CHAPTER 1

INTRODUCTION

1.1 Motivation for the Thesis

1.1.1 Importance of bubble column reactors

Bubble columns, as a simple and relatively inexpensive means of achieving gas-liquid or gas-liquid-solid contact, are widely used for carrying out reactions and mass transfer operations, in which a gas or a mixture of gases is distributed at the bottom and rises up in the form of a dispersed phase of bubbles in a continuous liquid phase. In the liquid there can be suspended or fluidized, reactive or catalytic solids. Accordingly, the device is termed a two- or three-phase (slurry) bubble column.

Bubble column reactors have been used in chemical, pharmaceutical, biochemical and other processes for many years. Some examples of industrial applications of bubble column reactors are listed in Table 1.1 and Table 1.2 (Carrà and Morbidelli, 1987; Shah and Sharma, 1987; Deckwer, 1992). From the two tables, it can be seen how important bubble column reactors are for industrial processes.

In fact, a few decades ago, no great scientific interest was shown in bubble column reactors. Very little literature was forthcoming from either industries or universities (Chisti, 1989; Deckwer, 1992). However, since the mid-1970s, the research and development interest in various types of bubble columns has dramatically increased. This is mainly because:

- A general recognition of the advantages such as
    - Simple structure and thereby low equipment investment,
    - No mechanically moving parts and thereby no sealing problems,
    - Good heat and mass transfer properties,
    - High thermal stability.

- The opening up of new fields of applications, especially in biotechnological areas such as effluent treatment, single-cell protein production, animal cell culture and antibiotic fermentation (Chisti, 1989).

Table 1.1 Examples of industrial-scale processes in two-phase bubble columns (Carrà and Morbidelli, 1987; Deckwer, 1992)

Process	Main product
Oxidation of	
ethylene (partially)	Vinyl acetate (Acetaldehyde)
cumene	Cumene hydroperoxide
butane	Acetic acid, MEK
toluene	Benzoic acid
xylene	Phthalic acid
Wet oxidation of effluents	
Oxychlorination of ethylene	Dichloroethane
Chlorination of	
aliphatic hydrocarbons	Chloroparaffin
aromatic hydrocarbons	Chlorinated aromatics
Alkylation of	
methanol	Acetic acid
benzene	Ethylbenzene, cumene
Isobutene hydration	*tert*-butanol
Oxysulphonation of paraffins	Paraffin sulphonate

Table 1.2 Examples of industrial-scale processes in three-phase bubble columns (Shah and Sharma, 1987; Deckwer, 1992).

Process	Solids
Production of Al-alkyls	$Ca(HSO_3)_2$ as reactant
Coal hydrogenation	Coal particles
SO_2 removal from tail gas	CaO and $CaCO_3$
Wet oxidation of effluent sludge	Sludge
Biotechnological processes	Biomass as reactant
Production of single-cell protein	Cells as reactant
Animal cell culture	Cells as reactant
Effluent treatment	Particles as reactant
Polymerization of olefines	Polyolefines
Oxamide synthesis of HCN oxidation	Oxamide
Production of biomass	Biomass as product
Hydrogenation of oils	Catalyst
Coal hydrogenation	Catalyst
Synthesis of methanol	Catalyst
Fischer-Tropsch synthesis	Catalyst
Numerous oxidation and hydrogenation processes	Catalyst

- A revival of interest in coal liquefaction and slurry phase Fisher-Tropsch synthesis, both relying greatly on bubble column technology, resulting from the oil crisis of 1973 and the subsequent search for alternative raw materials and synthetic fuels. Bubble columns also play a role in the development of C_1 chemistry (Deckwer, 1992).

On the world scale, for most countries, the oil required is much greater than that having been found and the oil resources are becoming exhausted. Even Norway as a fairly oil-rich country, has the known oil reserves that will only last for about 30-40 years with the present production rate (Bredesen, 1989). Within the next 10-15 years, several larger producers outside OPEC may cease to export and become only self-sufficient (Roterud, *et al.*, 1990). Therefore, developing new oil substitutes is the major national strategy in many countries and also in Norway.

The Norwegian natural gas reserves are large, and at present they are about 50% of the known reserves of Western Europe and cover more than 80% of the new proven gas reserves. These reserves will last more than 120 years at the present production level (Bredesen, 1989). Therefore, a great national research program, the SPUNG program (State R&D Program for Utilization of Natural Gas), was started up by the Norwegian government in 1987. The Chemical Conversion of natural gas into liquid products like fuels or chemical feed stocks is the largest program in the SPUNG.

