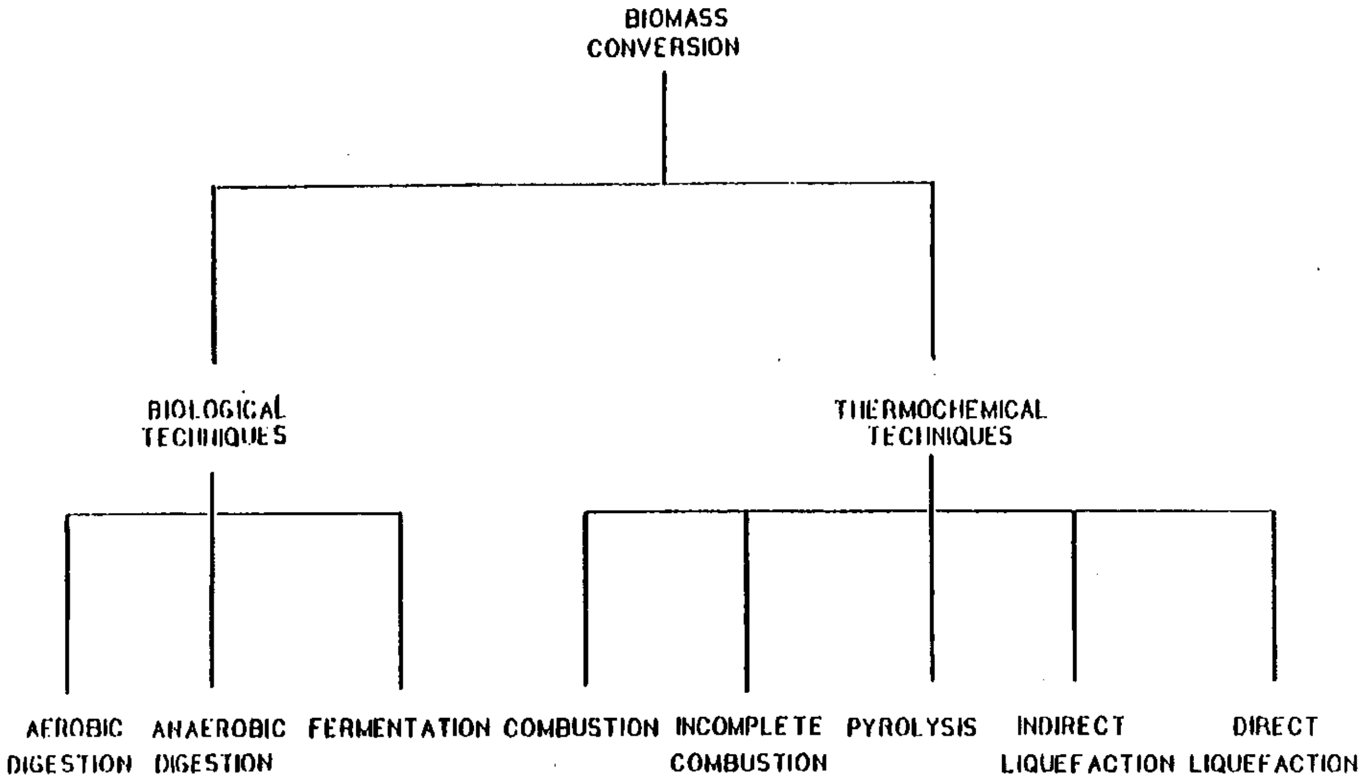

Figure 1. The general approaches to biomass conversion.

in order to convert the biomass into useful products. These techniques have the advantage of being much more flexible than biological processes. By careful manipulation of the temperature, pressure, and catalysts used, a wide range of products can be produced. It is possible to use thermochemical processes to produce materials that are completely interchangeable with currently available fuels. In addition, thermochemical techniques are much less sensitive to the type of biomass used than are biological techniques.

