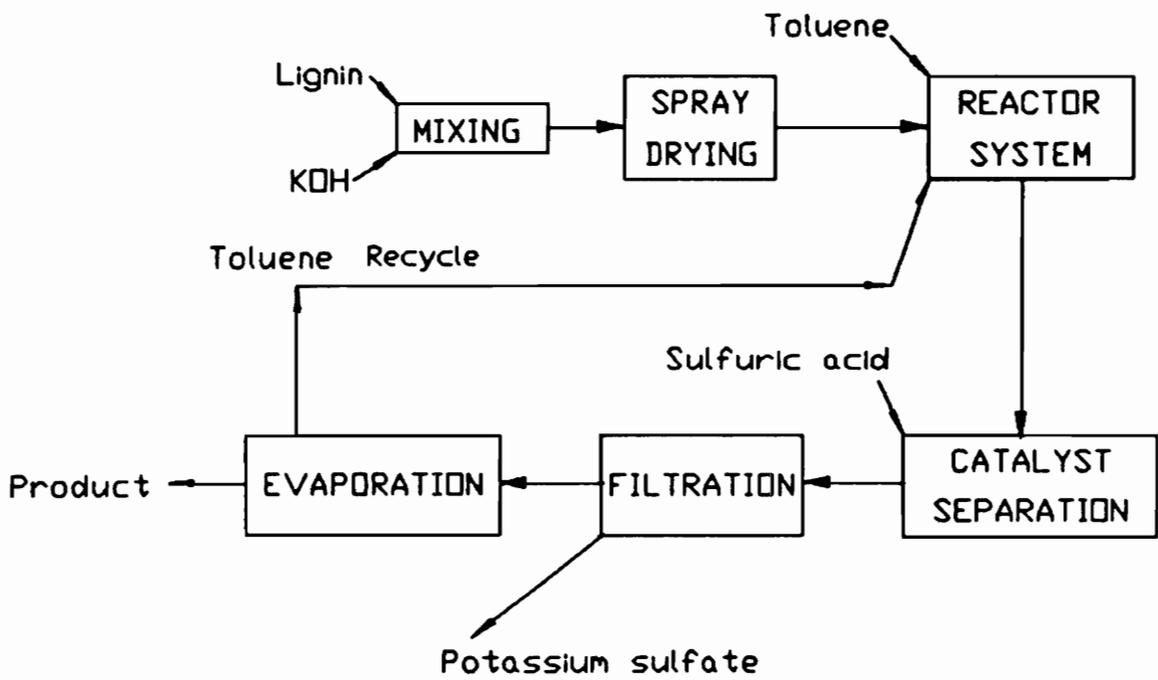


Figure B.1 Block diagram for continuous HPL synthesis process.

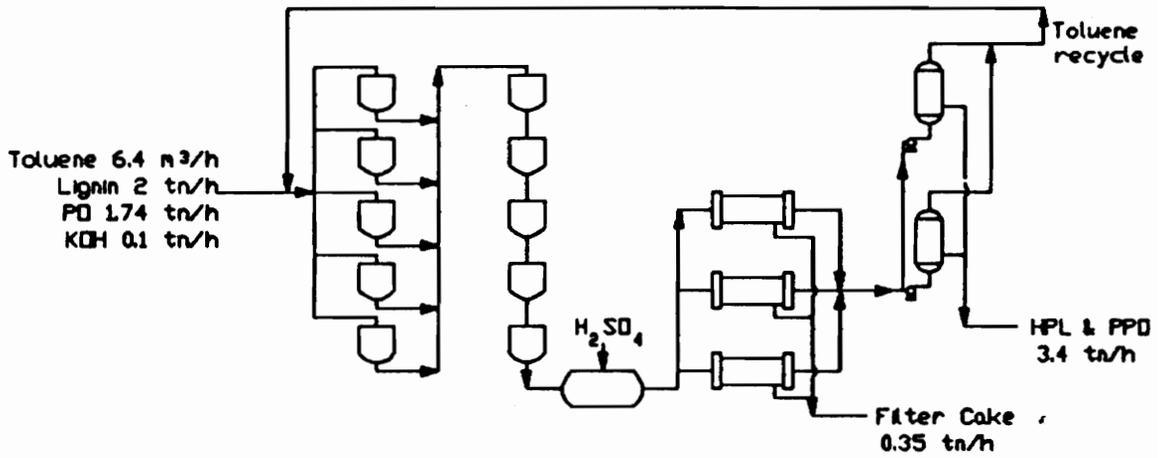


Figure B.2 Preliminary flow diagram for continuous HPL synthesis process.

