HABILITATION

The Concept of Chemical Similarity for Optimization and Design of Gas-Solid Processes

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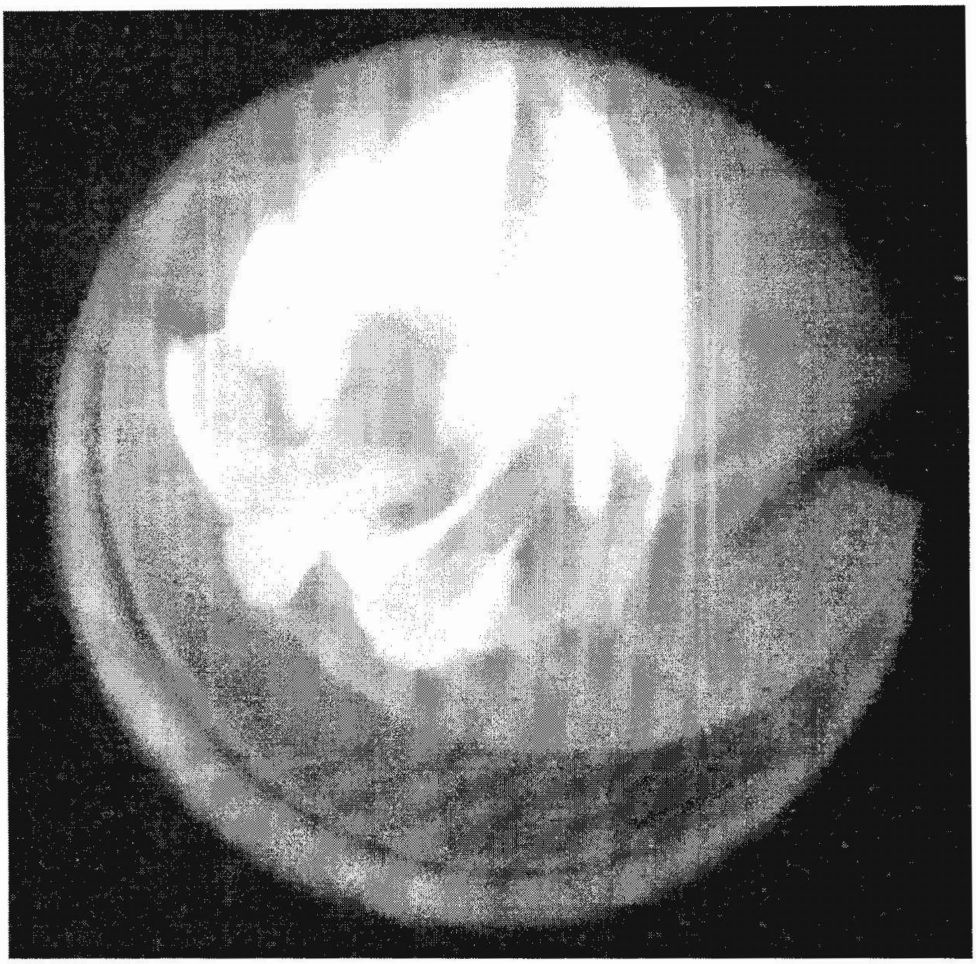

Burning coal particle (15 mm) in a circulating fluidized bed combustor.

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Abstract

The optimization and design of processes is one of the most important areas of process engineering. In practice the aims in the development of a new process are to minimize the risk of the new process, to minimize the costs for its development and to minimize the time for its development to compete with the constraints of a changing market.

Therefore experience and the development of reliable experimental and theoretical methods for scale-up and process design are necessary. Laboratory-scale units offer substantial information and are inexpensive, low in their operation costs, high in their availability, changes can be done quickly and at low costs and the operating conditions can be varied in a broad range. However, uncertainties exist and the results can be used incorrectly.

In this thesis the concept of chemical similarity between industrial-scale, pilot-scale and laboratory-scale units was introduced and demonstrated with examples from different gas - solid processes (the combustion of solid fuels, iron ore reduction, the sinter process and flue gas desulfurization). This concept was used to get important and reliable information from laboratory-scale units which can be used to optimize and design industrial-scale processes.

The basic principle of the concept of chemical similarity is that a finite volume of the industrial-scale reactor is mirrored in the laboratory-scale unit. To do this correctly certain similarity rules have to be fulfilled. For a pure homogeneous system these are at a given time: Gas temperature, total pressure, and species concentration, considering also the intermediate species.

In gas - solid reaction systems additional similarity rules exist:

- the particle temperature or the temperature of a certain zone in the particle
- the gas temperature inside the pores of the particle
- the pressure inside the particle which might differ from the bulk pressure
- the species' concentrations inside the pores of the particle to consider gas - phase reactions inside the pores and gas - solid reactions at the particle's internal surface
- the species' concentrations at the surface of the particle to consider gas - solid reactions at the particle's external surface
- the physical properties of the solid reactant such as external/internal surface area, pore structure (size of the pores and distribution)
- the chemical composition of the solid reactant (care has to be taken to impurities which might be catalytic active)

Because of the above mentioned similarity rules for gas - solid reaction systems, the actual solid reactant of the industrial-scale process has to be used in the laboratory-scale tests. Difficulties may arise in practice because the heating rates of the solid reactant have to be considered affecting the operating conditions in the laboratory-scale unit.

A similar problem which might be of importance for a proper scaling of the chemistry are fluctuations of the gaseous species and memory effects. If memory effects are dominant the application of kinetic data obtained from laboratory tests where the species' concentrations were kept constant will fail.

Also chemical and physical particle - particle interactions might be of importance. Particles of the same type and with the same or different size might interact via homogeneous or heterogeneous mechanism. Also particles of different types can interact. Heterogeneous mechanism will be of major importance especially under fixed bed conditions.

The concept of chemical similarity was demonstrated successfully in the following research areas:

The importance of radicals for CO and hydrocarbon oxidation and NO/N_2O formation was confirmed starting from the single burning particle, to burning batches of particles, further to combustion tests in a laboratory-scale CFBC up to a pilot-scale CFBC. A newly developed method was used, the method of iodine addition which enhances radical recombination reactions. Simultaneously it was shown that chemical similarity was obtained between the different test units.

In parallel, modeling work was done and a single particle model was developed and well tested in the formation rate unit. Then this model was incorporated into the CFBC NO/N_2O model which was also carefully tested in the laboratory-scale. Finally, this model was used successfully as a submodel in a global CFBC simulation model predicting NO and N_2O concentration profiles in an industrial-scale unit.

Additionally, the importance of the radicals as reactive intermediates was shown for the destruction of N_2O during CO oxidation in the laboratory-scale CFBC.

Similar trends as during the addition of iodine were found on CO, NO, and N_2O when SO_2 was added during the homogeneous oxidation of HCN studied in a laboratory-scale flow reactor. SO_2 also enhances radical recombination. This study was an important contribution to improve the understanding of trends observed from pilot-scale and industrial-scale units burning coals with different sulfur contents.

It was found that during the combustion of fuels with higher nitrogen contents more NO was formed but the conversion of fuel-nitrogen to NO decreased. This behavior was found in single particle combustion tests, during the combustion in a laboratory-scale fluidized bed combustor, and in a pilot-scale grate combustor. This behavior could be explained with the increased presence of nitrogenous species (e.g. NH_3, HCN) which reduced the NO generated by the oxidation of these same species.

The reactivities for devolatilization and char combustion of various different fuels ranging from coals to biomass to plastics and waste were determined in the laboratory-scale by integral and differential analysis. A classification system for the reactivities was established and calibrated with selected well-defined materials (graphite for char combustion and naphthalene-dicarboxylic acid anhydride for devolatilization). These standards can also be used to calibrate laboratory-scale units and procedures. The results were compared to experience well-known from industrial-scale units.

The propensity of a wide range of fuels (from petroleum coke to coals and biomass) for NO and N_2O formation was studied considering also the intermediates HCN and NH_3. Their NO and N_2O formation characteristics was obtained from transient concentration measurements during devolatilization and char combustion in a laboratory-scale unit. Generally, these characteristics can be found in pilot-scale and industrial-scale combustors, altered by destruction reactions.

In the laboratory-scale the reactivities of alternative fuels (dust from blast furnace, recycling material, fine metal, sinter coke, petroleum coke, anthracite) were studied for the sinter process and a classification system was derived. The reaction rate constants correlated well with sinter-pot results which corresponds to pilot-scale measurements. Design equations for the sinter process were derived, e.g. for the process productivity.

The reduction kinetics of iron ore fines with gas mixtures of H_2, H_2O, CO, CO_2 in nitrogen were studied in a laboratory-scale fluidized bed reactor at atmospheric and elevated pressures. The effects of temperature, gas composition, pressure, and iron ore particle size were investigated and quantified. The kinetic data were used to calculate the degrees of reduction for continuous operation of a laboratory-scale unit. Generally, good agreement was obtained.

To study fluid dynamics of fine particles which are strongly cohesive, the same principles were used which are the basis for the concept of chemical similarity. This concept was extended to focus on fluid dynamics and forces. Care was taken to have similar conditions in the laboratory-scale unit from the fluid dynamical point of view. The formation and destruction of agglomerates was studied and used for the development of the model describing the fluid dynamics of the desulfurization process. With this newly developed model the effect of reactor design, water injection and operating conditions on fluid dynamics were evaluated. Laboratory-scale and pilot-scale results were used for comparison, and the model applied for industrial-scale. However, to generalize the concept of similarity to design and optimize processes utilizing cohesive particles further work will be needed.

The concept of chemical similarity has proven to be a powerful tool which can be used for the optimization and design of gas - solid processes. In practice it is often not possible to fulfill all the very stringent similarity rules. However, useful information can be obtained, if the researcher is aware of the problems in designing laboratory-scale tests. He or she will know the limitations and will use the obtained results in a proper way depending on the aim of the work.