A reactor system using the thermochemical process of indirect liquefaction has been developed at Arizona State University under the direction of Dr. James Kuester. The technique makes use of two distinct steps in order to produce a liquid fuel. In the first step, biomass is pyrolyzed to produce a synthesis gas consisting of carbon monoxide, methane, carbon dioxide, hydrogen and water vapor. This gas is then introduced into a reactor that makes use of the Fischer-Tropsch synthesis in order to produce a liquid product. The product liquid is composed of an organic phase containing a mixture of long chain hydrocarbons very similar to diesel fuel or jet fuel and an aqueous phase consisting of water and various alcohols. (Wang, 1980) It is the organic phase that is of principle interest.

The system that currently implements this reaction scheme consists of three reactors as shown in Figure 2. The biomass is dried and ground into a coarse powder before being placed in the pressurized feeder. The feeder introduces the biomass into the pyrolyzer near the bottom of the fluidized bed. The biomass is very quickly gasified. The pyrolyzer consists of a bed of alumina particles fluidized by superheated steam. The reactor operates at about 700 °C and 1 atm. The steam serves not only to fluidize the bed but also shifts the reactions between the product gases so that more hydrogen and carbon monoxide are produced at the expense of methane and carbon dioxide and reacts with the small amount of ash formed to produce gaseous products. Oxygen is excluded from the pyrolyzer in order to limit the formation of oxidized species.

The second reactor in the system is the combustor. Since oxygen and oxidized species must be excluded from the pyrolyzer, the burners that provide the heat necessary to maintain the system's temperature are located in the combustor. Propane and oxygen are burned in order to provide the heat. The combustor contains a bed of fluidized particles that are identical to those in the pyrolyzer. The particles are circulated from one bed to the other in order to transfer heat from the combustor to the pyrolyzer where it is needed. Although solids are

