

Figure 17. A flow diagram for the slurry reactor.

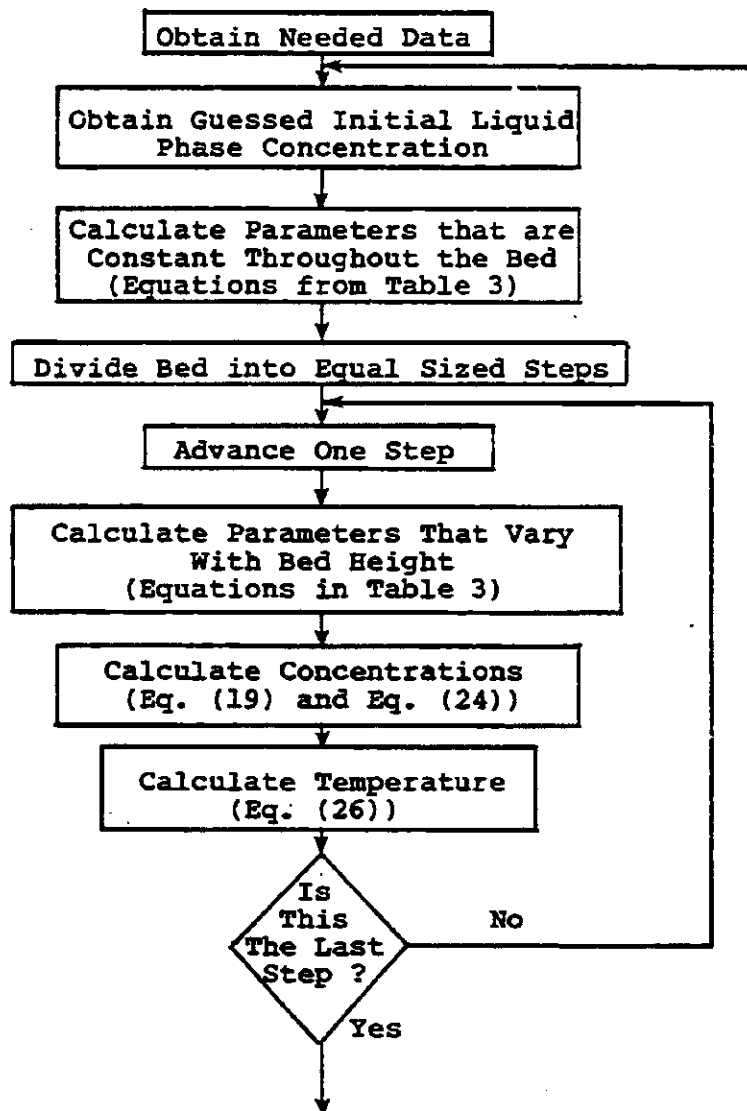
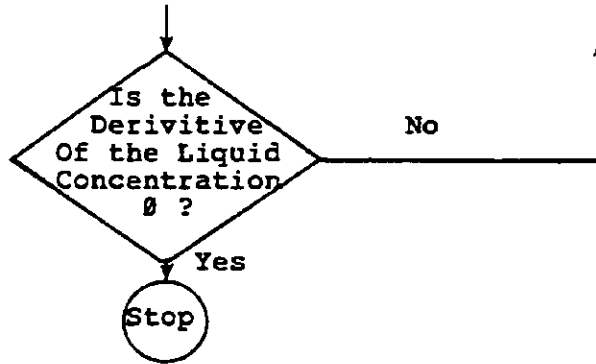


Figure 17. cont.



distributor plate was modeled using the correlation presented by Zhang and Ouyang. (1985)

Scrubber. In the scrubber the hot, dirty gas is passed through a water spray. The gas is cooled by the water and the tars and solids suspended in the gas stream are removed. Thus the major considerations of the model are the temperature change and the composition change that occur. The equations were developed assuming that the water and gas reached equilibrium. At higher gas velocities the validity of this assumption is likely to be doubtful, however for the purposes of the model the assumption was sufficiently accurate. Two other major assumptions were made in the development of the model. The gas was assumed to behave like an ideal gas and the volume change of the gas was entirely due to the temperature change and not to any composition change.