Kurzfassung

Eines der wichtigsten Gebiete der Verfahrenstechnik ist die Optimierung und die Auslegung des Verfahrens. Die Ziele dabei sind, die Risiken des neuen Verfahrens, sowie die Kosten der Verfahrensentwicklung und die Entwicklungszeit zu minimieren, um auf den sich schnell ändernden Märkten bestehen zu können.

Aus diesen Gründen sind Erfahrung und die Entwicklung von zuverlässigen experimentellen und theoretischen Methoden zur Maßstabsvergrößerung und Auslegung notwendig. Labormethoden können hierzu wichtige Informationen liefern, weiters sind sie kostengünstig, haben nur geringe Betriebskosten, sind gut verfügbar und Änderungen können schnell und mit geringen Kosten durchgeführt werden. Die Betriebsbedingungen können in einem weiten Bereich variiert werden. Jedoch Unsicherheiten bestehen in der richtigen Interpretation der Laborergebnisse für die Großanlage.

In dieser Arbeit wird das Konzept der Chemischen Ähnlichkeit zwischen Großanlage, Pilotanlage und Laboranlage vorgestellt und mit Beispielen von verschiedenen Gas - Feststoff Verfahren belegt (Verbrennung fester Brennstoffe, Eisenerzreduktion, der Sinterprozeß, Rauchgasentschwefelung). Dieses Konzept wurde verwendet, um zuverlässige Information zur Verfahrensoptimierung und Auslegung mittels Labormethoden zu gewinnen.

Das Grundprinzip des Konzeptes der Chemischen Ähnlichkeit besteht darin, daß man ein finites Volumenelement der Großanlage in einer Laboranlage korrekt abbildet, wodurch die Ähnlichkeitsbedingungen entstehen. Für ein rein homogenes System sind diese für einen bestimmten Zeitpunkt: Gastemperatur, Gesamtdruck und die Konzentrationen der Spezien, wobei auch kurzlebige Spezien berücksichtigt werden müssen.

In Gas - Feststoff Reaktionssystemen gelten noch zusätzliche Ähnlichkeitsbedingungen:

- Partikeltemperatur und die Temperatur in bestimmten Bereichen des Partikels
- die Gastemperatur in den Partikelporen
- der Gasdruck im Partikel
- die Spezienkonzentrationen in den Partikelporen, um die Gas - Gas und die Gas - Feststoff Reaktionen innerhalb des Partikels zu berücksichtigen
- die Spezienkonzentrationen an der äußeren Partikeloberfläche, um Gas - Feststoff Reaktionen zu berücksichtigen
- die physikalischen Eigenschaften des Feststoffes wie externe/interne Oberfläche, Porenstruktur (Größe und Verteilung)
- die chemische Zusammensetzung des Feststoffes (hier gilt auch ein besonderes Augenmerk den Spurenelementen, die katalytisch aktiv sein können)

Wegen der Vielzahl dieser Ähnlichkeitsbedingungen muß der tatsächliche Feststoff im Labor verwendet werden. Schwierigkeiten können entstehen, den die korrekten Aufheizraten des Feststoffes müssen berücksichtigt werden.

Ein weiteres Problem stellen Fluktuationen von Gasspezien und Gedächtniseffekte des Feststoffes dar. Wenn diese bestimmend für die Kinetik sind, werden die Aussagen, die im Labor mit konstanten Spezienkonzentrationen gewonnen wurden, versagen.

Auch chemische und physikalische Partikel - Partikel Wechselwirkungen können von Bedeutung sein. Partikeln der selben Zusammensetzung und mit gleichen oder unterschiedlichen Partikelgrößen können sich mittels homogener oder heterogener Mechanismen beeinflussen. Selbstverständlich gilt das auch für Partikeln mit unterschiedlicher Zusammensetzung. Heterogene Mechanismen sind insbesonders für Reaktionssysteme im Festbett von großer Wichtigkeit.

Das Konzept der Chemischen Ähnlichkeit wurde anhand folgender Beispiele demonstriert:

Die große Bedeutung der Radikale bei der Verbrennung von CO, Kohlenwasserstoffen und der NO/N_2O Bildung wurde gezeigt, ausgehend von einem brennenden Einzelpartikel, über einen Batch an Brennstoffpartikeln bis zu einer CFBC Laboranlage und einer CFBC Pilotanlage. Eine neue Methode wurde entwickelt, die Methode der Iod Zugabe, die Radikalabbruchreaktionen verstärkt. Gleichzeitig wurde gezeigt, daß chemische Ähnlichkeit zwischen den einzelnen Anlagen besteht.

Parallel zu den experimentellen Arbeiten wurden die entsprechenden Modelle erstellt. Ein Einzelpartikelmodell wurde entwickelt und umfangreich in der Bildungsratenmeßanlage getestet. Anschließend wurde dieses

Modell als Unterprogramm des CFBC NO/N_2O Modells verwendet, welches in einer Laboranlage erneut getestet wurde. Dann wurde dieses Modell als ein Unterprogramm in einem globalen CFBC Simulationsmodell zur Berechnung der NO und N_2O Konzentrationsprofile einer Großanlage verwendet.

Zusätzlich wurde die Wichtigkeit der Radikale als reaktive, intermediäre Spezien für den N_2O Abbau während der CO Oxidation in der CFBC Laboranlage aufgezeigt.

Ähnliche Trends wie bei der Zugabe von Iod wurden bei CO, NO und N_2O gefunden, als SO_2 während der homogenen Oxidation von HCN in einem Laborströmungsreaktor zugegeben wurde. SO_2 verstärkt ebenso wie Iod die Rekombinationsreaktionen der Radikale. Diese Studie war ein wichtiger Beitrag, um die Trends, die in Pilot- und Großanlagen beobachtet wurden, zu verstehen.

Brennstoffe mit einem höheren Stickstoffgehalt erzeugen mehr NO, jedoch der Konvertierungsgrad des Stickstoffes zu NO nimmt mit einem höheren Stickstoffgehalt ab. Dieses Verhalten wurde bei Einzelpartikeltests, bei Verbrennungsversuchen in einer Laborwirbelschichtanlage und in einer Pilotanlage gefunden, und konnte mit der erhöhten Konzentration an stickstoffreichen Spezien in der Gasphase (z.B. NH_3, HCN), die das schon gebildete NO wieder reduzieren können, erklärt werden.

Die Reaktivität der Entgasung und des Koksabbrandes wurde von zahlreichen verschiedenen Brennstoffen (von Kohle bis Biomasse, Kunststoffen und Abfall) in einer Laboranlage durch integrale und differentielle Auswertemethoden bestimmt. Ein Klassifikationsschema für die Reaktivitäten wurde etabliert und mit ausgewählten Substanzen (Graphit für den Koksabbrand, Anhydrid der Naphthalindicarbonsäure für die Entgasung) kalibriert. Diese Substanzen können auch zur Kalibrierung von Laboranlagen und Methoden verwendet werden. Die erhaltenen Ergebnisse wurden mit Erfahrungen von Großanlagen verglichen.

Die Bildung von NO und N_2O von unterschiedlichen Brennstoffen (von Petroleum Koks bis zu Kohle und Biomasse) wurde untersucht, wobei die Zwischenprodukte HCN und NH_3 berücksichtigt wurden. Während der Entgasung und während des Koksabbrandes wurde die zeitabhängige NO und N_2O Bildung in einer Laboranlage charakterisiert. Dieselben Charakteristika können auch in Pilotanlagen und Großanlagen gefunden werden, jedoch müssen Abbaureaktionen berücksichtigt werden.

In einer Laboranlage wurden die Reaktivitäten von alternativen Brennstoffen (Gichtstaub, Recyclingmaterial, Feinmetall, Sinterkoks, Petroleumkoks, Anthrazit) für den Sinterprozeß untersucht und ein Klassifikationssystem entwickelt. Die Geschwindigkeitskonstante korrelierte mit Ergebnissen aus Sinterpfannenversuchen, welche einen Pilotanlagenmaßstab darstellen. Auslegungsgleichungen für den Sinterprozeß wurden abgeleitet, z.B. für die Produktivität.

Die Reduktionskinetik von feinem Eisenerz mit H_2, H_2O, CO, CO_2 wurde in einer Laboranlage bei Atmosphärendruck und erhöhten Drücken untersucht. Die Effekte der Temperatur, Gaszusammensetzung, Druck, Partikelgröße des Eisenerzes wurden bestimmt und quantifiziert. Die kinetischen Daten wurden zur Modellierung von kontinuierlichen Versuchen im Labormaßstab verwendet. Im allgemeinen wurde eine gute Übereinstimmung erhalten.

Die Grundsätze des Konzeptes der Chemischen Ähnlichkeit wurden für die Untersuchung des Strömungsverhaltens von stark kohäsiven, sehr feinen Partikeln in analogem Sinne angewandt. Das Konzept wurde ausgedehnt und lokale Kräfte und Strömungszustände berücksichtigt. Sorgfältig wurden die Laborbedingungen so gewählt, daß lokale Ähnlichkeit aus strömungsmechanischer Sicht zwischen Laboranlage und Großanlage waren. Die Bildung und der Zerfall von Agglomeraten wurden studiert und zur Modellentwicklung verwendet, welches die Strömungsmechanik des Entschwefelungsverfahrens beschreibt. Mit diesem neu entwickelten Modell können die Einflüsse von geometrische Änderungen, Wassereindüsung und Betriebsbedingungen untersucht werden. Labormessungen und Messungen in einer Pilotanlage wurden miteinander verglichen, und das Modell für Großanlagen angewandt. Jedoch zur Verallgemeinerung des Konzeptes der Ähnlichkeit zur Verfahrensoptimierung und Verfahrensentwicklung mit kohäsiven Partikeln sind weiterführende Arbeiten notwendig.

Das Konzept der Chemischen Ähnlichkeit hat sich als ein sehr leistungsstarkes Werkzeug bewährt, das zur Verfahrensoptimierung und Auslegung von Gas - Feststoff Reaktionssystemen verwendet werden kann. In der Praxis ist es häufig nicht möglich, alle Ähnlichkeitsbedingungen zu erfüllen. Jedoch wichtige Information kann erhalten werden, wenn sich die Forscher den Problemen der Maßstabsübertragung bewußt sind, dann sind die Grenzen bekannt und die Ergebnisse werden in richtiger Weise zur Erreichung der Ziele verwendet.