Many of the processes making oil substitutes from natural gas such as the Fisher-Tropsch synthesis step in the production of middle distillates from synthesis gas ($CO + H_2$), the methanol synthesis from synthesis gas and the coal liquefaction or coal hydrogenation processes all rely greatly on bubble column reactors. This is because the reactors have such advantages as mentioned above and also because CO-enriched synthesis gas ($H_2{:}CO$ = 0.6-0.7) can directly be used to the reactors. Using this composition, low cost and high thermal efficiency may be obtained for the Fisher-Tropsch synthesis (Shinnar and Kuo, 1978).

Norway is active in the research and development of these processes. For instance, a process for the production of middle distillates from natural gas, via synthesis gas, has be developed by STATOIL. One of the key steps is the conversion of the synthesis gas to wax in a Fisher-Tropsch reaction. This reaction takes place in a slurry bubble column where the Cobalt and Rhenium catalyst is suspended in the molten wax phase, and can give conversion levels of 95% per pass (Roterud, *et al.*, 1990).

A new low temperature and high conversion process for methanol from synthesis gas has been developed by SINTEF (Onsager *et al.*, 1989; Hansen, R., 1990). The methanol synthesis takes place in a slurry bubble column with a suspended Copper-Chromite catalyst. Because of the active catalyst and low temperature

(110-130 °C), high conversion levels per pass (>90%) can be achieved even with air based synthesis gas (high N_2 content).

Another new process for co-production of methanol and acetic acid from natural gas, via synthesis gas, has also been developed by SINTEF (Onsager and Andersen, 1990). The conversion of synthesis gas to methanol and methyl formate is achieved in a slurry bubble column reactor at temperature 90-140 °C and pressure 30-80 bar, where a heterogeneous copper-chromite catalyst and a homogeneous alkaline-earth-alcoxides catalyst are used. The conversion of CO is also > 90% per pass. 97% pure methyl formate is obtained from a fractional column and isomerized to acetic acid (Both conversion and selectivity > 99%).

The bubble column reactor technology is also important for China, since she is an oil-poor country, but new gas fields have been found in Xinjiang and in other areas of central and western China (Wang, 1993). Particularly, the technology of bubble column reactors for coal liquefaction processes may have a more significant effect on the economic development of China, since China has large coal resources (about 80 billion tons of reserves). Coal hydrogenation is the reaction of coal with hydrogen at high temperature and pressure. The finely milled dried coal is suspended with a catalyst in a suitable hydrocarbon oil and proceeds to react with hydrogen in a slurry bubble column reactor (Shah and Sharma, 1987). Various coal liquefaction projects have received governmental supports not only in oil-poor countries like the former West Germany, but also in the oil-rich countries like USA (Deckwer, 1992).

In the present age of biotechnology, bubble columns as bioreactors have the greatest potential and have widely been used (Schügerl *et al.*, 1977; Blenke, 1979; Chisti, 1989). An example is the biological effluent treatment plant operated by Hoechst where the reactor has 5 m diameter and 22 m effective height, and the treatment ability is about 2 ton BOD_5 per day (Leistner *et al.*, 1979). As another example, bubble columns have successfully been used for the production of single-cell protein (Sittig *et al.*, 1979; Westlake, 1986).

1.1.2 The importance of reactor modeling

The design or scale-up of bubble column reactors is one of the basic and common problems frequently occurring in practice. Earlier, one often resorted to completely empirical models, *e.g.* correlations obtained through dimensional analysis, for solving this kind of problems. These empirical methods are not only prodigal (time-consuming and need many steps of pilot-scale units), but also unreliable (*i.e.* as well known, a scale-up method using dimensional analysis fails in cases with chemical reactions). With increased knowledge about the phenomena governing multi-phase reactor systems, the empirical methods should and can, to a large extent, be avoided. However, the recognized level of understanding is still not sufficient to build completely theoretical models for such types of reactors. This is due to the complex fluid dynamic conditions prevailing and their sensitivity to material and fluid properties.