#### Staged Unit Configuration.

The configuration of the staged unit must meet several requirements. First, the gas flow must proceed from the pyrolyzer to the scrubber to the Fischer-Tropsch reactor. The gas flow from the combustor can not be mixed with the general gas flow. Second, it must be possible to

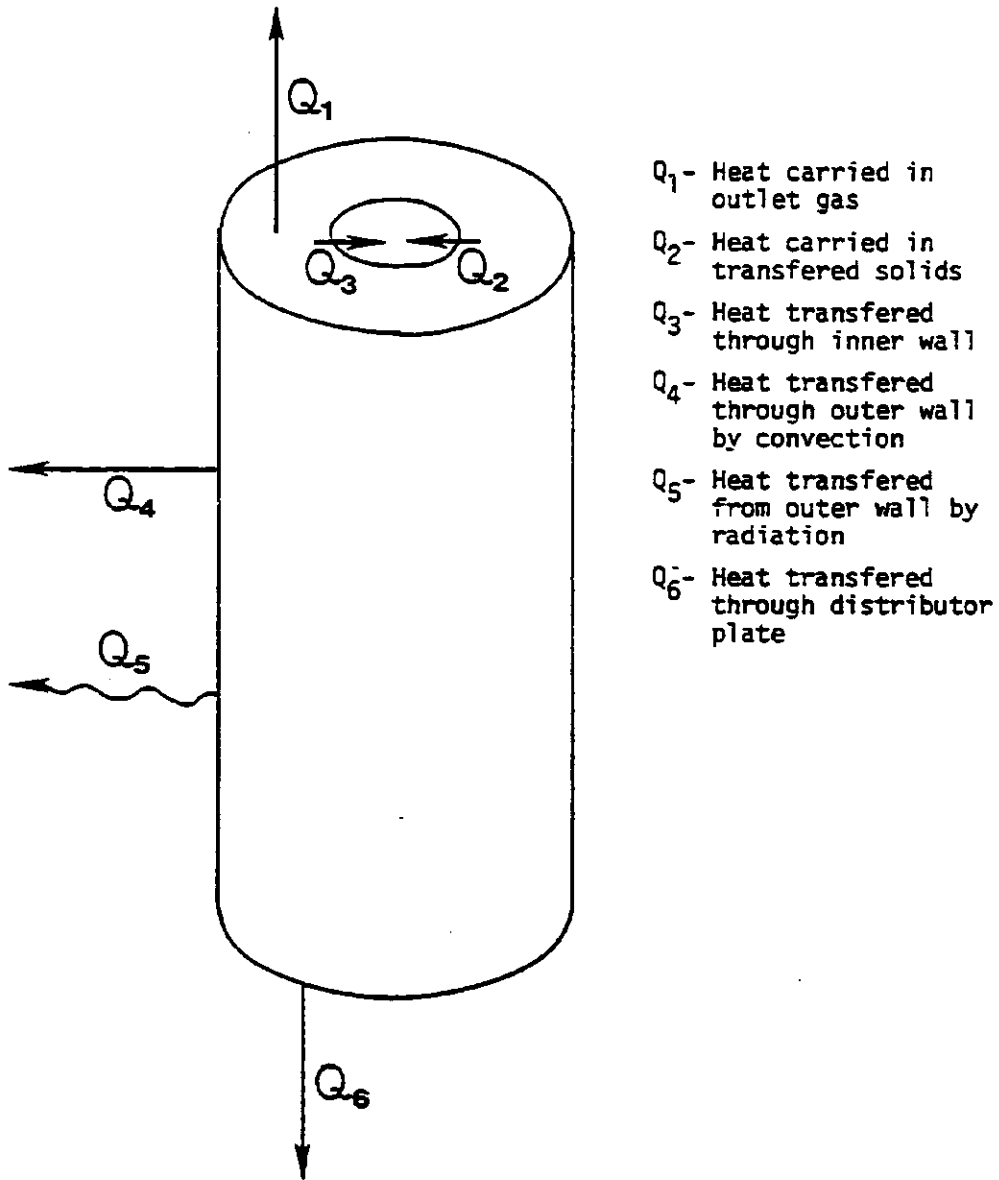


Figure 18. Modes of heat loss from the combustor.

circulate solids between the combustor and the pyrolyzer. Third, there must be efficient heat transfer from the combustor to the pyrolyzer.

The flow order requirement is reasonably easy to satisfy by placing the reactors one atop the other. It has been found, however, that the operation of fluidized beds in series is difficult. The placement of the combustor is the greatest challenge in developing the configuration of the system. Three possible configurations are shown in Figure 19. The side by side configuration shown in Figure 19(a) is used in the current indirect liquefaction system. Using it in the staged reactor would limit the amount of improvement that the staged reactor would be capable of achieving. The main problem associated with the configuration is poor heat transfer from the combustor to the pyrolyzer.