| Eq. Identification              | Units | Base Bare Module Cost |
|---------------------------------|-------|-----------------------|
| Reactor                         | 10    | 600,000.00            |
| Blow tank                       | 1     | 20,000.00             |
| Feeder                          | 10    | 500.00                |
| Lignin storage                  | 5     | 45,000.00             |
| KOH storage                     | 2     | 9,000.00              |
| PO storage                      | 5     | 45,000.00             |
| Toluene storage                 | 10    | 150,000.00            |
| HPL storage                     | 10    | 100,000.00            |
| Evaporator                      | 2     | 3,000,000.00          |
| Filter                          | 3     | 120,000.00            |
| TOTAL BARE MODULE (CTBM)        |       | 4,089,500.00          |
| Start up exp. (0.08 CTBM)       |       | 327,160.00            |
| Contingency and fee (0.18 CTBM) |       | 736,110.00            |
| TOTAL MODULE CAPITAL            |       | 5,152,770.00          |
| Auxiliary facilities (0.3 CTBM) |       | 1,226,850.00          |
| TOTAL FIXED CAPITAL             |       | 6,379,620.00          |

| Raw materials                                   | tons/hour | \$/kg | Recycling % | Total \$/hour |
|---|-----------|-------|-------------|---------------|
| Lignin  | 2.00      | 0.55  |             | 1,100.00      |
| KOH   | 0.14      | 2.91  |             | 407.40        |
| PO  | 1.74      | 1.05  |             | 1,827.00      |
| Toluene   | 5.54      | 0.26  | 90.0        | 144.04        |
| Sulfuric acid                                   | 0.12      | 0.15  |             | <u>18.00</u>  |
| Cost of Total raw materials (without optionals) |           |       |             | 3,496.44      |

| Table B.4 Preliminary Economic Analysis of Cost of Continuous HPL Synthesis Process. |       |               |
|--|-------|---------------|
| Economic Analysis  | \$/kg | \$/year       |
| CFC: Fixed Capital   |       | 6,379,620.00  |
| CWC: Working Capital (15%CFC)  |       | 956,943.00    |
| CTC: Total Capital   |       | 7,336,563.00  |
| ATE: Annual Total Expenses   | 1.34  | 22,726,860.00 |
| AS: Annual sales   | 1.43  | 24,310,000.00 |
| ANNP: Annual Net Profits after taxes   |       |               |
| ANNP = (AS - ATE) (1-t)  |       | 791,570.00    |
| t = 0.5  |       |               |
| ABD: Depreciation  |       |               |
| ABD = CFC (1 - 0.1)/s  |       | 574,165.00    |
| s = 10 years   |       |               |
| PROFITABILITY = (ANNP/CTC) 100   |       | 10.79         |
| RATE OF RETURN = (ANNP + ABD) 100/CTC  |       | 18.62         |

of return is 18.62% per year for a product selling price of 1.43 \$/kg, or in 5.4 years the investment could be recovered. However, this simple rate of return is limited as a measure of profitability. A project normally extends over many years before completion, and during this time the economic parameters change. The time factor needs to be considered in a final design step.

If a batch process were selected there will be several reactors working in parallel. A time scale for these reactors needs to be established to transfer the

reaction product to the following process steps. In a batch process, more storage is required, for both raw materials and intermediate products.

The design here presented was based upon the pre-pilot plant designed in *Chapter 7*. We called it a pre-pilot plant because it is not possible to scale-up some of its equipment. Since the best process conditions are still under research many changes will be made to this full scale design. The objective at this point was to estimate the plant capacity and the equipment and capital required. It is possible that this plant will not be constructed as an independent plant but with either a wood fractionation plant or a polyurethane foam production plant.

Finally, is listed the following information needed from the pilot plant to produce a more complete plant design: (a) the overall properties of the reactor mixture, that is, heat capacity, density, and viscosity; (b) the reaction kinetics, that is time vs. lignin conversion; (c) the best reaction temperature or temperature gradient; (d) the design pressure or pressure gradient; (e) the heat of reaction, to calculate the required area of heat exchange; (f) the percentage of recycle of solvents, to calculate the exact mass balance; and (g) the yield loss of HPL to by-products in the reactor, regardless of conversion, to adjust the net production.