Thus, the realistic, reliable and economical way to solve such problems is through establishing suitable mathematical models on the basis of the theoretical knowledge recognized at the time. The so-called "suitability" of mathematical models implies that they must provide a practical description of what are the main processes or phenomena actually taking place, without having to represent exactly the real processes. Hence, they may be founded on a combination of experience and fundamental physical and chemical understanding as well as experimental results. Inside the models, there may exist one or more unknown constants that need to be determined by experiments, but should not have strong correlations with the conditions of a real process (as little as possible), for example the scale of equipment. Only by using these kinds of models can such problems as design and scale-up or scale-down be solved in a reasonable length of time. Figure 1.1 gives an overview of the main elements involved in the modeling of multi-phase reactors.

Good mathematical models are needed not only for the design and scale-up or scale-down, but also for optimization purposes, process control and performance diagnosis. Thus, much work has been done in the area of modeling bubble column reactors (Deckwer and Schumpe, 1987; Deckwer, 1992; Torvik and Svendsen, 1990; Jakobsen, 1993).

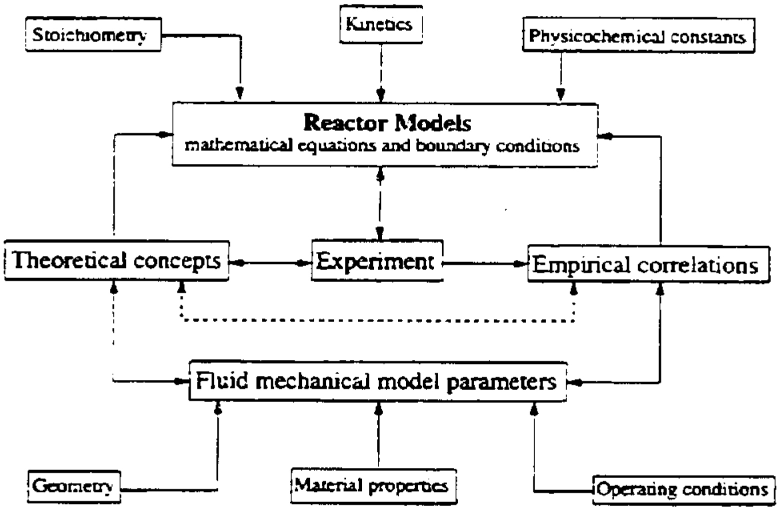

Figure 1.1 The main features of modeling for multi-phase reactors.

1.1.3 The need for determining model parameters

As pointed out by Deckwer (1992), the set of equations resulting from most mathematical models for bubble column reactors contains numerous, often highly uncertain parameters. These parameters have to be quantified before using the models. This is not an easy task since the parameters may be difficult to obtain and strongly correlated with each other, as shown in Figure 1.2.

The non-adjustable or self-adjustable operating conditions (*e.g.* phase holdups, bubble size distributions and specific interfacial areas) and the model parameters (*e.g.* dispersion coefficients and mass transfer coefficients), as shown in Figure 1.2, will depend upon reactor geometry, type of phase distribution, the adjustable operating conditions (*e.g.* superficial gas and liquid velocities and energy input) and the process data. Such non-adjustable operating conditions as phase holdups are often used as parameters in the reactor models, thereby often also called "model parameters". In addition, some of the model parameters *e.g.* mass transfer coefficients and dispersion coefficients may be calculated according to the non-adjustable operating conditions such as bubble size distributions and local liquid velocities.

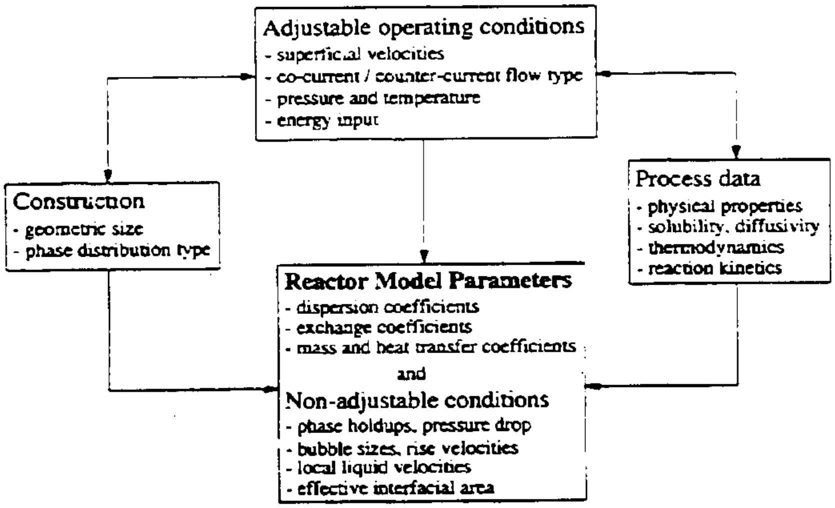

Figure 1.2 Relationships between the adjustable and self-adjustable operating conditions, the construction and the process-specific data.