Figure 19(b) shows the combustor below the pyrolyzer. Once again the heat transfer is inefficient. In addition, there will be difficulty separating the gas flow from the combustor from that of the pyrolyzer.

Figure 19(c) shows the combustor and pyrolyzer in a concentric configuration. This arrangement has much better heat transfer characteristics than either of the other configurations. It also has the advantage of being a simpler system. However, it has the potential of being

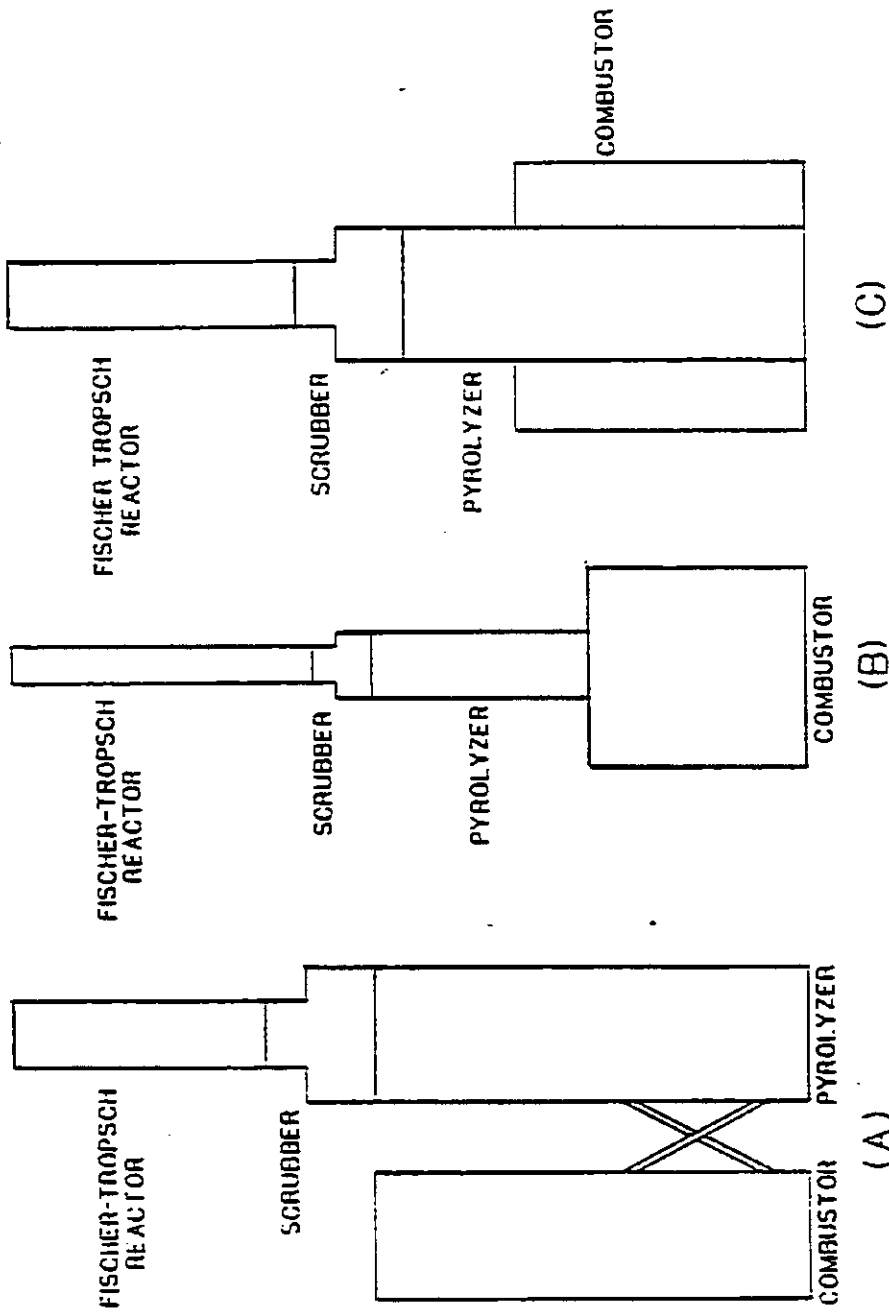


Figure 19. Three possible staged unit configurations.