*Appendix C*  
*Program BUBBLET*

C\$NOWARNINGS

C\$NOEXTENSIONS

```
C *****
C   BUBBLE CALCULATIONS - CALCULATE THE COMPOSITION
C   OF A SYSTEM Y AND TEMPERATURE GIVEN PRESSURE AND X
C *****
  IMPLICIT LOGICAL (A-Z)
  INTEGER IX, J
  REAL*8 X1, X2, Y1, Y2, Q1, Q2
  REAL*8 GA1, GA2, P1S, P2S, LA12, LA21, T
  REAL*8 P, T1S, T2S
  REAL*8 EPS, DT, TNEW
  REAL*8 BS01, BS02, BS11, BS12, B11, B22, TC12, ZC12,
#   VC12, PC12, BS012, BS112, B12, DEL12
  REAL*8 VL1, VL2, R, AA1, AA2, BB1, BB2, CC1, CC2,
#   L12, L21, PC1, PC2, TC1, TC2, VC1, VC2,
#   ZC1, ZC2, W1, W2, W12
  DATA VL1, VL2, R, AA1, AA2, BB1, BB2, CC1, CC2,
#   L12, L21, PC1, PC2, TC1, TC2, VC1, VC2,
#   ZC1, ZC2, W1, W2/
#   70.75D-6, 106.85D-6, 8.31439D0, 7.01443D0, 6.95087D0,
#   1086.369D0, 1342.310D0, -44.406D0, -53.813D0,
#   3768.28D0, -2185.26D0, 4.92D6, 4.21D6, 482.2, 593.1,
#   186.0D-6, 316.6D-6, 0.258, 0.264, 0.2, 0.257/
C
  OPEN (1, FILE='BUBLT.DAT', STATUS='OLD')
  WRITE(*,*) 'ENTER PRESSURE (PA) = '
  READ(*,*) P
  WRITE(1,400)
```

```

DO 10 IX = 0,20
X1 = IX/20.0
X2 = 1.0 - X1
Q1 = 1.0
Q2 = 1.0
T1S = (BB1/(AA1 - LOG10(P*750.061D-5))) - CC1
T2S = (BB2/(AA2 - LOG10(P*750.061D-5))) - CC2
T = X1*T1S + X2*T2S
P1S = 10**(AA1 - BB1/(CC1 + T)) / 750.061D-5
P2S = 10**(AA2 - BB2/(CC2 + T)) / 750.061D-5
LA12 = VL2/VL1*EXP(-L12/(R*T))
LA21 = VL1/VL2*EXP(-L21/(R*T))
GA1 = EXP(-LOG(X1+LA12*X2) + X2*(LA12/(X1+LA12*X2) -
#   LA21/(LA21*X1+X2)))
GA2 = EXP(-LOG(X2+LA21*X1) - X1*(LA12/(X1+LA12*X2) -
#   LA21/(LA21*X1+X2)))
P1S = P/((X1*GA1/Q1)*(P1S/P1S) + (X2*GA2/Q2)*(P2S/P1S))
T = BB1/(AA1 - LOG10(P1S*750.061D-5)) - CC1
J = 0
100  J = J + 1
      IF(J.LT.10000) GOTO 110
      WRITE(*,*) 'LOOP ON T, J' ,J
      GOTO 200
110  CONTINUE
P1S = 10**(AA1 - BB1/(CC1 + T)) / 750.061D-5
P2S = 10**(AA2 - BB2/(CC2 + T)) / 750.061D-5
Y1 = X1*GA1*P1S/(Q1*P)
Y2 = X2*GA2*P2S/(Q2*P)
BS01 = 0.083 - 0.422/((T/TC1)**1.6)
BS02 = 0.083 - 0.422/((T/TC2)**1.6)
BS11 = 0.139 - 0.172/((T/TC1)**4.2)
BS12 = 0.139 - 0.172/((T/TC2)**4.2)

```

```

B11 = (R*TC1/PC1)*(BS01+W1*BS11)
B22 = (R*TC2/PC2)*(BS02+W2*BS12)
TC12 = DSQRT(TC1*TC2)
ZC12 = (ZC1+ZC2)/2
VC12 = ((VC1**(1.0/3.0) + VC2**(1.0/3.0))/2)**3
PC12 = ZC12*R*TC12 /VC12
BS012 = 0.083 - 0.422/((T/TC12)**1.6)
BS112 = 0.139 - 0.172/((T/TC12)**4.2)
W12=(W1+W2)/2.0
B12 = (R*TC12/PC12)*(BS012+W12*BS112)
DEL12 = 2*B12 -B11 -B22
Q1 = EXP((B11*(P - P1S) + P*Y2**2*DEL12)/(R*T))
Q2 = EXP((B22*(P - P2S) + P*Y1**2*DEL12)/(R*T))
LA12 = VL2/VL1*EXP(-L12/(R*T))
LA21 = VL1/VL2*EXP(-L21/(R*T))
GA1 = EXP(-LOG(X1+LA12*X2) + X2*(LA12/(X1+LA12*X2) -
# LA21/(LA21*X1+X2)))
GA2 = EXP(-LOG(X2+LA21*X1) - X1*(LA12/(X1+LA12*X2) -
# LA21/(LA21*X1+X2)))
P1S = P/((X1*GA1/Q1)*(P1S/P1S) + (X2*GA2/Q2)*(P2S/P1S))
TNEW = BB1/(AA1 - LOG10(P1S*750.061D-5)) - CC1
DT = TNEW - T
EPS = 1.0D-6
T = TNEW
IF (DT.GT.EPS) GOTO 100
C *****
C RESULTS FOR THE BUBBLE T
C *****
200 WRITE(1,500) X1, X2, Y1, Y2, T
WRITE (*,*) 'T (K)'
WRITE (*,*) T
WRITE(*,*) 'X1, X2, Y1, Y2'