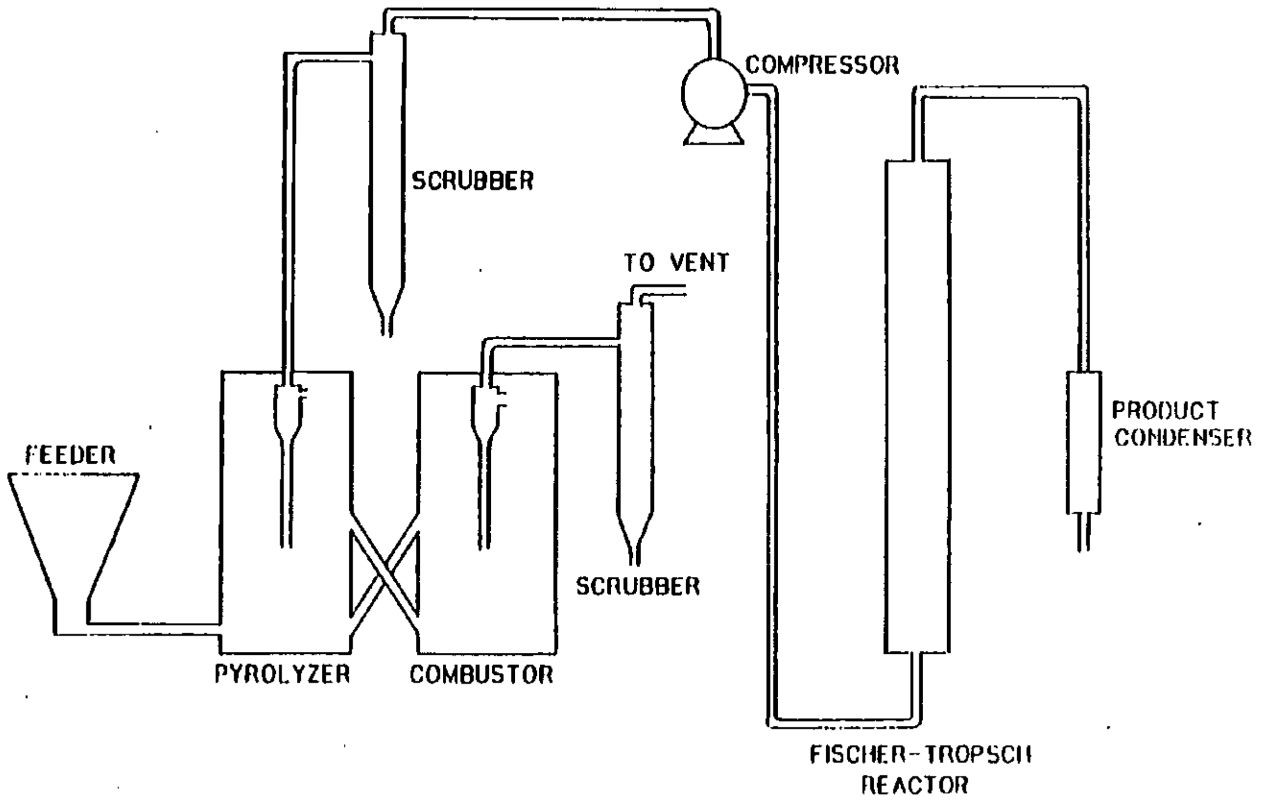

Figure 2. The current indirect liquefaction system at Arizona State University.

transferred from one reactor to the other, the pressures are maintained in such a way that there is never any transfer of gas. The exhaust gas from the combustor is cleaned and vented to the atmosphere.

After leaving the pyrolyzer, the synthesis gas is scrubbed and filtered to remove tars and solid particles from the stream. The clean gas is compressed to about 10 atm. and injected into the third reactor. The third reactor is filled with a Fischer-Tropsch catalyst. Generally this catalyst is a transition metal supported on an inert solid. The system developed at ASU is effective using cobalt supported on alumina.(Wang, 1980) The reactor consists of either a packed bed, a fluidized bed, or a slurry. The fluidized bed and slurry reactors have proven the most effective due to their ability to transfer the large amount of heat produced by the Fischer-Tropsch synthesis away from the reactive sites thus preventing catalyst deactivation. The slurry reactor consists of a liquid in which the catalyst support is suspended. The slurry reactor can be operated over a wider range of flow conditions than the fluidized bed but does not have the close contact between the reactant gases and the catalyst. The reactor operates at 300°C and 10 atm. The products leave the reactor as vapors which are condensed in a trap cooled by chilled water and ice to 0°C.

Modification of the current system could improve the efficiency of the conversion process. An increase in effecincy would in turn make a smaller reactor feasible. This is important because biomass is expensive to ship the distances that would be required to provide sufficient quantities to operate a large plant in most regions of the country.

The first step in increasing the efficiency of the the process would be to resize all the reactors and reset all the flows involved. The reactors in the current system were all sized independently and are consequently not optimally sized for integrated operation. The second step, would be to examine the overall configuration of the system and attempt to eliminate as much of the pumping and plumbing as is possible. These two steps could produce a reactor that is more efficient than the current system.

Many of the configurational problems of the current system could be eliminated by the combination of the three reactors into a single staged unit. A staged unit would be simpler than the current system but would have to operate at a single pressure. This is a disadvantage because pyrolysis produces the most desirable products at low pressures while the Fischer-Tropsch reactor produces the most desirable products at high pressures. Recent studies, however, have indicated that it is possible to operate pyrolysis reactors at elevated pressures.(Beck and Wang, 1980) At the same time there has been work that indicates that it may not be necessary to perform the Fischer-Tropsch synthesis at 10 atm.(Dry, 1976) In this light, it seems likely that a staged reactor would be possible to construct and operate. The staged reactor would not only be smaller and more efficient than the current system, it would also be more portable. A small, portable reactor can be moved to locations where stockpiles of biomass have been accumulated. The reactor could then process the biomass until it has used up the stockpile. Once the store has been depleted the reactor would be moved to another site. The advantages of this type of reactor system have prompted several different research efforts.

In order to design a new staged system, it is first necessary to develop mathematical models of the processes involved. These models can be used to predict the performance of the reactor under various operating conditions. Since the final reactor configuration may vary considerably from the current reactor, the models must be based, as much as is feasible, on fundamental phenomena.