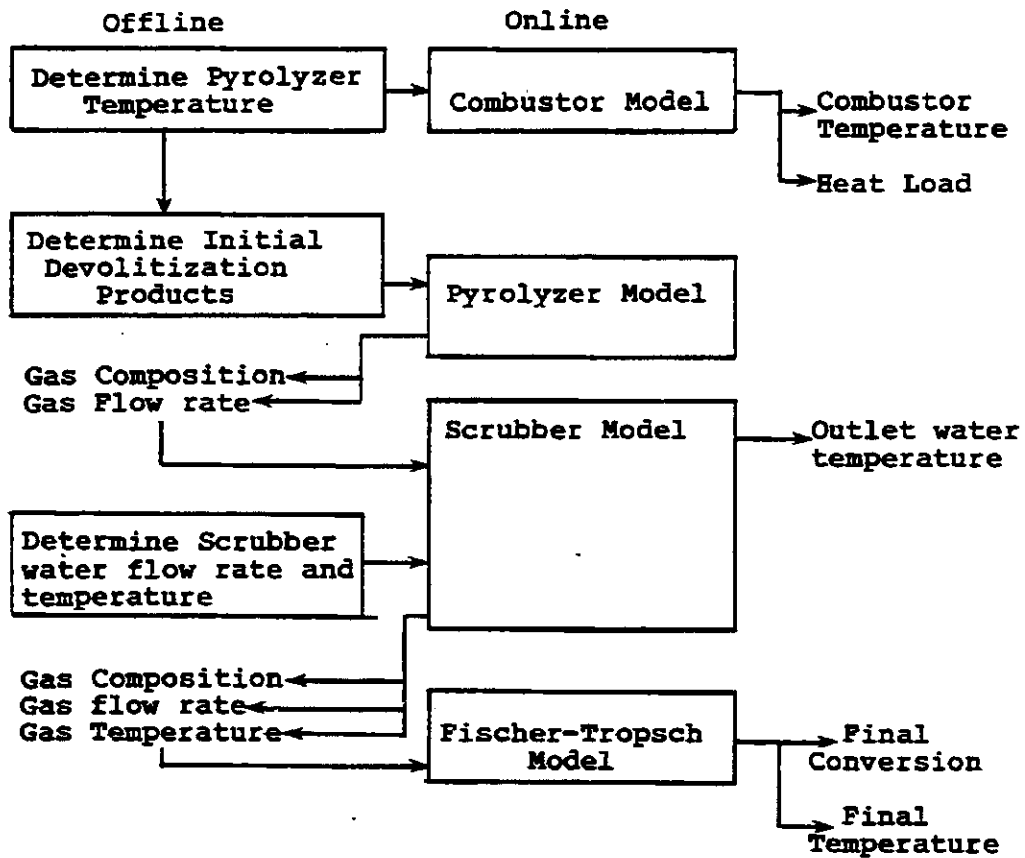
hard to operate and may present difficulties in trying to keep the gas flow from the combustor separate from that of the pyrolyzer. Studies on similar systems indicate that these problems may be overcome. (Kuramoto et al., 1982) Thus the concentric configuration was chosen for testing.

Once the overall configuration was determined a strategy for operating the models to simulate the complete system could be developed. Figure 20 shows the overall flow diagram. The control of each component model was handled off line to maintain flexibility in modeling different configurations.

## KINETICS

The reactions occurring in the pyrolysis reactor and the Fischer-Tropsch reactor are actually combinations of a large number of interrelated reactions. Obtaining useful kinetic expressions is not a simple task. Fortunately there has been considerable work on both reaction systems. The studies have made considerable progress in obtaining useful kinetic expressions. However, researchers have yet to obtain a generally accepted expression for either reaction.

Figure 20. A flow diagram for the staged reactor model.





### Pyrolysis

Biomass is composed of long chain oxygenated hydrocarbons and water. When it is subjected to heat the water is driven off and the hydrocarbons break down to form shorter chains. It is generally accepted that the pyrolysis occurs in stages. (Raman et al., 1980)

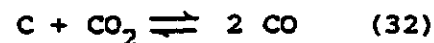
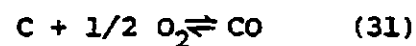
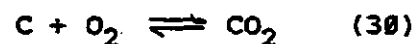
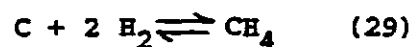
The first stage consists of the devolatilization of the biomass. Biomass contains many compounds that have low vaporization pressures as well as loosely bonded compounds that easily break down to form volatile substances. These volatiles are driven off with the water in this first step. Devolatilization leaves the heavier tars, and char behind. The relative amount of volatile material in biomass can vary depending on the characteristics of the biomass. In general biomass contains around 70 percent volatile material. (Bungay, 1981) Biomass like peat and sludge produce less volatiles and more char while leaves and straw produce much more volatile material and less char.