```

```
WRITE(*,300) X1, X2, Y1, Y2
10  CONTINUE
300  FORMAT(4(1PE11.4))
400  FORMAT('* BUBLT'/'*',4X,'X1',4X,'X2',9X,'Y1',9X,'Y2',9X,'T')
500  FORMAT(5(1PE11.4))
STOP
END
```

*Appendix D*  
*Program FLASH*

C\$NOWARNINGS

C\$NOEXTENSIONS

```
C      *****
C      FLASH CALCULATIONS - CALCULATE THE COMPOSITION
C      OF A SYSTEM Y AND X
C      GIVEN T, P AND THE OVERALL COMPOSITION
C      *****
      IMPLICIT LOGICAL (A-Z)
      INTEGER I,II,J,JJ,JJJ
      REAL*8 X1, X2, Y1, Y2, Z1, Z2, Q1, Q2, LPO, LTO, LM, VM
      REAL*8 GA1, GA2, P1S, P2S, V, LA12, LA21, T, NT
      REAL*8 K1, K2, X1NEW, X2NEW, Y1NEW, Y2NEW, VJP1, P
      REAL*8 DV, DY1, DY2, DX1, DX2, F, DFDV, L, EPS
      REAL*8 BS01, BS02, BS11, BS12, B11, B22, TC12, ZC12,
#      VC12, PC12, BS012, BS112, B12, DEL12, XT,
#      GA1NEW, GA2NEW, DGA1, DGA2, PDEWNEW, DPDEW
      REAL*8 PDEW, PBULB, X1DEW, X1BULB, X2DEW, X2BULB,
#      Y1DEW, Y1BULB, Y2DEW, Y2BULB, Q1DEW, Q1BULB,
#      Q2DEW, Q2BULB,GA1DEW, GA1BULB, GA2DEW, GA2BULB,
#      W12, DPBULB, PBULBNEW, INT
      REAL*8 VL1, VL2, R, AA1, AA2, BB1, BB2, CC1, CC2,
#      L12, L21, PC1, PC2, TC1, TC2, VC1, VC2,
#      ZC1, ZC2, W1, W2, N
      DATA VL1, VL2, R, AA1, AA2, BB1, BB2, CC1, CC2,
#      L12, L21, PC1, PC2, TC1, TC2, VC1, VC2,
#      ZC1, ZC2, W1, W2/
#      70.75D-6, 106.85D-6, 8.31439D0, 7.01443D0, 6.95087D0,
#      1086.369D0, 1342.310D0, -44.406D0, -53.813D0,
#      3768.28D0,-2185.26D0, 4.92D6, 4.21D6, 482.2, 593.1,
```

```

#    186.0D-6, 316.6D-6, 0.258, 0.264, 0.2, 0.257/
WRITE(*,*) 'ENTER TEMPERATURE (K) = '
READ(*,*) T
WRITE(*,*) 'ENTER PRESSURE (PA) = '
READ(*,*) P
WRITE(*,*) 'ENTER TOTAL COMPOSITION OF PO ='
READ(*,*) Z1
WRITE(*,*) 'ENTER TOTAL COMPOSITION OF TOLUENE ='
READ(*,*) Z2
WRITE(*,*) 'ENTER TOTAL NUMBER OF MOLES (MOLES) ='
READ(*,*) NT
C    *****
C    DEW P CALCULATIONS WITH {Yi = Zi}
C    *****
Y1 = Z1
Y2 = Z2
Q1 = 1.0
Q2 = 1.0
GA1 = 1.0
GA2 = 1.0
P1S = 10**(AA1 - BB1/(CC1 + T)) / 750.061D-5
P2S = 10**(AA2 - BB2/(CC2 + T)) / 750.061D-5
PDEW = 1.0 / (Y1*Q1/(GA1*P1S) + Y2*Q2/(GA2*P2S))
X1 = Y1*Q1*PDEW/(GA1*P1S)
X2 = Y2*Q2*PDEW/(GA2*P2S)
LA12 = VL2/VL1*EXP(-L12/(R*T))
LA21 = VL1/VL2*EXP(-L21/(R*T))
GA1 = EXP(-LOG(X1+LA12*X2) + X2*(LA12/(X1+LA12*X2) -
#    LA21/(LA21*X1+X2)))
GA2 = EXP(-LOG(X2+LA21*X1) - X1*(LA12/(X1+LA12*X2) -
#    LA21/(LA21*X1+X2)))
PDEW = 1 / (Y1*Q1/(GA1*P1S) + Y2*Q2/(GA2*P2S))