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Curriculum Vitae

1. GAS-SOLID PROCESSES

In this thesis I want to show how the problem of optimizing or designing a gas-solid process can be approached by using the concept of chemical similarity. The problem of scaling a gas-solid process especially at elevated temperatures is very complex and chemistry as well as fluiddynamics has to be considered. Fluiddynamics is of great importance because stable operating conditions are necessary to study or optimize chemical reaction kinetics.

This thesis is based on the experience I gained in eight years of research in the field of gas-solid processes. In this time experimental and modeling tools have been developed and tested in the area of fluidized bed, grate and pulverized fuel combustion, fluidized bed iron ore reduction, characterization of cokes and alternative fuels for the iron ore sinter-process, and flue gas desulfurization in circulating fluidized bed reactors.

The concept of chemical similarity will be described and demonstrated and discussed with actual examples from the above listed processes. First, an overview of the gas - solid processes studied will be given, followed by an overview about laboratory-scale methods.

Combustion of Solid Fuels

Four different combustion techniques have been developed to burn solid fuels as efficiently as possible: grate combustion, fluidized bed combustion, pulverized fuel combustion and rotary tube combustion. Pulverized fuel combustion and fluidized bed combustion are the most important technologies for industrial heat and power generation.

Fluidized bed combustion

The importance of fluidized bed combustion is increasing continuously because of its advantages of low temperature combustion, low NO_x emissions, *in-situ* sulfur capture, fuel and load flexibility combined with a high efficiency.
Different types of fluidized bed combustors with their own advantages and disadvantages have been developed, e.g. the bubbling fluidized bed combustor (FBC), the externally circulating fluidized bed combustor (CFBC) (refer to Fig. 1.-1), the internally circulating fluidized bed combustor (ICFB), the pressurized bubbling fluidized bed combustor (PFBC) and the pressurized circulating fluidized bed combustor (PCFB).

Besides the many advantages of fluidized bed combustion further optimization of the combustion process as well as the reduction of the emissions (NO_x, N_2O, SO_2, CO) is necessary because of the growing public concern about the environmental effects and combustion as an anthropogenetic source of emissions.

The nitrogen oxides NO (nitric oxide) and NO_2 (nitrogen dioxide), respectively NO_x, and N_2O (nitrous oxide) are the major nitrogen containing pollutants generated in the fluidized bed combustion process.

The NO_X emissions can be divided by their formation paths into three different classes: The thermal - NO_X, the prompt - NO_X and the fuel - NO_X. In fluidized bed combustion it has to be focused only on the NO_X emissions generated by the oxidation of the fuel bound nitrogen (fuel - NO_X) because of the typically low combustion temperatures. But these low temperatures cause a strong increase of the N_2O emissions. Thus, N_2O has the potential of being a major drawback of the fluidized bed combustion technology.
Nitrogen oxides are very harmful emissions because they cause health injuries e.g. illnesses of the respiratory organs like asthma, general decrease in vitality. Other dangerous effects are the formation of acid rain and the formation of ozone at the ground level.

Additionally to these ecological reasons there also exist economical ones: The cost of the fuel constituents a major part of the operating cost of a combustor and a gain in the percentage range in the combustion efficiency can save a large amount of money in terms of operating cost of the boiler over its lifetime.
A primary reduction of emissions achieved by optimizing the process parameters of the combustor is much cheaper than highly expensive secondary abatement technologies like SCR (selective catalytic reduction) - techniques because of expensive catalysts.

These ecological and economical reasons cause the urgent need for a deeper understanding of the very complex structure of the combustion process.

The fuel is one of the most important parameters affecting the whole combustion process and the design of the combustor. The knowledge of the behavior of the fuel is the basis to increase combustion efficiency and to decrease emissions of an existing combustion process.

If chemical kinetics and physical properties of the burning fuel are qualitatively and quantitatively described, characterizing fuel parameters will be obtained. These fuel parameters represent important input parameters of general combustor models. These models together with practical experience (time, temperature and turbulence) allow the optimization of the whole combustor .
Especially in fluidized bed combustion where a broad variety of different fuels is used optimization of the process parameters and boiler design is essential. A classification system which allows to predict the behavior of an unknown fuel will save much time and money.

The conditions in fluidized bed combustion can differ a lot if for instance a circulating fluidized bed combustor is compared with a bubbling fluidized bed combustor (refer also to Table 2.-3). The superficial gas velocity varies in a range from 0.5 (FBC) to 9 m/s (CFBC), the typical bed temperature is between 750 to 900 °C (optimum for sulfur capture, no thermal - NO_X), the oxygen concentration varies from 21 (air-nozzles) to almost 0 vol-%, the bed voidage from 0.6 (FBC)to almost 1 (CFBC), the pressure varies from 1 to 20 bar (PFBC, PCFB), the fuel particle size varies from pulverized fuel (ca. 100 μm) to 30 mm, the solid fuel varies from bituminous coal, sub-bituminous coal, wood to plastics from municipal waste. The typical power range varies from 1 to 20 MW(thermal) (FBC) to 20 - 500 MW (thermal) (CFBC) and 200 - 500 MW(thermal) (PFBC).

Straight on from the inlet of the fuel feeding system the combustion of solid fuel is a very complex process especially under fluidized bed conditions:

The fuel particle is surrounded from bed solids like silica sand, sorbents (like CaO), ash particles and other fuel particles (although the typical fuel concentrations are rather low, about 0.5 - 5 w-%) as well as gas.

In bubbling fluidized bed combustors the bed density is high (about 1000 kg/m3) and the bed voidage is low (about 0.6). The fluidized bed can be mainly divided into two different phases: the bubble phase and the particulate phase. The main gas transport takes place in the bubbles which move through the suspended particulate phase and cause the vigorous circulation of the bed material. This vigorous circulation leads to good mixing inside the combustor and cause the typical behavior of the fluidized bed which has many attributes of a liquid. The relatively strong pressure drop of the combustor height separates the bed region from the freeboard. The voidage of the freeboard is almost 1. The superficial gas velocity is between the minimum fluidization and the terminal velocity.

The riser of a circulating fluidized bed combustor consists of the bed region (lower part in the riser with a typical voidage between 0.8 and 0.98) and the transport zone (upper part in the riser, voidage between 0.99 and 1) but without well defined boundaries. No bubbles can be observed. The pressure loss is more or less continuously decreasing. One main phase, gas with suspended particles, and particle clusters can be observed. Additionally, the cross section area can be divided in a thin particle rich zone at the annulus and a gas rich zone at the core. High velocities (several times higher than the terminal velocity) cause a good turbulence in the combustor and a typical height of 30 m guarantees a long residence time of the small fuel particles.

These different features cause a very complex structure of fluid dynamics as well as mass and heat transfer in the combustor. Beside the mass and heat transfer mechanisms between bubble and particulate phase (FBC) or core and annulus (CFBC) the mass and heat transport mechanisms between the fuel particles and the fluidized bed is very important. These mechanisms determine the mass and heat flow to and from the fuel particle during its lifetime in the combustor. To characterize these processes various different conditions have to be taken into consideration: If the fuel particle gets in contact with a bubble carrying oxygen rich gas the fuel particle is surrounded by oxygen and the burning rates will increase significantly (yellow diffusion flames can be observed). But if the fuel particle is in the particulate phase the oxygen concentration around the fuel particle is much lower, the burning rate will be low, too and no flames will be seen. The contact and residence times are important but often uncertain parameters for these processes.

After the feeding of the fuel in the combustor the fuel particle starts drying. Parallel to the drying devolatilization takes place. These two processes are mainly controlled by external and internal heat transfer. The fuel particle releases the volatile matter which is transported by convection and diffusion in the particulate and bubble phase (FBC) or gas phase (CFBC) within the combustor while homogeneously reacting with oxygen and other species with or without flame. The burning of the volatile matter and its site are important parameters for the heat balance of the combustor and the operating conditions.

With decreasing devolatilization the combustion of the remaining char starts. This process is about an order of magnitude slower than the fast release of volatiles. The oxygen has to be transported to the fuel carbon by external and internal mass transfer before the heterogeneous chemical reaction can take place. Therefore char combustion is often governed by a combined process of mass transfer and chemical kinetics. During the char combustion period the fuel particle shrinks in size and density changing its physical and chemical properties and fluid dynamic characteristics. A loss of combustion efficiency is often caused by insufficient burn out of the char (a too short residence time in the combustor).

Additionally, the following mechanisms of swelling of the fuel particle, fragmentation and attrition can be observed in a fluidized bed combustor.

The formation of NO_X and N_2O emissions is at least as complex as the mechanisms of carbonaceous species during devolatilization and char combustion. The combustion process is the basis for the formation and destruction paths of NO_X and N_2O. The reverse influence, effects from the nitrogen chemistry on the combustion chemistry, can be neglected because the concentrations of nitrogen containing species are relatively low in comparison to the carbonaceous species and the nitrogen chemistry neither effects heat generation nor heat consumption.

During devolatilization and char combustion nitrogen containing species are released from the fuel matrix. Their possible reaction paths already start in the porous structure of the fuel particle and follow the flow of the volatile matter, carbon dioxide and carbon monoxide. Nitrogen containing species can react homogeneously with the volatiles or with the combustion gases in order to form or to reduce NO_X and N_2O. Beside the complex structure of these homogeneous reactions there exist heterogeneous or heterogeneously catalyzed reactions. These heterogeneous reactions interfere with the radical based homogeneous chemistry. The sum of possible different reaction conditions increase the difficulty in NO_X, N_2O emission predictions.

These complex processes can be studied as separately as possible with single fuel particle experiments under well defined conditions in conjunction with modelling work.