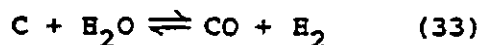
The effects stemming from the operating conditions at which the pyrolysis is carried out are as important to the initial product split as the type of biomass used. Higher temperatures and higher heating rates decrease the amount of char produced. (Cullis et al., 1983) It is possible to obtain as little as 5 percent char. Lower

temperatures and high pressures tend to cause the reaction to favor the production of tar and char. Thus for systems that require the production of synthesis gas it is best to operate at low pressures and high temperatures and use high heating rates.

Immediately after the initial devolatilization each of the groups of compounds begins to react further to produce secondary products. The initial devolatilization occurs very rapidly, often in less than 0.5 s. (Raman et al., 1980) The secondary reactions are considerably slower. Thus, in modeling, these secondary reactions are of interest.

The char reacts with gases formed by the initial devolatilization and the gases introduced to fluidize the bed. It has been found that the following reactions predominate: (Shariat, 1984)



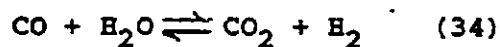


The last reactions is one of the principle reasons for the addition if steam to the reactor. In systems that produce significant amounts of char, these reactions act to convert the char into gases. Since char is generally considered waste these reactions serve to increase the efficiency of the reactor.

The tars are cracked to form shorter chain hydrocarbons. Most studies on the effects of catalysts on the pyrolysis of biomass have focused on catalyzing these reactions. These reactions proceed rapidly, though not as fast as the initial devolatilization. (Shariat, 1984) These are the most complex reactions and correspondingly the least well understood. The products of these reactions have been examined by Lipska and Wodely. (1969)

The reactions between the gases formed both by the secondary reactions of tars and char and the initial devolatilization are of principle interest in this project. The heating rates and use of steam as the fluidizing gas in the indirect liquefaction system insure that only very small amounts of char are formed. The tars that are formed react swiftly until there is only an insignificant amount left. The gas phase reactions are slow enough of be of

concern. The main reaction occurring is : (Raman et al., 1981)



the water gas shift reaction. The rate constants for this reaction have been determined by Raman et al. (1981) to be 94.56 ml<sup>2</sup>/mole-s for the forward reaction and 94.11 ml<sup>2</sup>/mole-s for the reverse. The final rate expression used in the model of the pyrolyzer is thus :

$$r = 94.56 * (C_{\text{CO}})(C_{\text{H}_2\text{O}}) - 94.11(C_{\text{CO}_2})(C_{\text{H}_2}) \quad (35)$$

#### Fischer-Tropsch Reactions

The Fischer-Tropsch reactions have been studied for several decades. Among the most important of the recent work done on the system is that of Deckwer et al., (1982) Satterfield et al., (1985) and Stern et al. (1985) Basically the mechanisms involve carbon monoxide being adsorbed onto active sites on the catalyst to form an activated carbon. This carbon then reacts with hydrogen or other carbon chains to produce a longer chain. The rate limiting step appears to be the reaction of the hydrogen

with the carbon which basically serves as the terminating step in the chain formation.

The mechanisms are too involved to allow a direct Langmuir (Froment and Bischoff, 1979) type approach. However, Lu (1985) was able to obtain an effective expression using a simplified mechanistic scheme. The rate expression he found to most effective for the catalysts used at ASU is

$$r = \frac{a e^{-E/RT} k_{H_2} k_{C_2H_4} k_{CO}^2 P_{H_2}^2 P_{C_2H_4} P_{CO}}{(1 + k_{H_2} P_{H_2} + k_{C_2H_4} P_{C_2H_4} + k_{CO} P_{CO} + k_{C_2H_6} P_{C_2H_6} + k_{CH_4} P_{CH_4} + k_{CO_2} P_{CO_2})^3} \frac{1}{(1 + (k_{H_2} P_{H_2})^{1/2} + (k_{CO} P_{CO})^{1/2})^3} \quad (36)$$