Fluidized bed and slurry reactors are very difficult to model accurately. Many of the small scale phenomena that occur must be predicted by empirical correlations. In addition, the details involved in the construction and operation of fluidized bed reactors are impossible to predict at all. Thus it is inappropriate to use only mathematical models to design the reactor system. A cold flow simulator of the reactor must also be used. The simulator used in the design of the staged unit was a full scale simulator made out of transparent acrylics. The mathematical models were used to predict the size of the simulator. The simulator was used in turn to revise the models and to locate weaknesses and oversights in the design.

Once the simulator and the models behaved satisfactorily a final reactor design was produced. The reactor was not actually built in conjunction with this research effort since the selection of proper catalysts would be beyond the scope involved.

# THEORY

There are two major areas that must be considered in conjunction with the design of a staged reactor system. They are the fluid dynamic characteristics of the reactors and the chemical characteristics of the reactions involved. In the design of a staged indirect liquefaction reactor, both areas present considerable complexities. The fluid dynamics of gases in a fluidized bed or a slurry reactor depend on a number of factors some of which are not easy to measure. Thus, it is necessary to resort to correlations in order to describe some parameters. However, both reactor types have been subjected to a large amount of research. Due to this research, much of the behavior of the two reactor types has been either explained or accurately correlated. The kinetics of the reactions involved are considerably less well understood. The difficulty of obtaining measurements as well as the complexity of the reacting systems have made the study of the reactions extremely difficult. There has been enough research, however, to obtain kinetic expressions that can be used in rough models.

# FLUID DYNAMICS

## Fluidized Beds

Behavior. A fluidized bed consists of a fluid moving up through a bed of solid particles at such a rate that the drag force exerted on the particles by the fluid is sufficient to offset the force of gravity on the particles. As a result, the particles are lifted apart. The bed then takes on many of the characteristics of a fluid with small local variations in the flow pattern causing the particles to move about in the bed in a random manner. This homogenous bed is said to be in particulate fluidization. Particulate fluidization is usually encountered only in a narrow range of flow rates just above the minimum flow rate required to fluidize the bed. However if the density of the fluid moving up through the bed approaches that of the particles, particulate fluidization can be found in a much wider range of gas velocities.

As the fluid flow rate is increased beyond the rate where particulate fluidization occurs, a new phenomena is observed. The bed loses its homogeneity as areas that are relatively free solid particles form. These areas rise through the bed much like bubbles rise through a liquid. Generally the voids are called "bubbles" but the term must be applied with caution. As will be discussed later, there are some very fundamental differences between real bubbles and the voids in a fluidized bed. Figure 3 shows the behavior of a bed of solid particles as the flow rate of the fluid is increased.

It is possible to predict which type of fluidization will predominate in a given system. Geldart (Cheremisinoff and Cheremisinoff, 1984) developed a method for making these types of predictions. His technique is generally accepted throughout the literature. The method is based on the graph shown in Figure 4. This graph groups potential fluidized systems into four categories. Category A systems exhibit extensive regions of particulate fluidization before aggregate fluidization is encountered. Category B consists of systems where the primary form of fluidization encountered is aggregate fluidization. Category C consists of those systems where particle to particle interactions are significant. These systems are extremely difficult to fluidize. Category D systems can not be fluidized. The particles are too large. Generally beds of this type exhibit such phenomena as by-passing and spouting where the flow is directed mainly through a small portion of the bed.

The behavior of fluidized beds has been subjected to many comprehensive studies. Cheremisinoff and Cheremisinoff (1984), Kunii and Levenspiel (1977), and