Grate combustion

Biomass and waste are the most important fuels burned on the grate. In principle the fuel undergoes the same changes as described in the previous section but the operating conditions differ significantly. The superficial gas velocities are much lower in grate combustors (typically 1-2 m/s, refer to Table 2.-3). Mass and heat transfer rates are lower and significant temperature and concentration gradients exist in the fuel bed. Fuel temperatures are typically in a range between 400 and 1000°C. The fuel particle size can be quite large (typically 10 to 100 mm) and the heating rates are low.

In Fig. 1.-1 the bottom part of an industrial-scale grate combustor is given. Many grate combustors can be found below 5 MW_{th} but some operate up to 30 MW_{th}. The area of the grate is between 2-3 m^2 and up to 30 m^2 with boiler heights of 20 m.

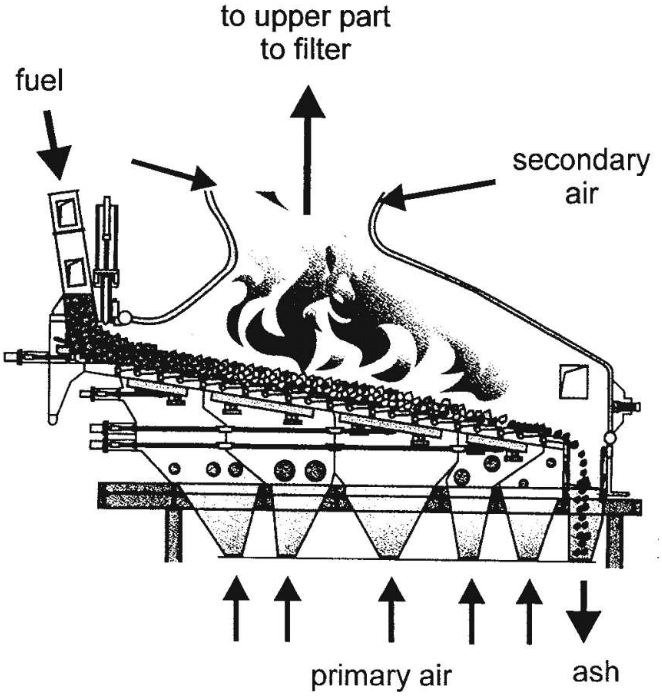

Figure 1.-1: Scheme of the bottom part of an industrial-scale grate combustor (modified from Kvaerner Pulping brochure 1996: The Trollhättan boiler).

Pulverized fuel combustion

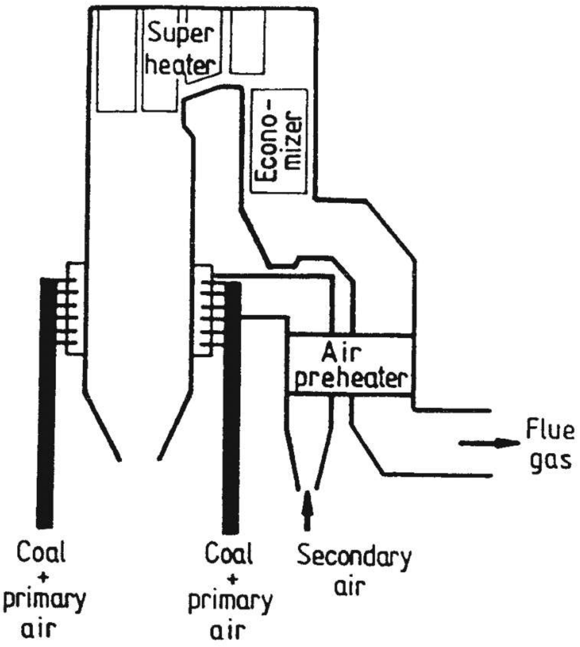

Figure 1.-2: Scheme of an industrial-scale pulverized coal combustor (*Tomeczek 1994*).

Usually bituminous and sub-bituminous coals are burned in large boilers (up to 1000 MW_{th}). The coals are grinded to a fine powder (10 - 100 µm) and undergo drying, devolatilization and char combustion in the entrained flow of the boiler. Superficial gas velocities are in a range of

5 to 10 m/s and fuel temperatures of 1700°C can be found (refer to Table 2.-3). The heating rates of the fine fuel particles are very high. Recently, tests are performed to burn the coal together with biomass (co-combustion).

Because of the locally high temperatures in the boiler, thermal - NO_x gains more importance (compare fluidized bed combustion). But in the last years low-NO_x burners have been developed and the thermal - NO_x was reduced significantly. Additionally, air staging, reburning and SNCR (selective non-catalytic reduction) techniques are used for a further reduction of NO_x.

Fluidized Bed Iron Ore Reduction

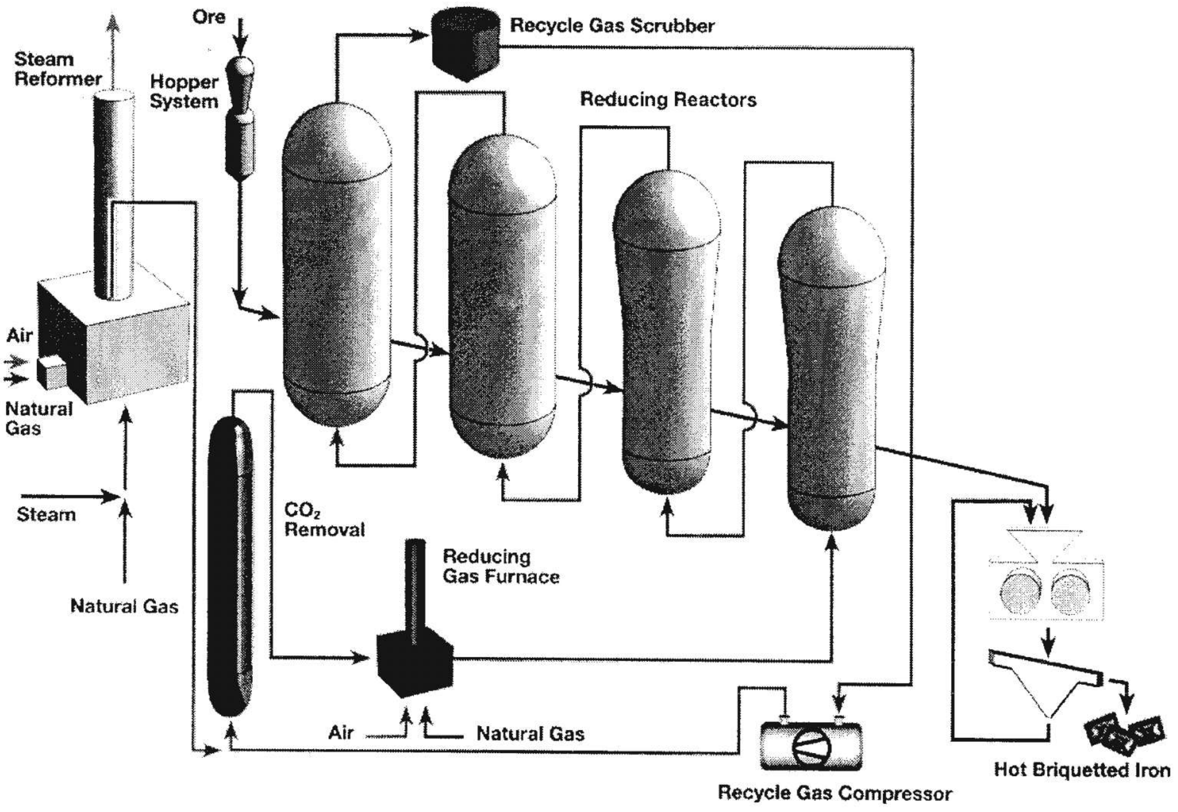

Figure 1.-3: The fluidized bed iron ore reduction process (from Voest Alpine Industrieanlagenbau brochure 1997: The FINMET process).

The fine iron ore (typical particle size 0.05 to 6 mm) is charged through a lock hopper system into a series of fluidized bed reactors (refer to Fig. 1.-3). The pressure within the reactors is between 10 and 12 bar. The iron ore is preheated in the first reactor by the incoming gas from the previous reactor of the series. After a certain residence time the partially reduced iron ore is transferred to the next reactor of the series by a transfer line. The temperatures in the reactors range from 600 up to 850°C (refer to Table 2.-3). The superficial gas velocity is in a range of 0.8 to 1.2 m/s.

The reducing gas (H_2, CO, CH_4) is generated from the catalytic conversion of natural gas and steam in a reformer. Higher hydrocarbons are completely cracked. Excess CO_2 is removed from the gas stream. The gas enters the series of reactors in the opposite direction to the iron ore route reducing the iron ore fines in counter-flow. The degree of metallization typically lies between 91 and 92 %. After exiting from the last reactor the gas is cleaned and cooled before being recycled to the first reactor.
Additionally to the bubbling fluidized bed, also circulating fluidized bed reactors are used for iron ore reduction.

The Iron Ore Sinter-Process

Fine iron ore can not be used directly in the blast furnace which operates in the counter-flow mode. To obtain the optimal mechanical properties (size, voidage, mechanical stability, etc.), the iron ore is sintered.
The fine iron ore is mixed with coke (typical particle size between 0.2 to 5 mm, refer to Table 2.-3) which is the fuel for the sinter process and with additives. Recently, also the utilization of alternative fuels (e.g. metallurgical waste) are in discussion. Then the solids are put on a moving grate (refer to Fig. 1.-4, typical grate size: 3 to 4 m in width and 50 to 70 m in lenght, typical bed height: 0.5 to 1 m). With a burner at the beginning of the grate, the coke is ignited at the top of the bed.