```

```

BS01 = 0.083 - 0.422/((T/TC1)**1.6)
BS02 = 0.083 - 0.422/((T/TC2)**1.6)
BS11 = 0.139 - 0.172/((T/TC1)**4.2)
BS12 = 0.139 - 0.172/((T/TC2)**4.2)
B11 = (R*TC1/PC1)*(BS01+W1*BS11)
B22 = (R*TC2/PC2)*(BS02+W2*BS12)
TC12 = DSQRT(TC1*TC2)
ZC12 = (ZC1+ZC2)/2
VC12 = ((VC1**(1.0/3.0) + VC2**(1.0/3.0))/2)**3
PC12 = ZC12*R*TC12 /VC12
BS012 = 0.083 - 0.422/((T/TC12)**1.6)
BS112 = 0.139 - 0.172/((T/TC12)**4.2)
W12=(W1+W2)/2.0
B12 = (R*TC12/PC12)*(BS012+W12*BS112)
DEL12 = 2*B12 -B11 -B22
J = 0
100  J = J + 1
      IF (J.LT.10000) GOTO 110
      WRITE(*,*) 'DEW P CALCULATION IN Q1,Q2'
      GOTO 600
110  CONTINUE
      Q1 = EXP((B11*(PDEW - P1S) + PDEW*Y2**2*DEL12)/(R*T))
      Q2 = EXP((B22*(PDEW - P2S) + PDEW*Y1**2*DEL12)/(R*T))
      JJ = 0
200  JJ = JJ + 1
      IF(JJ.LT.10000) GOTO 210
      WRITE(*,*) 'DEW P CALCULATION IN X1,X2'
      GOTO 600
210  CONTINUE
      X1 = Y1*Q1*PDEW/(GA1*P1S)
      X2 = Y2*Q2*PDEW/(GA2*P2S)
      XT = X1 + X2

```

```

X1 = X1/XT
X2 = X2/XT
GA1NEW = EXP(-LOG(X1+LA12*X2) + X2*(LA12/(X1+LA12*X2) -
#   LA21/(LA21*X1+X2)))
GA2NEW = EXP(-LOG(X2+LA21*X1) - X1*(LA12/(X1+LA12*X2) -
#   LA21/(LA21*X1+X2)))
DGA1 = GA1NEW - GA1
DGA2 = GA2NEW - GA2
GA1 = GA1NEW
GA2 = GA2NEW
EPS = 1.0D-3
IF (DGA1.GT.EPS) GOTO 200
IF (DGA2.GT.EPS) GOTO 200
PDEWNEW = 1/(Y1*Q1/(GA1*P1S) + Y2*Q2/(GA2*P2S))
DPDEW = PDEWNEW - PDEW
PDEW = PDEWNEW
EPS = 1.0
IF (DPDEW.GT.EPS) GOTO 100
X1DEW = X1
X2DEW = X2
Y1DEW = Y1
Y2DEW = Y2
GA1DEW = GA1
GA2DEW = GA2
Q1DEW = Q1
Q2DEW = Q2
WRITE(*,*) PDEW
C   *****
C   BULB P CALCULATIONS WITH {Xi = Zi}
C   *****
X1 = Z1
X2 = Z2