Ledakowicz et.al. (1985) have determined a similar expression for potassium promoted iron catalysts. Their expression is

$$-r_{CO + H_2} =$$

$$\frac{K C_{H_2}}{1 + \frac{k_{H_2O}}{k_{CO}} \frac{C_{H_2O}}{C_{CO}} + \frac{k_{CO_2}}{k_{CO}} \frac{C_{CO_2}}{C_{CO}}} \quad (37)$$

Deckwer et.al. (1982) used a simplified rate expression that depends on the hydrogen concentration of the feed gas only. The rate expression is first order in hydrogen. The rate constant proposed by Deckwer is dependant on the reactor temperature. At 300°C it is 0.00545 (s % catalyst in slurry)<sup>-1</sup> Deckwer uses a term called the usage factor to relate the hydrogen consumption to the consumption of other feed compounds. This factor varies slightly with reactor conditions and catalyst used and has a value of 1.5.

The majority of the rate expressions that have been developed for the Fischer-Tropsch reaction focus on the rate at which feed material is used up to avoid the complexity of predicting the product composition. The researchers make use of some technique such as the Schultz-Flory distribution in order to predict the product character.

Stern et. al. developed kinetic expressions that predict the C/H ratio of the products based on the rate of chain growth. Stern's expression is the most complex of the group. It has only been used in conjunction with iron

catalysts but it has provisions for being adapted to other catalysts.

The expression developed by Deckwer was chosen to represent the Fischer-Tropsch kinetics in the model of the staged reactor. The expression was the simplest and thus the best suited for use in combination with a sophisticated fluid dynamic model. A more complex kinetic expression would greatly increase the difficulty in solving the system of equations without correspondingly increasing the accuracy of the model since most of the error stems from the simplifications required to produce a fluid dynamic model of the system.

## EXPERIMENTAL PROCEDURES AND APPARATUS

### MODEL PARAMETER STUDIES

The computer models of each section of the reactor were developed and tested using data from the current indirect liquefaction reactor system and data reported in the literature. Table 4 shows the results obtained from the fluidized bed pyrolysis model and the actual results obtained from the current pyrolysis reactor operated at 790°C and 1 atm. with a steam to biomass feed ratio of 2. (Prasad, 1986) Wang's study of the fluidized bed Fischer-Tropsch reactor found that 90 % of the hydrogen in the inlet stream was used up by the time the gas exited a 150 cm bed. (Wang, 1980) The fluidized bed Fischer-Tropsch model predicts that 87 % would be used. The scrubber and combustor models could not be checked against the current system because inadequate data from the current system is available. Appendix B contains listings of the programs used to simulate each portion of the reactor.

After the models had been checked against the current indirect liquefaction system they were used to generate data needed to produce a design for the plastic flow simulator. The critical dimensions that the models



Table 4. A comparison of predicted and experimental concentrations in the pyrolysis product gas stream.

Gas	Predicted Concentration, (moles/liter)	Actual Concentration, (moles/liter)
H <sub>2</sub>	0.0889	0.0443
CO	0.0909	0.0765
CO <sub>2</sub>	0.0414	0.0470
CH <sub>4</sub>	0.0342	0.0354
C <sub>2</sub> H <sub>4</sub>	0.0478	0.0153

were used to determine were the height of each reactor and the diameter of the combustor. Appendix A contains a full description of the criteria used to produce all of the critical dimensions for the simulator.

The sensitivity of the models to changes in various parameters was then examined. All key input parameters as well as several important internally generated parameters were examined. Each parameter was tested independently rather than using a factorial approach since the models were easy to run and the results of single variable experiments are easier to visualize.

## SIMULATOR STUDIES

### Simulator Description

The cold flow simulator was constructed using an acrylic whose trade name is plexiglass. Both preformed tubing and sheets of plexiglass were used. The rationale for the reactor sizing is presented in Appendix A. The initial design was subjected to several modifications that were prompted by experience gained from operating the simulator. Figure 21 shows the initial and final reactor designs.