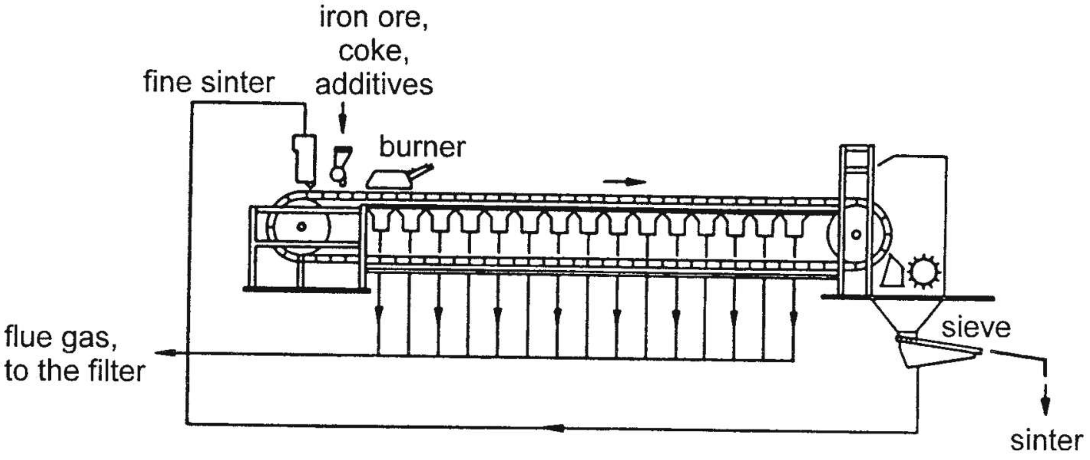

Figure 1.-4: The iron ore sinter-process.

The air for the combustion of the coke is sucked with a fan through the bed of the solids (typical superficial gas velocities 1 m/s). The temperature front (with peak temperatures above 1400°C) follows the air flow and moves from the top of the bed downwards while the bed is moving to the end of the unit. Within the temperature front the sintering of the iron ore as well as a partial reduction (by CO) takes place. For optimal sinter properties and operating conditions it is essential that the temperate front has passed the bottom part of the bed at the end of the sinter unit. Bed height, bed composition, grate length and moving velocity are key parameters.
At the end of the unit the sponge-like sinter is removed from the grate and sieved. The fine sinter is recycled whereas the sinter with a size range between 5 and 50 mm is transported to the blast furnace.

Fluidized Bed Flue Gas Desulfurization

The semi-dry flue gas desulfurization processes is carried out in a circulating fluidized bed reactor. The flue gas generated from pulverized coal combustion or from solid waste combustion is rich in CO_2, SO_2, HCl and other pollutants. After passing a filter (which is optional) the flue gas (with a temperature of approx. 150°C) enters the CFB-reactor (refer to Fig. 1.-5). The superficial gas velocities are about 1-5 m/s (refer to Table 2.-3). Very fine $Ca(OH)_2$ is used as sorbent with a particle size of about 5 µm. In the bottom part of the CFB-reactor water is injected to promote the chemical reactions. At low temperatures (below 80°C) desulfurization is improved but the formation of agglomerates increases which might lead to process difficulties. Therefore only a narrow temperature window exists. $Ca(OH)_2$ reacts with the gaseous pollutants to $CaSO_3$, $CaSO_4$, $CaCO_3$, $CaCl_2$ and other solid species. After the solids have passed the riser they are partly recycled after passing a dust filter system and partly removed from the process.
The main advantages of the fluidized bed flue gas desulfurization process are that it can be used for existing combustors with low investment and running costs. The pressure drop is very small and no special water treatment is required.

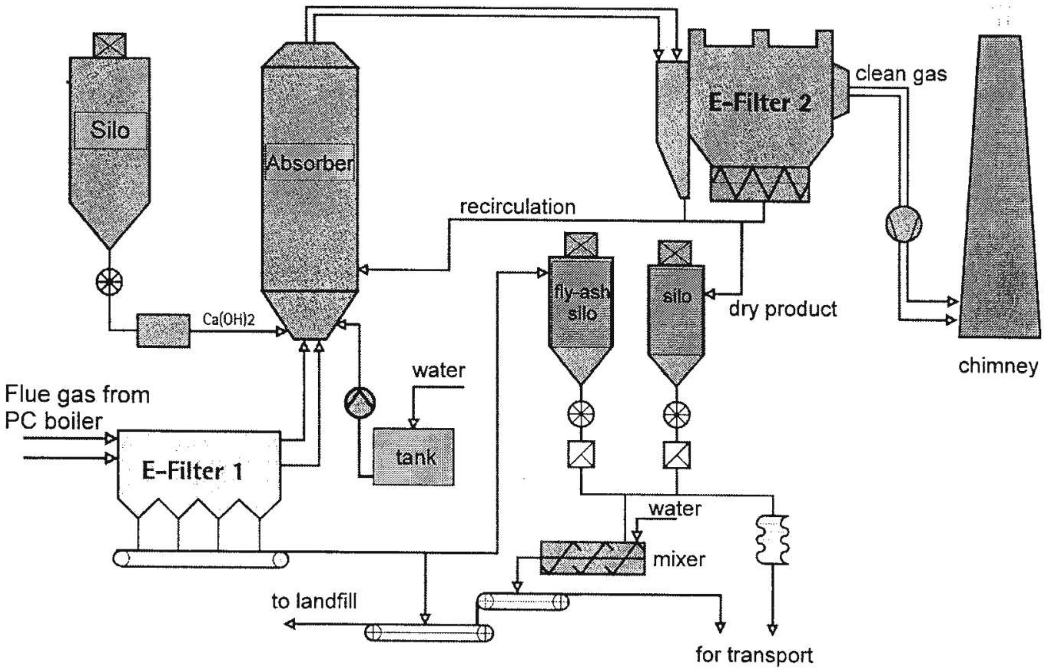

Figure 1.-5: The fluidized bed flue gas desulfurization process (modified from Draukraft brochure 1997: Dampfkraftwerk Zeltweg).

The difficulties of this process are that the on-going fluiddynamical processes are very complex and not well understood. The fine solids are group C particles (cohesive, Geldart classification system, *Geldart 1986*) with high inter-particle forces. Those particles are difficult to fluidize and tend to form agglomerates which affect the fluiddynamical properties. The injection of the water even increases the complexity. Scale-up of such systems is very difficult.

References

Tomeczek, J. (1994): *Coal Combustion*, Krieger Publishing Company, Malabar, Florida.
Geldart, D. (1986): *Gas Fluidization Technology*, John Wiley & Sons, New York.

2. LABORATORY-SCALE METHODS

In this chapter an overview of the different characterization methods is presented and their typical applications and features are described (refer also to *Winter et al. 1997*). The different methods are grouped according to their basic fluidization characteristics. For instance, in a thermogravimetric analyzer (TGA) the particles do not move. Therefore TGA will be considered as a fixed particle method.

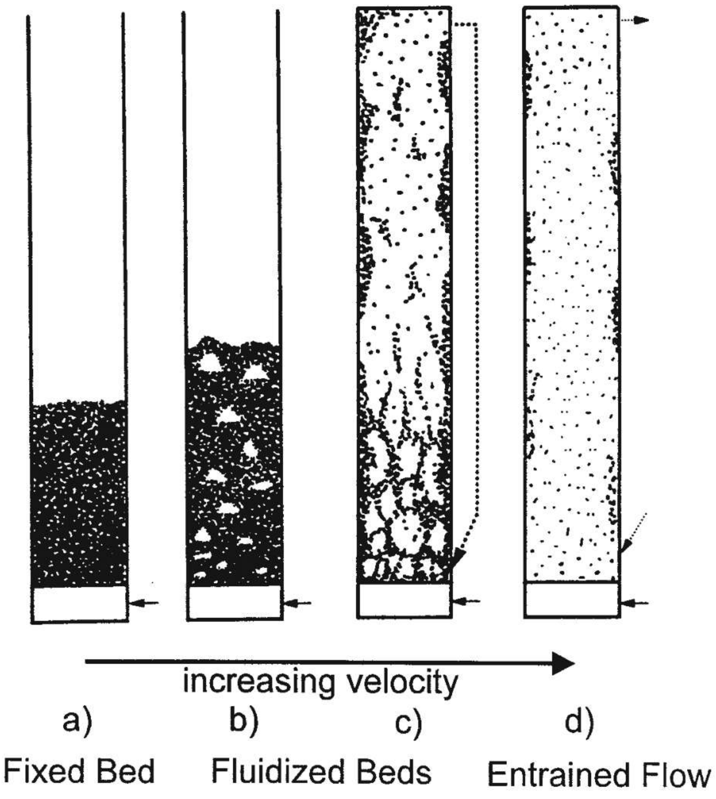

Figure 2.-1: The different flow regimes of particles. With increasing velocity the fixed bed (a) turns into a bubbling fluidized bed (b) or circulating fluidized bed (c). At higher velocities the particles are entrained and entrained flow conditions (d) are obtained. (modified from *Grace (1986)*).

Fixed Particles - Methods

Fixed particle methods are often used in laboratory-scale to perform experiments with solid reactants. They can be divided into thermogravimetric methods and others:

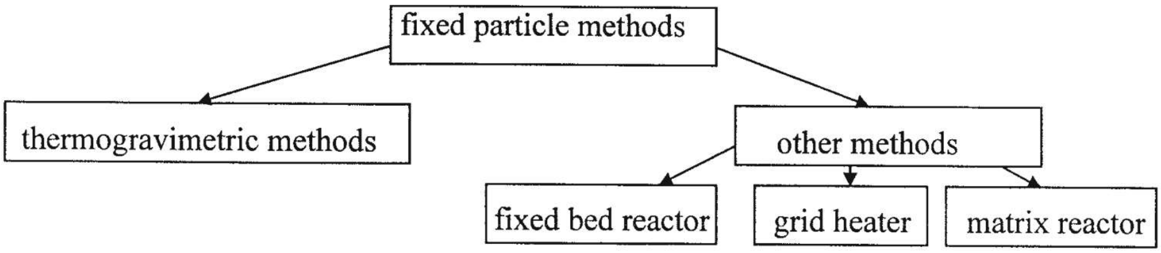

Figure 2.-2: Overview of the fixed particle methods

Thermogravimetric analyzer (TGA)

The TGA is often used to investigate gas-solid reactions where changes of the mass of the sample provide the key information on the reaction mechanisms and reaction kinetics because during an experiment solid mass is recorded continuously. The TGA technique is employed when only comparably slow reaction phenomena are to be expected. The thermogravimetric analyzer is also used to carry out precise density measurements and sorption measurements. Furthermore this tool is used for analysis purpose of the solid material.