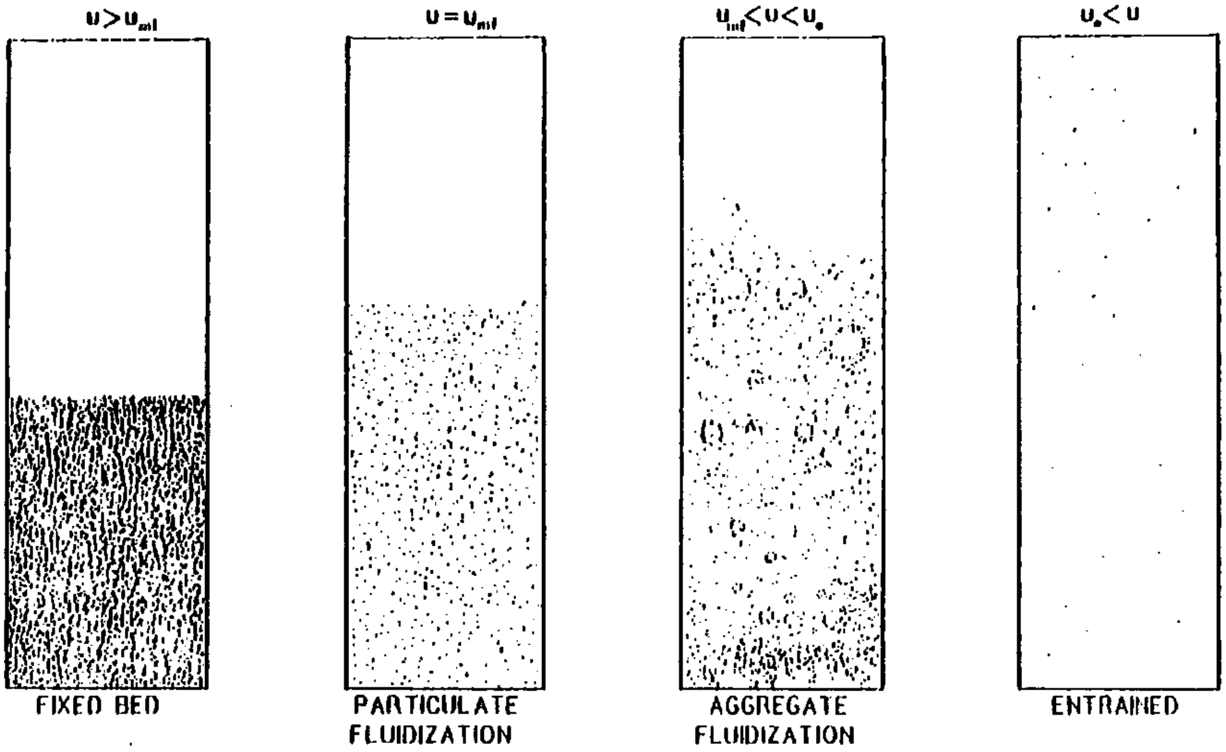

Figure 3. The behavior of a bed of particles with a gas flowing through it at an increasing rate.