```

```

Q1 = 1.0
Q2 = 1.0
P1S = 10**(AA1 - BB1/(CC1 + T)) / 750.061 D-5
P2S = 10**(AA2 - BB2/(CC2 + T)) / 750.061 D-5
LA12 = VL2/VL1*EXP(-L12/(R*T))
LA21 = VL1/VL2*EXP(-L21/(R*T))
GA1 = EXP(-LOG(X1+LA12*X2) + X2*(LA12/(X1+LA12*X2) -
#   LA21/(LA21*X1+X2)))
GA2 = EXP(-LOG(X2+LA21*X1) - X1*(LA12/(X1+LA12*X2) -
#   LA21/(LA21*X1+X2)))
PBULB = X1*GA1*P1S/Q1 + X2*GA2*P2S/Q2
JJJ = 0
300  JJJ = JJJ + 1
      IF(JJJ.LT.10000) GOTO 310
      WRITE(*,*) 'JJJ', JJJ
      WRITE(*,*) 'BULB P CALCULATION IN Y1,Y2'
      GOTO 600
310  CONTINUE
      Y1 = X1*GA1*P1S/(Q1*PBULB)
      Y2 = X2*GA2*P2S/(Q2*PBULB)
      Q1 = EXP((B11*(PBULB - P1S) + PBULB*Y2**2*DEL12)/(R*T))
      Q2 = EXP((B22*(PBULB - P2S) + PBULB*Y1**2*DEL12)/(R*T))
      PBULBNEW = X1*GA1*P1S/Q1 + X2*GA2*P2S/Q2
      DPBULB = PBULBNEW - PBULB
      PBULB = PBULBNEW
      EPS = 1.0
      IF (DPBULB.GT.EPS) GOTO 300
      X1BULB = X1
      X2BULB = X2
      Y1BULB = Y1
      Y2BULB = Y2
      GA1BULB = GA1

```

```

GA2BULB = GA2
Q1BULB = Q1
Q2BULB = Q2
WRITE(*,*) 'PBULB FINISH'
WRITE(*,*) PBULB
C *****
C INITIAL VALUES
C *****
IF (PDEW.LT.P.AND.PBULB.GT.P) GOTO 10
WRITE(*,*) 'THE MIXTURE IS NOT IN V-L CONDITION'
STOP
10 CONTINUE
C *****
C FLASH
C *****
INT = P - PDEW/(PBULB - PDEW)
GA1 = GA1DEW + INT*(GA1BULB - GA1DEW)
GA2 = GA2DEW + INT*(GA2BULB - GA2DEW)
Q1 = Q1DEW + INT*(Q1BULB - Q1DEW)
Q2 = Q2DEW + INT*(Q2BULB - Q2DEW)
V = (PBULB - P) /(PBULB - PDEW)
WRITE(*,*) 'VINITIAL', V
C
I = 0
500 I = I + 1
IF (I.LT.100000) GOTO 510
WRITE(*,*) ' LOOP IN X , Y '
GOTO 600
510 CONTINUE
K1 = GA1 *P1S/(Q1*P)
K2 = GA2 *P2S/(Q2*P)
C

```

```

II=0
400  II=II+1
    IF(II.LT.10000) GOTO 410
    WRITE (*,*) 'LOOP IN V', II
    WRITE(*,*) 'ENTER N'
    READ (*,*) N
    V = (PBULB - P)/(PBULB - PDEW)*N
    II = 0
    GOTO 410
410  CONTINUE
    F = Z1*(K1-1)/(1+V*(K1 -1)) + Z2*(K2-1)/(1+V*(K2-1))
      DFDV =- Z1*(K1-1)**2/(1+V*(K1-1))**2 - Z2*(K2-1)**2/(1+V*(K2-
1))**2
    VJP1 = V - F/DFDV
    DV = VJP1 - V
    V = VJP1
    IF (ABS(DV).GT.1.0E-5) GOTO 400
C
X1NEW = Z1/(1+V*(K1-1))
X2NEW = Z2/(1+V*(K2-1))
Y1NEW = K1*X1
Y2NEW = K2*X2
DX1 = X1NEW - X1
DX2 = X2NEW - X2
DY1 = Y1NEW - Y1
DY2 = Y2NEW - Y2
Y1 = Y1NEW
Y2 = Y2NEW
X1 = X1NEW
X2 = X2NEW
Q1 = EXP((B11*(P - P1S) + P*Y2**2*DEL12)/(R*T))
Q2 = EXP((B22*(P - P2S) + P*Y1**2*DEL12)/(R*T))