These non-adjustable operating conditions or model parameters are usually determined by experiments, empirical and semi-theoretical (rarely theoretical) correlations. There exist, for example, a large number of correlations for gas holdup and volumetric mass transfer coefficient (Shah *et al.*, 1982). However, most of these correlations are completely empirical.

Since completely empirical correlations for model parameters have limited reliability, supplementary experimental work is necessary for many cases. However, experimentation may, for industrial-scale systems and conditions, not only be time-consuming and expensive, but also be impossible. Hence, it is desirable to develop semi-theoretical or theoretical models for estimating the basic parameters such as bubble size and local liquid velocity distributions from which other reactor model parameters, *e.g.* dispersion coefficients in a phenomenological reactor model, can be estimated.

1.2 Problem Formulation

1.2.1 Overview

The purpose of this research work is to improve our understanding of the characteristic behavior of bubble column reactors and to develop semi-theoretical or theoretical models on which reactor model parameter predictions can be based. This thesis is especially concerned with:

- A semi-theoretical rate model for binary bubble coalescence is developed in Chapter 3, based on the theory of turbulence and coalescence mechanisms including the approach model also developed in this thesis (Chapter 4). This model together with a rate model for binary bubble breakup will be used to predict bubble size distributions using the population balance technique.

- A theoretical rate model for binary bubble breakup is also developed in Chapter 3, based on the theories of turbulence and probability. This model also predicts breakage daughter size distributions, that are needed for describing breakup processes but are usually more or less arbitrarily chosen by previous authors due to the lack of sufficient understanding for the distributions.

- Two theoretical approach models for both two equal and unequal sized bubbles is developed in Chapter 4, based on the parallel film concept. From these model, the interaction time and contact film area can be predicted. The interaction time model is needed for development of the bubble coalescence rate model.

- The prediction of local bubble size distributions in a bubble column is given in Chapter 5, using a one-dimensional population balance model together with the rate models for bubble coalescence and breakup.

- Two semi-theoretical models are proposed for liquid circulation in bubble columns, as given in Chapter 6, using the pseudo-homogeneous fluid and two-fluid concepts respectively.

- Development and experimental verification of a phenomenological model for determining the gas holdup structure and the Sauter mean bubble diameter or the specific interfacial area, from measured data by using the dynamic gas disengagement technique, are given in Chapter 7.

- In order to understand bubble behavior in bubble columns and verify the modeling work mentioned above, bubble size distributions, bubble velocities and local gas holdups have been measured using a commercial five-point conductivity micro-probe technique. This work is briefly summarized in Chapter 2.

1.2.2 Coalescence and breakup rates

Together with the conditions created by the inlet distributor design, bubble coalescence and breakup are among the most important characteristics of a gas-liquid or gas-liquid-solid dispersion. They may not only dominate the bubble size distributions, but also directly affect mass transfer by the renewal of bubble surfaces. If the inlet bubble characteristics and the processes of bubble coalescence and breakup are well known, then the local bubble size distribution in a bubble column can be determined using population balance models. Thereby the Sauter mean diameter or specific interfacial area, both which are needed in the reactor models, can be obtained. To do this, prior knowledge concerning the underlying mechanisms such as the bubble-bubble approach process and the coalescence probability is needed. This modeling process is visualized in Figure 1.3.

Since the 1950's, a lot of effort has been spent in trying to establish rate models for bubble or drop coalescence and breakup. However, most of the previous models were based on many assumptions. For example, for coalescence probability and breakage daughter size distribution, various function types were usually assumed.