The thermogravimetric analyzer (or apparatus) TGA consists of two main parts: The mass balance and the reactor where the solid sample is located in a sample holder. Furthermore there exists a gas supply system and mostly an analysis system for the evolved gas.

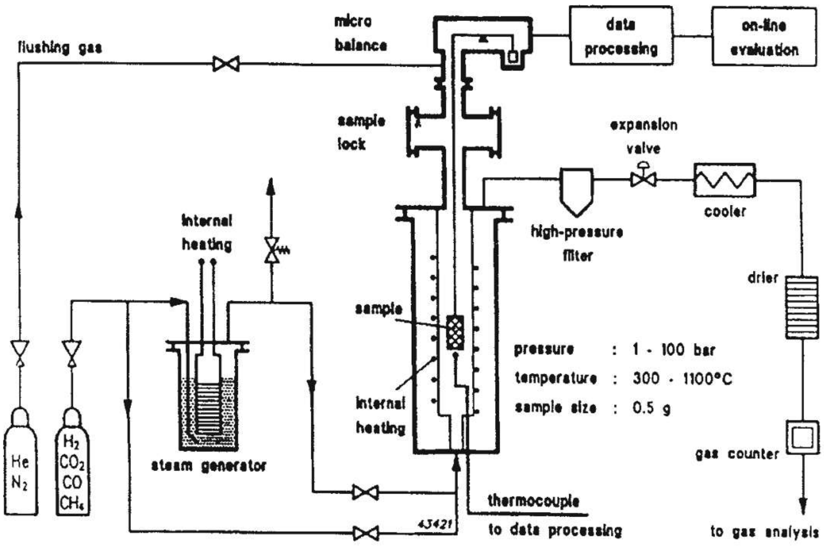

Figure 2.-3: Typical setup for a high pressure TGA experiment with a gas supply system, the sample in the sample holder that is connected with a mass balance, the high pressure reactor together with an electric heater, filter, expansion valve, cooler, drier and gas analysis for the exiting gas *(van Heek and Mühlen, 1991)*.

Usually the sample material is located in or attached to a sample holder. The sample holder is in contact with a balance where the mass of the sample together with the sample holder is measured and recorded continuously (refer to Fig. 2.-3)

Grid heater

Only when the screen or grid are used for heating or cooling, the setup is regarded as a grid heater here.

The screen heater (Fig. 2.-4) is mainly used when fast reactions are investigated since fast heating (or cooling) rates can be achieved. Usually the sample size is kept small which makes off-line analysis of the solid material difficult.

The grid heater consists of a reactor, a heating (or cooling) device, and a screen or grid. The solid sample is located on the screen (or grid).

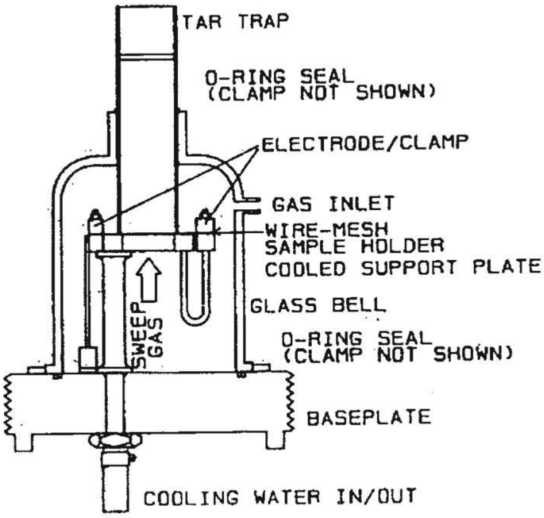

Figure 2.-4: Typical setup for heated grid experiments (*Cai et al. 1993*)

Particles in a matrix - matrix reactor

In this method the solid reactant is located in a matrix which is heated in a chamber (Fig. 2.-5). As matrix, glass wool (*Kambara et al. 1993*) or other inert fabrics can be used. This experimental tool is used when fast heating rates are required and the possibility of particle to particle interactions should be kept small.

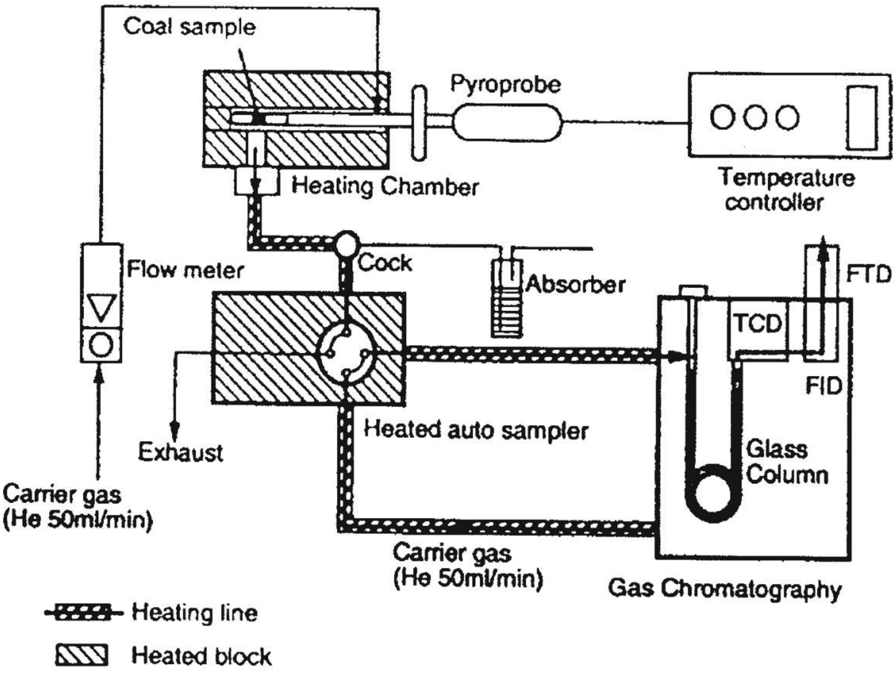

Figure 2.-5: Typical setup for experiments with the solid reactant fixed in a matrix (Kambara *et al. 1993*)

Borgwardt 1985, used a solid sample of 10 mg in his reactor. The heating rates, which can be obtained by those method range up to 75·10^3 K/s but the fuel heating rate is 1·10^3 K/s (*Kambara et al. 1993*). A gas flow is usually provided through the quartz wool fabric. It must be taken care that the solid particles are not carried out of the chamber by the gas stream. The fuel temperature is measured by a thermocouple in the center of the quartz wool fabric. The maximum fuel temperature which can be reached is around 1800°C (*Kambara et al. 1993*).

The mass balance is obtained by weighing and analyzing the solid reactant at the beginning of the experiment and after a certain time. Also the tars, which are collected from the glass wool, are weighed in pyrolysis experiments (*Kambara et al. 1993*).

Fixed bed reactor

The fixed bed reactor is often used to investigate gas-solid reactions where gas analysis data of the exiting gas provide key information on the reaction mechanisms. The solid material can be characterized after the reaction. Fixed bed experiments are often used to obtain breakthrough curves (see *Irabien et al. 1992*). *Sherwood et al. 1975,* for example used breakthrough curves to derive kinetic data.

The fixed bed reactor consists of a reaction chamber where the solid sample is located on top of a frit. A heating device is required to heat the reactor together with the solid sample material in the reactor. Also a feeding and withdrawal device can be available to fill the reactor and to empty it before and after the experiment, respectively. Furthermore a gas supply system must be available.

Figure 2.-6 shows the schematic of a fixed bed reactor that can also be operated as a fluidized bed reactor.

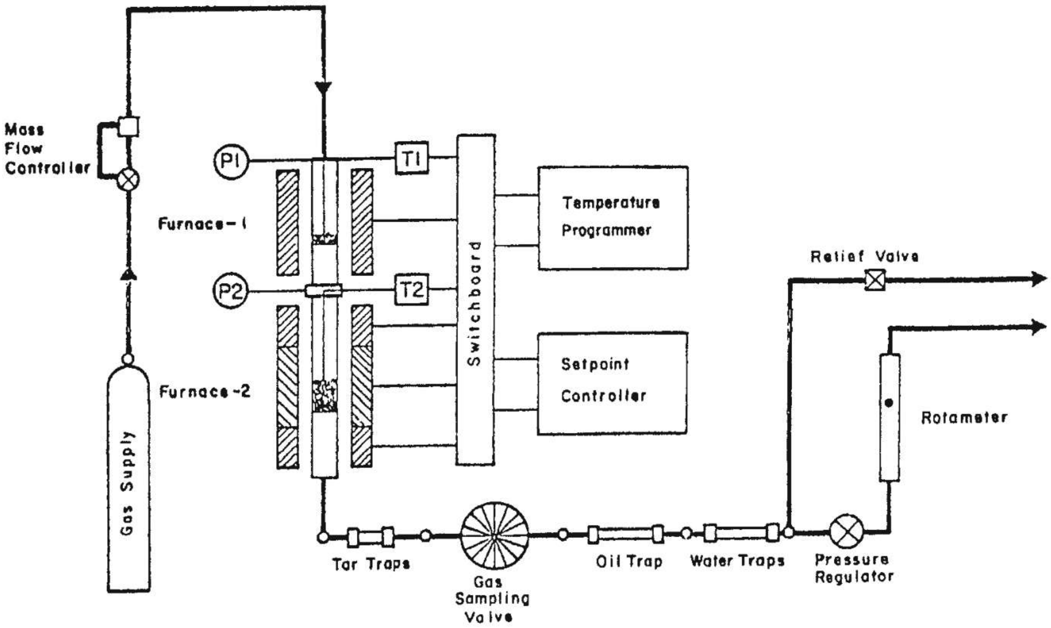

Fig. 2.-6: Fixed bed reactor: used *by Boroson 1987* for characterization of the secondary reactions of sweet gum hardwood tars

The solid sample can be distributed in inert bed material which was realized *by Klingspor et al. 1984*, who had lime dispersed in a sand bed. There the solid bed was located on a gas permeable frit.