```

```

LA12 = VL2/VL1*EXP(-L12/(R*T))
LA21 = VL1/VL2*EXP(-L21/(R*T))
GA1 = EXP(-LOG(X1+LA12*X2) + X2*(LA12/(X1+LA12*X2) -
#   LA21/(LA21*X1+X2)))
GA2 = EXP(-LOG(X2+LA21*X1) - X1*(LA12/(X1+LA12*X2) -
#   LA21/(LA21*X1+X2)))
EPS = 1.0D-2
IF (ABS(DX1).GT.EPS) GOTO 500
IF (ABS(DX2).GT.EPS) GOTO 500
IF (ABS(DY1).GT.EPS) GOTO 500
IF (ABS(DY2).GT.EPS) GOTO 500
L = 1.0 - V
LPO = X1*L*NT*58.08/0.859
LTO = X2*L*NT*92.13/0.866
LM = LPO + LTO
VM = 3785.0 - LM
C   *****
C   RESULTS FOR THE FLASH CALCULATIONS
C   *****
600  WRITE (*,*) 'VAPOR VOLUME (MOLES/MOLES TOTAL)'
      WRITE (*,*) V
      WRITE (*,*) 'LIQUID VOLUME (MOLES/MOLES TOTAL)'
      WRITE (*,*) L
      WRITE (*,*) 'LIQUID VOLUME (ML)'
      WRITE (*,*) LM
      WRITE (*,*) 'VAPOR VOLUME (ML)'
      WRITE (*,*) VM
      WRITE (*,*) 'Y1 = '
      WRITE (*,*) Y1
      WRITE (*,*) 'Y2 = '
      WRITE (*,*) Y2
      WRITE (*,*) 'X1 = '

```

```
WRITE (*,*) X1
WRITE (*,*) 'X2 = '
WRITE (*,*) X2
C   WRITE (*,*) 'P1S = '
C   WRITE (*,*) P1S
C   WRITE (*,*) 'P2S = '
C   WRITE (*,*) P2S
C   WRITE (*,*) I
1000 STOP
END
```

*Appendix E*  
*Program DCB*

C\$NOWARNINGS

C\$NOEXTENSIONS

IMPLICIT REAL\*8 (A-Z)

CHARACTER\*4 FLAG,RESET\*2

INTEGER DELTA

C \*\*\*\*\*

C F1: FOR REACTION ONLY

C F2: FOR REACTION AND LOADING

C \*\*\*\*\*

C

F1(T,K,C0) = C0\*EXP(-K\*T)

F2(T,K,F0,V0,Q) = (EXP(-K\*T)/(V0+Q\*T))\*

# (F0\*V0+((Q\*CI/K)\*(EXP(K\*T)-1)))

C

OPEN(1,FILE='DCB.DAT',STATUS='OLD')

OPEN(2,FILE='DCBH.DAT',STATUS='OLD')

OPEN(3,FILE='DCBAFR.DAT',STATUS='OLD')

OPEN(4,FILE='LIM.DAT',STATUS='OLD')

OPEN(5,FILE='GRID.DAT',STATUS='OLD')

C \*\*\*\*\*

C INPUTS

C \*\*\*\*\*

C

WRITE(\*,\*) 'ENTER CL:'

READ (\*,\*) CL

WRITE(\*,\*) 'ENTER CH:'

READ (\*,\*) CH

WRITE(\*,\*) 'ENTER TOTAL TIME (sec):'

```

READ (*,*) TT
WRITE(4,*) 0,CL,CH
WRITE(4,*) TT,CL,CH
CI=1.461D4
V0=1.5D-3
WRITE(*,*) 'ENTER K0'
READ (*,*) K0
WRITE(*,*) 'ENTER TK0, K1'
READ (*,*) TK0,K1
WRITE(*,*) 'ENTER TK1, K2'
READ (*,*) TK1,K2
WRITE(*,*) 'ENTER TK2, K3'
READ (*,*) TK2,K3
WRITE(*,*) 'ENTER TK3, K4'
READ (*,*) TK3,K4
WRITE(5,'(5E15.5)') 0.0,TK0/3600,TK1/3600,TK2/3600,TK3/3600
WRITE(5,'(5E15.5)') CH,TK0/3600,TK1/3600,TK2/3600,TK3/3600
Q=1.0D-7
Q1=4.0D-8
C *****
C   INITIALIZATION
C *****
C
VTOT=0.0D0
C=0D0
F0=0D0
C0=0D0
T1=0D0
T2=0D0
TT1=0d0
TT2=0d0
OLDTT1=0D0

```

```

K=K0
DELTA=36
J=0
TLOAD=0.0 - DELTA
TUNLOAD=0.0 - DELTA
VLOAD=0.0
FLAG='LOAD'
C *****
C PROGRAM STARTS, TOTAL TIME 100 HOURS
C *****
DO 10 T=0,36E4,DELTA
  J=J+1
  IF(J.GT.10) J=J-10
  RESET='OF'
  IF(T.EQ.4320) THEN
    T2=T-DELTA
    T1=T-DELTA
    F0=C
    C0=C
    V0=V0+(TT1-TT2)*Q
    VLOAD=VLOAD+(TT1-TT2)*Q
    TT2=TT1
    Q=Q1
  ENDIF
  IF(T.EQ.TK0) THEN
    WRITE(*,*) K1
    K=K1
    RESET='ON'
  ENDIF
  IF(T.EQ.TK1) THEN
    WRITE(*,*) K2
    K=K2