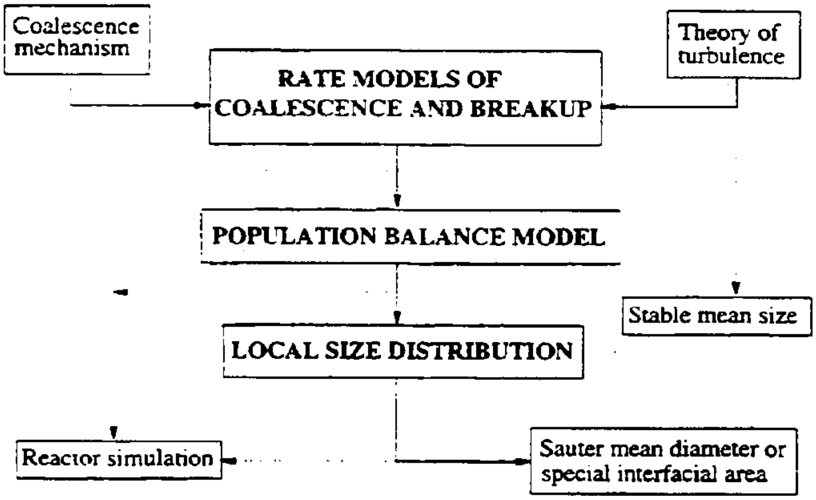

Figure 1.3 Sketch of the work to predict local bubble size distributions from the rate models of bubble coalescence and breakup.

This thesis proposes a semi-theoretical coalescence rate model based on the theories of molecular collision, turbulence, bubble-bubble approach and coalescence. Since approach models for two unequal sized bubbles are not available (a few approach models for two equal sized bubbles exist), an approach model for both two equal and unequal sized bubbles has been developed, based on the parallel film concept.

A theoretical rate model for binary bubble breakage is developed based on the theories of turbulence and probability. All parameters in this model can be calculated from the constants of turbulence theory and it has none unknown or tuned parameters. In addition, the breakage daughter bubble size distribution can be obtained directly from the model, instead of making more or less arbitrary assumptions as done by most of the previous authors in this field.

Based on rate models for coalescence and breakup, the local bubble size distribution in a bubble column is predicted using a one-dimensional population balance model. Obviously, this is a foundation for estimating the Sauter mean diameter and the specific interfacial area for the reactor models.

The work drawn by the dotted lines in Figure 1.3 is not included in this thesis, but which may be done in the future. For example, the modeling of local bubble size distributions considering the coalescence and breakage processes, may be used for reactor simulations. The estimation of the stable mean bubble size from the theory of turbulence, as shown in Figure 1.3, is earlier work by Hinze (1955) and Hughmark (1971), in which only bubble or drop breakup was considered.

1.2.3 Liquid circulation

The liquid circulation is also an important hydrodynamic characteristic of bubble columns and is a complex function of geometry, operating conditions and physical properties of the system fluids. It directly affects the mixing properties and is a decisive factor for some reactor model parameters, *e.g.* the axial and radial dispersion coefficients. The pseudo-homogeneous fluid and the two-fluid concepts have both been used in the literature for modeling liquid circulation.

However, in most previous work using the pseudo-homogeneous fluid concept, the way for determining the liquid velocity was inconsistent with the concept (that is, two-phase flow concept was used for determining the liquid velocity). In the previous two-fluid liquid circulation models, a very questionable assumption was introduced. This assumption made the two-fluid models obtain the same equation of motion as the pseudo-homogeneous fluid concept.

This work tries to clarify the pseudo-homogeneous fluid and the two-fluid concepts and their use of modeling for the liquid circulation. The expressions for the liquid velocity profiles have been developed along the lines of these two concepts, combining with a turbulent viscosity distribution model for single-phase pipe flows and an empirical gas holdup distribution model for bubble columns.

1.2.4 Dynamic gas disengagement

The gas holdups and bubble size distributions are very important model parameters or self-adjustable operation conditions. They may be difficult to measure in many cases, *e.g.* for non-transparent columns, at operating conditions of high temperature or pressure and with adverse system properties like low conductivity and high turbidity, as well as for pilot-scale or industrial-scale columns. In such cases, the dynamic gas disengagement (DGD) technique for estimating gas holdup and bubble sizes may be found very useful.

The DGD technique is based on obtaining bubble rise velocity information through analyzing the liquid surface drop data, recorded by visual or non-visual methods, after cutting off the gas supply. As estimation of bubble sizes is based on the bubble rise velocities obtained from the DGD data, the most critical part of this technique is how to obtain as correct bubble rise velocities as possible from the DGD data.