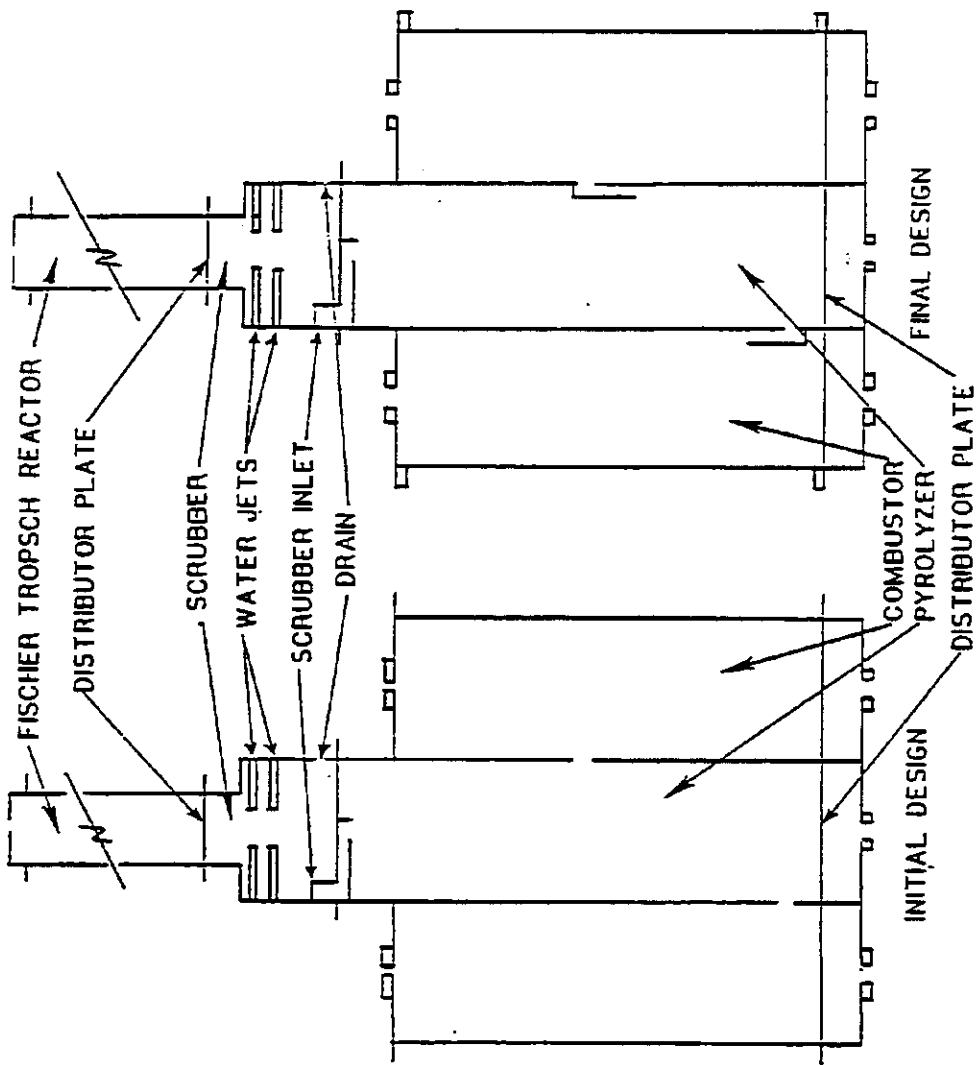


Figure 21. The initial and final simulator designs used.

The bottom head is made of 0.64 cm (1/4 in.) thick plexiglass. It has three gas inlets, two in the section providing air to the combustor and one in the section feeding the pyrolyzer. The flange consists of a single 0.64 cm (1/4 in.) sheet. The distributor plate is made of 0.32 cm (1/8 in.) aluminum sheet. The layout of the orifices is shown in Figure 22. Each orifice consists of a single threaded central hole with two small extensions on either side. A bolt with a star washer is inserted into each hole. This promotes radial flow along the distributor plate and eliminates the chance of dead zones forming between holes. The details of the hole construction and the expected air flow patterns are shown in Figure 23. The plate makes use of two sizes of orifices in order to insure a desirable solids circulation pattern. The pattern that the plate was designed to produce is shown in Figure 24. The ratio of open area to total plate area is 0.011 for the combustor and 0.014 for the pyrolyzer.

The combustor/pyrolyzer stage was made of two concentric tubes of 0.64 cm (1/4 in) plexiglass. The upper and lower flanges were 1.91 cm (3/4 in) thick, consisting of a 0.64 cm (1/4 in.) flange attached to a 1.27 cm (1/2 in.) flange. The extra thickness was used to resist the torque that was placed on the joint between the flange and the reactor when moderate pressures is applied to the