```

```

    RESET='ON'
ENDIF
IF(T.EQ.TK2) THEN
    WRITE(*,*) K3
    K=K3
    RESET='ON'
ENDIF
IF(T.EQ.TK3) THEN
    K=K4
    WRITE(*,*) K4
    RESET='ON'
ENDIF
IF(RESET.EQ.'ON') THEN
C
C   RESET EVERYTHING WHEN THE CONSTANT CHANGES
C
    T2=T-DELTA
    T1=T-DELTA
    F0=C
    C0=C
    IF(FLAG.EQ.'LOAD') THEN
        V0=V0+(TT1-TT2)*Q
        VLOAD=VLOAD+(TT1-TT2)*Q
        TT2=TT1
    ENDIF
ENDIF
IF (FLAG.EQ.'LOAD') GOTO 1
IF (FLAG.EQ.'UNLO') GOTO 2
C--TT2:ABSOLUTE TIME LOAD BEGINS
C--TT1:ABSOLUTE TIME UNLOAD BEGINS
C.LOAD
1   C=F2(T-T2,K,F0,V0,Q)

```

```

C   CLL=CL*0.9
C   IF (T.GT.182000.AND.C.LT.CLL) GOTO 999
TLOAD=TLOAD+DELTA
IF(J.EQ.1) WRITE(1,*) T/3600,C
C0=C
T1=T
TT1=T
IF(C.GT.CH) THEN
  FLAG='UNLO'
  V0=V0+(TT1-TT2)*Q
  VLOAD=VLOAD+(TT1-TT2)*Q
  VTOT=VTOT+VLOAD*1.0D3
  TCYCLE=TLOAD+TUNLOAD
  AFR = VLOAD*3600*1.0D6/TCYCLE
  WRITE(2,901) T,TLOAD,VLOAD,AFR
  WRITE(3,'(2E15.6/2E15.6)') OLDDTT1/3600,AFR,T/3600,AFR
  OLDDTT1=T
  TUNLOAD=0.0 - DELTA
ENDIF
GOTO 10
C.UNLOAD
2   C=F1(T-T1,K,C0)
TUNLOAD=TUNLOAD+DELTA
IF(J.EQ.1) WRITE(1,*) T/3600,C
F0=C
T2=T
TT2=T
IF(C.LT.CL) THEN
  FLAG='LOAD'
  WRITE(2,902) T,TUNLOAD
  VLOAD=0.0D0
  TLOAD=0.0 - DELTA

```

```
    ENDIF
10  CONTINUE
    WRITE(2,*)
    WRITE(2,*) 'TOTAL VOLUME FED =',VTOT
901  FORMAT(' begin NO-feed cycle=',f9.0,' FEEDING time was=',f9.0/
*      ' volume fed=',1pe15.6,' Average feeding rate =',1pe15.6)
902  FORMAT(' begin feed cycle...=',f9.0,' no-feeding time was=',f9.0)
    GOTO 1000
999  WRITE (*,*) 'Problems'
    STOP
1000 END
```

## VITA

*Ana Maria Marengo de Barbero* was born in Rio Cuarto, Cordoba, Republica Argentina. She graduate from "F.M. Esquiú" High School, first in the class of 1979. From 1980 to 1986 she attended the National University of Rio Cuarto. In June 23, 1986 she presented her thesis "*Design of an Egg Solids Production Plant*" to the College of Engineering and obtained her degree in Chemical Engineering, with a minor in Food Science and Technology, graduating first in the class of 1986. After graduation she worked as a Junior Engineer at a private company designing chemical equipment for the food processing industry. She was also involved in continuing education, attending courses in the area of Industrial Cost Management. She married Ever Jose Barbero in April, 1985. In March 1988 she enrolled at Virginia Polytechnic Institute and State University for a Master of Science degree in Chemical Engineering. In June 1989 she was awarded with the Cunningham Master's Summer Thesis Fellowship for the completion of her thesis, "*Process and Reactor Design Study of Lignin Propozylation*". She moved to Morgantown, West Virginia in October 1989, where his husband became a professor in Mechanical Engineering at West Virginia University. On January 1990 their first son, Daniel, was born. She is planning to join the West Virginia University as a research associate.

A handwritten signature in cursive script, reading "Ana M. Barbero". The signature is written in black ink and is positioned at the bottom right of the page.