Usually the reactor is equipped with a heating (electrically) and/or cooling device which is important to either maintain constant temperature conditions or to run certain heating (or cooling) profiles. The temperature is measured by a thermocouple that is located in the vicinity of the reacting bed or in the reacting bed itself. The gas flow can be maintained through the reactor which is either directed from the bottom to the top or vice versa. Also a gas flow from the side is possible.

Fixed bed reactors are usually operated at temperatures below 1300 K (e.g. *Marban et al. 1995*). Also experiments at elevated pressures can be performed: *Simons et al. 1987,* e.g. carried out experiments in a solid bed reactor at a pressure up to 10 bar.

Advantages and limitations

In Table 2.-1 the heating rates are given but it can also be of imminent importance to know the rates of other changes of reaction conditions such as rate of total pressure change, rate of cooling, rate of total gas flow change, and rate of concentration change.

It is questionable whether the solid sample itself experiences the heating rate. A large sample size, geometry and mass of the sample holder, distance of the heating device, and limited gas flow rates can provide poor mass and heat transfer conditions and they are major restrictions of the actual heating rate of the entire sample (and not only of the outer surface of the sample or sample holder).

experiemental method	sample size [mg]	heating rate [K/s]	temperature [°C]	pressure [bar]
TGA	> 0.01	< 3.3 < 200 [a] < 1000 [b]	< 1800	$1.3 \cdot 10^{-9}$ - 100
Grid Heater	5-30	< 10000	< 1700	vacuum - 240
Matrix Reactor	5-30	< 10000	< 1700	?
Fixed Bed Reactor	> 10	< 1.5 $< 1 \cdot 10^{6}$ [c]	< 1300	< 100

Table 2.-1: Overview of the application range of the different fixed particle methods
a This heating rate can be achieved by lowering the sample from a cold pre-rector zone into a hot reactor zone by an electric winch system
b This heating rate can be obtained when in an already heated reactor a cooled shield is quickly removed from the sample pan.
c laser heating (e.g. CO_2 or Nd:YAG)

In Table 2.-2 a summary of the advantages and drawbacks is given.

Method	Advantages	Disadvantages
TGA	• continuous temperature measurements in the vicinity of the sample • well defined heating rate • continuous weight measurement • good reproducibility • large range of sample size and particle diameters	• slow heating rate
heated grid	• high heating rate • little secondary reactions	• restricted to small particle diameters • uncertainties in particle temperature
matrix reactor	• high heating rates • good particle distribution • little secondary reactions	• restricted to small particle diameters • large uncertainties in particle temperature
fixed bed reactor	• large sample size • continuous temperature measurement	• slow heating rates • large particle to particle interactions • secondary reactions

Table 2.-2: Comparison of fixed particle characterization methods

The thermogravimetric analyzer TGA has the intriguing benefit that continuous measurements of the mass can be performed. This experimental tool is well established and commercially available. But there are also some major drawbacks: The slow heating and cooling rates, a large sample size, and poor heat and mass transfer conditions restrict the field of application of the TGA to reactions with slow rates or reactions where the latter state of the reaction (i.e. equilibrium state) is the matter of investigation. The determination of initial reaction rates is often difficult or impossible. Particle-to-particle interference can sometimes not be excluded which complicates deriving intrinsic kinetic data. Extensive calibration measurements are required to evaluate the influence of the temperature, pressure and concentration on the recorded mass of the sample. This calibration data are finally required to extract the actual mass and its changes from the recorded mass signal which includes the drag force.

The screen (grid) heater and matrix reactor allow much faster heating rates but continuous measurements are restricted to temperature transients and sometimes gas analysis data. Usually only a (too) small amount of solid material is available for off-line characterization. The matrix reactor has the benefit that particle to particle interactions are reduced but the actual temperature and heating rate are difficult to determine.

The fixed bed reactor allows only the investigation of comparably slow reactions. They however have the advantage that more sample material can be used which makes off-line analysis of the solid products easier. Continuous measurements are mostly restricted to gas analysis. However there exist also setups of fixed bed reactors where only a small sample is used which is heated by e.g. a high energy laser. The characteristic features of such a setup is similar to those of a grid heater.

Single particle experiments can be performed with an electrodynamic balance (EDB), an ultrasonic levitator, an upstream reactor, or an hybrid reactor where electrodynamic, ultrasonic, and gas pressure forces are combined. Also forces such as photophoretic force or photon pressure forces can provide at least a contribution to levitate a particle. These methods allow containerless processing since no neighboring particles or surfaces are in physical contact with the particle under investigation. Particle to particle interactions and contact with other surfaces do not occur and therefore intrinsic kinetics can be derived more easily. These methods are usually very expensive to apply and mostly not commercially available. Furthermore they are difficult to handle especially when fast heating rates are required and temperature transient are measured. The electrodynamic balance is used when small particles are subject of the investigation whereas the upstream and the ultrasonic reactor are used for larger particles. The upstream reactor requires a precise flow profile control: Variations of the transfer conditions are very restricted since gas flow corresponds with the particle size, shape and mass. The ultrasonic reactor gives much more variability as far as transfer conditions are concerned since a gas flow can be introduced simultaneously.

Especially for single particle experiments but also for experiments where only small samples are used, it is extremely difficult to prepare a representative solid sample especially when the base solid material is inhomogeneous. Only numerous experiments at equal experimental conditions can finally provide results representative for the material under investigation. Also off-line characterization of the sample material becomes increasingly difficult with decreasing sample size. Therefore it is crucial to extrapolate especially from single particle experiments toward the base material.

Fluidized Bed Methods

The conditions in fluidized bed reactors can vary in a broad range, for instance the superficial gas velocity varies in a range from 0.03 (*Hayhurst and Lawrence 1995*) to 9 m/s (*Winter et al. 1995a*).

Two different fluidization regimes can be distinguished, the bubbling fluidized bed regime and the fast fluidized bed regime. In bubbling fluidized bed reactors (FB) the bed density is high (about 1400 kg/m^3) and the bed voidage is low (about 0.6). The bubbling fluidized bed can be mainly divided into two different phases: the bubble phase and the particulate phase. The main gas transport takes place in the bubbles which move through the suspended particulate phase and cause the vigorous circulation of the bed material. This vigorous circulation leads to good mixing inside the reactor and causes the typical behavior of the fluidized bed that has many attributes of a liquid. The voidage of the freeboard is almost 1. The superficial velocity is between the minimum fluidization and the terminal velocity (typical superficial gas velocity 0.03 to 5 m/s, depending on the bed material size).

In fast fluidized bed reactors (FF) the superficial gas velocity is higher than the terminal velocity. The reactors consist of the dense region (lower part in the riser with a typical voidage between 0.8 and 0.98) and the transport zone (upper part in the reactor, voidage between 0.99 and 1) but without well-defined boundaries. No bubbles can be observed. Additionally, the cross section area can be divided in a thin particle rich zone at the annulus and a gas rich zone at the core. High velocities cause a good turbulence in the reactor.

This difference features cause a very complex structure of fluid dynamics as well as mass and heat transfer in the reactor. Beside the mass and heat transfer mechanism between bubble and particulate phase (FB) or core and annulus (FF) and the mass and heat transport mechanisms between the reacting particles and the fluidized bed is very important. These mechanisms determine the mass and heat flow to and from the reacting particle during its lifetime in the reactor.

Bubbling fluidized beds:

The typical laboratory scale fluidized bed reactor is a tube with a diameter between 25 and 150 mm and a height between 100 and 2300 mm. Typically the reactor is divided in two zones, the preheating zone and the reaction zone (see Fig. 2.-7). The experimental setup includes different parts, a flow control system to control the gas flow and mixtures of different gases, an external heating system with temperature control to vary the temperature in the reaction zone independently from load of the solid reactant, the feeding system, and an analytical part.

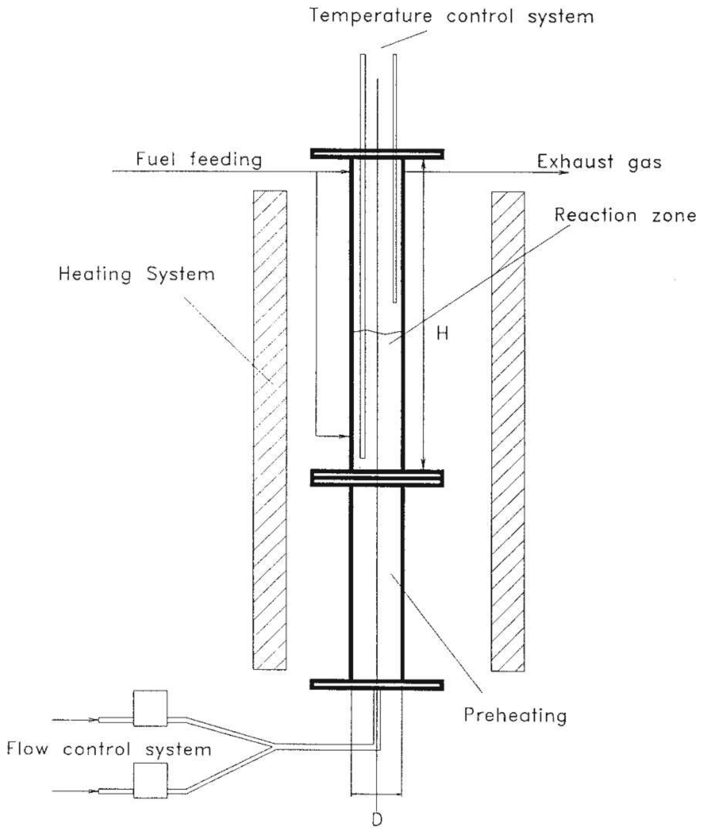

Figure 2.-7: Typical laboratory-scale fluidized bed reactor with flow control system, preheating and reaction zone, and heating and temperature control system.