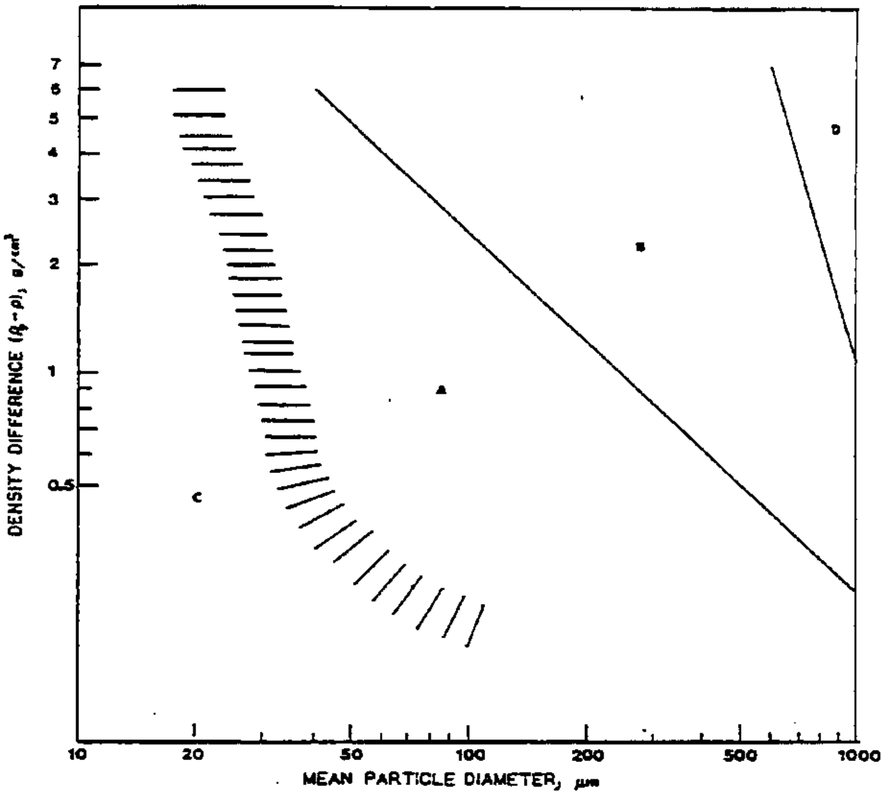

Figure 4. Geldart's classification of fluidized systems.

Davidson and Harrison (1982) have published extensive reviews of the material available on the subject of fluidized beds. Due to the extensive interest in fluidized beds, all the major phenomena that occur in them have been observed by one researcher or another. It is possible to obtain a good qualitative idea of how fluidized beds behave.

As gas is introduced into a fluidized bed the component that it encounters first is the distributor plate. This plate is designed to support the bed and distribute the flow of gas evenly over the cross-section of the reactor. Thus, it is usually metal pierced by holes of one type or another. The details of the distributor plate's construction play a key role in determining the character of the fluidized bed.(Fakhimi et al.,1983) The minimum requirement for the distributor plate is that the force required to push air through the plate be significantly larger than the force resisting the rearrangement of the gas flow. Richardson (1961) has developed an equation that predicts the ratio of the area of the holes to the area of distributor that is required to produce a large enough pressure drop across the plate to insure an even gas distribution.

Two types of distributor plates have been used. One is a porous or sintered metal plate. These plates have a large number of very small holes in them. They are ideal for smaller diameters but become too expensive and weak for larger beds. The second type uses a smaller number of larger holes. Usually some provision is made to insure that the solid particles can not enter these larger orifices. A number of different designs for these multiple orifice plates have been developed. (Fakhimi et al., 1983, Peng et al., 1985, Hsu, 1979) In the past, it has been assumed that an even initial distribution of the gas was the ideal to strive for. More recent studies have found that by designing a plate that induced an uneven initial distribution it is possible to over come the tendency of the bubbles to move toward the walls of the reactor and thus produce an even gas distribution higher in the bed. (Peng et al., 1985) An example of such a design is shown in Figure 5. Gas entering through the small holes will have a higher velocity than gas entering through the large holes. This will create a radial pressure gradient that will turn cause the flow to move toward the region with smaller holes. A diagram of the flow patterns produced is shown in Figure 6.

The behavior of the bed from this point on depends on whether the bed is experiencing particulate or aggregate fluidization. Since gas-solid systems are nearly always in the aggregate fluidization mode the examination of the

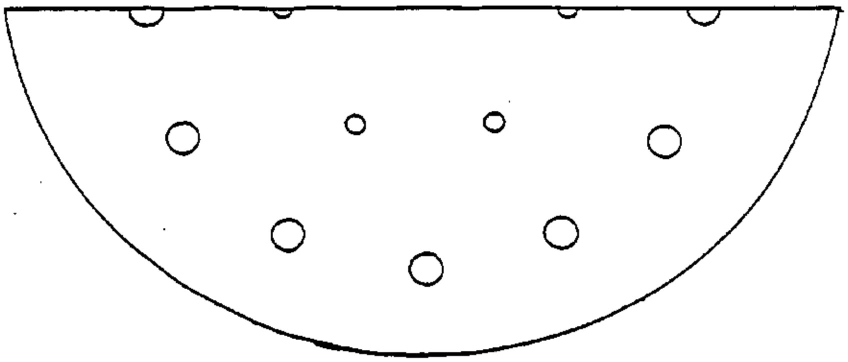

Figure 5. A distributor design that will produce an uneven gas flow.

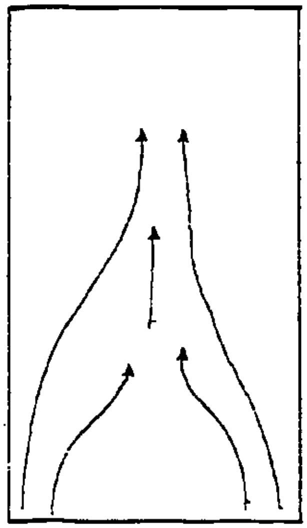

Figure 6. The gas flow pattern produced by a distributor plate with the pattern of holes shown in figure 5.

phenomena occurring in fluidized beds will focus on that type of fluidization.

Once the gas has passed the distributor plate, it encounters the bottom of the bed of solid particles. The gas tends to push the particles immediately around each orifice away to form elongated voids or jets extending up from the plate into the bed. (Cheremisinoff and Cheremisinoff, 1984) The region between the plate and the approximate end of these voids is called the jetting region and has different characteristics than the rest of the bed. Perhaps the most important difference is the lack of any gas circulation between the voids and the rest of the bed. The jetting region generally extends only 2 to 7 cm. into the bed. Figure 7 is a sketch of a typical jetting region. The figure is based on photographic and x-ray data from two-dimensional and three-dimensional beds. (Harrison et al., 1961,Massiimilla and Westwater, 1960)

At the top of the jetting region the ends of the elongated voids break off to form the "bubbles" that move up through the remainder of the bed. The main portion of the bed is characterized by the presence of two distinct, interacting "phases". The rising voids comprise one phase known as the "bubble" or "lean" phase and the rest of the bed comprises the second phase which is called the "emulsion" or "dense" phase. The emulsion phase contains

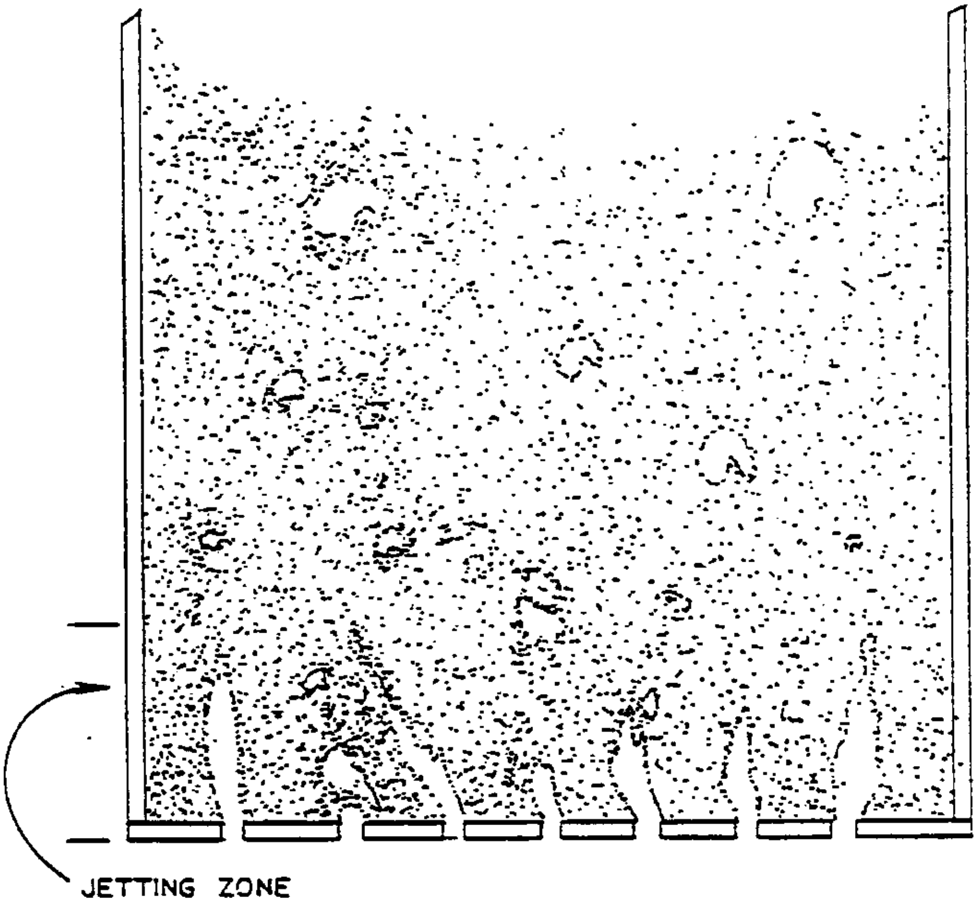

Figure 7. The jetting zone in a fluidized bed.

the bulk of the solid particles and a small gas flow. It is generally assumed that the gas flowing through this phase has a velocity relative to the solid particles that is independent of the total gas flow rate and equal to the minimum flow required to fluidize the bed. Experimental studies show that this assumption is probably true but are not conclusive. (Kunii and Levelspiel, 1977)

Any gas in excess of the minimum required to fluidize the bed is thus carried in the bubble phase. Like liquid bubbles, the voids that make up this phase are relatively free of the surrounding material and rise through the bed at a rate that increases with their size. As the voids in a fluidized bed rise, they both coalesce into larger voids and break down into smaller ones. In general, however, the rate of coalescence is greater than the rate of break up. The rates are related to the size of the bubbles so that in any given bed there exists some size where the rates are equal. This size is the maximum stable bubble size and is dependant on the conditions prevalent in the reactor. (Viswanathan, 1985)

As was mentioned earlier there are fundamental differences between the voids in a fluidized bed and the bubbles in a liquid. The most obvious difference is the shape of the voids. Figure 8 is a diagram of some typical voids. The voids can vary in shape much more than bubbles

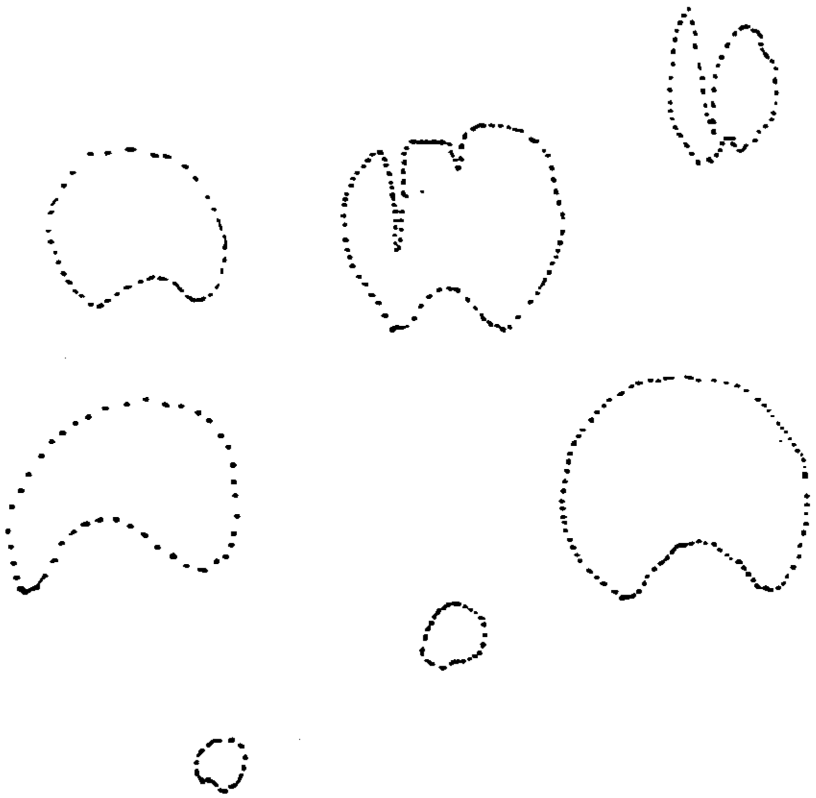

Figure 8. Some typical voids in a bed experiencing aggregate fluidization.