To minimize catalytic effects of the reactor wall (i.e. NO, N_2O, and NH_3 destruction) and to allow insight into the reactor, a lot of researchers use reactors made of quartz glass. In this case two different setups are used: the whole reactor is made of quartz glass (*Winter et al. 1995b*) or the quartz reactor is put inside a steel vessel (*Tullin et al. 1993*).

Beside laboratory-scale fluidized bed reactors different research groups operate bench-scale or pilot-scale fluidized bed reactors. These reactors are made of steel. The reactors are heated up by natural gas or a gas preheating system is used. The solid reactant is fed into the reactor with a feeding system from the top or from the bottom of the reactor directly into the fluidized bed.

Fast fluidized beds

Figure 2.-8 shows a typical laboratory-scale circulating fluidized bed reactor. Typically the reactor is divided in 4 parts, the riser, the cyclone, the downcomer and the return leg with a non mechanical valve. The experimental setup includes different parts, similar to the bubbling fluidized beds. A flow control system to control the gas flow and mixtures of different gases, an external heating system with temperature control, feeding of the solid reactant and an analytical part.

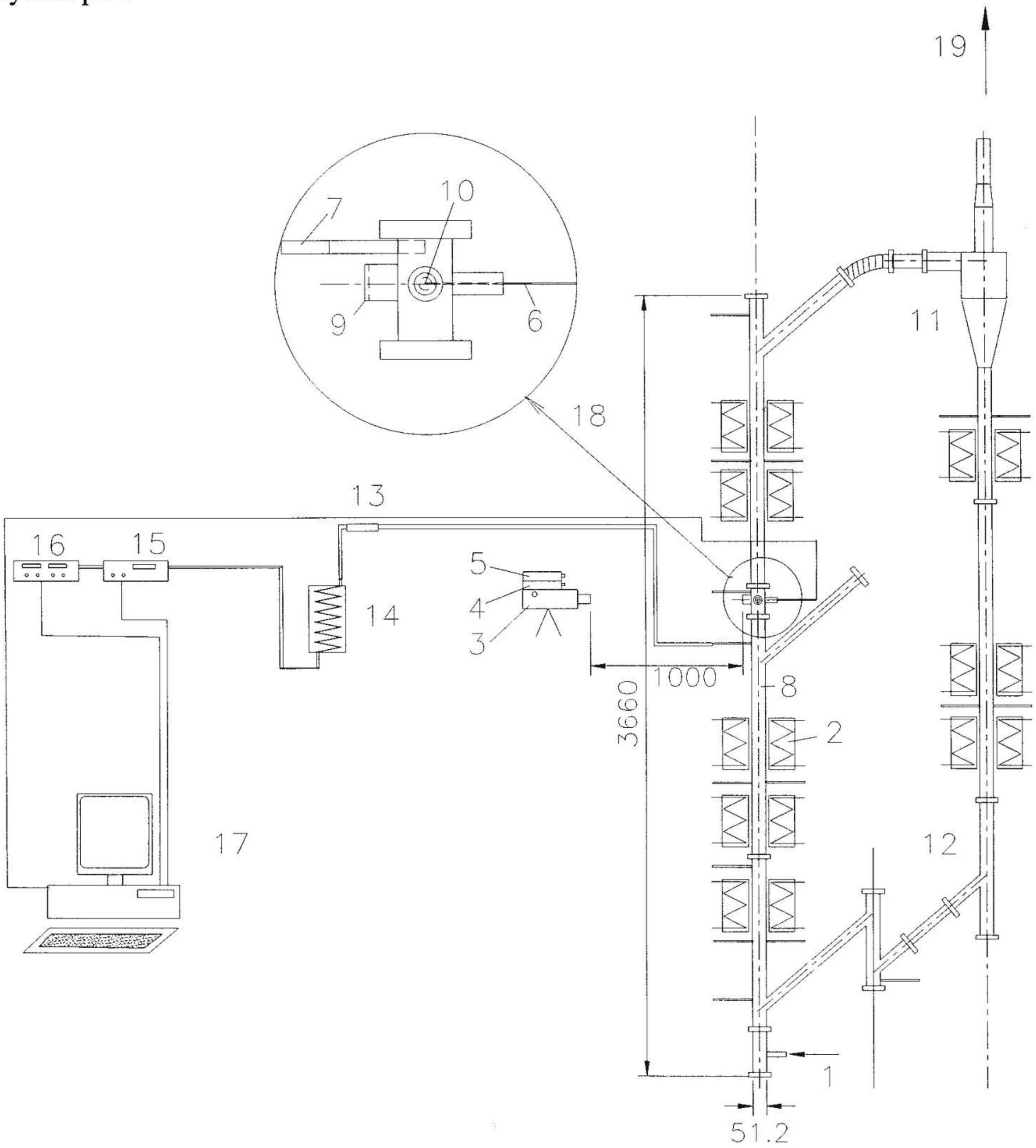

Figure 2.-8: Laboratory-scale circulating fluidized bed reactor, University of Technology Vienna, Institute of Chemical Engineering, Fuel and Environmental Technology. Single particle behavior was studied with a video camera. 1...Air inlet, 2...Heaters, 3...Video camera, 4...Laser, 5...Pyrometer, 6...Thermocouple, 7...Tap for gas analysis, 8...Riser column, 9...Quartz window, 10...Fuel particle, 11...Cyclone, 12...Return leg, 13...Filter, 14...Cooler, 15...O2 analyzer, 16...CO_2/CO analyzer, 17...Data acquisition 18...Video camera equipment, 19...to chimney (*Winter et al. 1995a*).

Usually silica sand is used as bed material (particle size 100 µm to 2 mm). The operating conditions vary in a broad range. Depending on the fluidization mode the superficial velocity varies between 0.1 to 3 m/s (bubbling fluidized bed) and 1.5 to 9 m/s (fast fluidized bed). The bed temperature varied between 600 to 900 °C for combustion and iron ore reduction tests, 300 to 1000 °C for pyrolysis, and 750 to 850 °C for gasification. For studying desulfurization the typical temperature range is from 60 to 150 °C. The range of the particle size is very broad, particles between 0.1 and 50 mm are used. The reactors are operated as differential reactors or as integral reactors. Depending on the size of the reacting particle the operating conditions can be isothermal (small particles) or non-isothermal (large particles).

To investigate conversion of the solid reactant in laboratory-scale fluidized bed reactors two principal methods are used, the single particle or the multiple particle method. Single particle conditions in laboratory-scale fluidized bed will be obtained when the numbers of particles are small enough so that the emissions from one reacting particle will not interfere with the neighboring particles.

Depending on the aim of the investigation different species in the flue gas are quantified. In order to investigate the kinetics of carbon conversion different carbon species (e.g. CO, CO_2, total hydrocarbons (THC)) are quantified and a carbon mass balance is performed (see *Winter et al. 1995b*, *Brunello et al. 1996*). Other research groups measure the size of the fuel directly with video cameras (refer to *Fuertes et al. 1993* and *Winter et al. 1995a*) or collect the particles after immediate nitrogen quenching and measure particle diameter or particle mass (*Halder et al. 1993, Fuertes et al. 1993, Samolada and Vassalos 1991, Wildeger-Gaismaier and Agarwal 1990, Zhang et al. 1990)*. Figure 2.-8 shows the experimental setup to obtain the fuel size during combustion directly with a video camera. The particle is fixed on a thermocouple in the riser and is observed with a video camera through a quartz window.
Fuertes et al. 1993 located the sample material in a separate basket to prepare partially combusted coke fractions. The basket comprised a bed of sand particles supported by a mesh of stainless steel. When the operation temperature was reached the coke particles were added. At a given time the bed was quenched with nitrogen and the coke particles separated by sieving. The burnoff was evaluated by weighing.

To obtain accurate concentration measurements, deposition, chemical reactions and adsorption in the sampling line must be minimized. This may require special materials, heated sample lines, or quenching of the reactions. For example, in order to quantify HCN and NH_3 in combustion gases it is necessary that the gas sample line and the gas cell are heated above 100°C, because in a cold sample line the water condenses and NH_3 and HCN are absorbed (*Wartha et al. 1997*). Tubes should be as short as possible. Enlargements, fittings, etc., should be avoided in order to minimize axial dispersion along the sample lines.
In-bed concentrations of oxygen at high temperature can also be measured by zirconia electrochemical cells (*Stubington and Clough 1997, Kleindienst et al. 1997*).
In order to determine gas concentration profiles it is required to measure gas concentration at different points of the reactor. A requirement for sampling is that the sampling rate is sufficiently small, that there is negligible interference with the surrounding bed, and that a layer of solids does not build up on the sample tube. These conditions are considered to be satisfied if the sampling tube is much smaller than the bed dimensions and if the mean gas velocity in the tube is the minimum fluidization velocity or less. The end of the sampling tube must be covered with a fine mesh or a porous tip to prevent the inflow of particles.

Advantages and limitations

Reactivities are commonly measured with fixed bed reactors, entrained flow reactors, and thermogravimetric techniques. But the reactivities measured by conventional techniques may be significantly different from that of the *in-situ* fluidized bed environment. Beside the chemical reaction, the overall reaction kinetics is complicated by other processes such as mass transfer and heat transfer. The different heating rates in the conventional techniques (compare fluidized bed methods) are also a problem. Specially for pyrolysis the product yields depend on the heating rates. To measure reactivities for fluidized bed processes it is necessary to develop an experimental technique which ensures fluidized bed conditions (e.g. high heating rates, high heat transfer). *Stubington et al. 1997* compared two different experimental methods (TGA and FBC) for determining coal particle devolatilization times. The results show a longer devolatilization times (by a factor of 2-4) for TGA experiments compared to fluidized bed experiments. *Kleindienst et al. 1997* compared kinetic experiments from a TGA, a fluidized bed and a drop tube reactor. The kinetic constants can not be compared to each other.

An essential element for the investigation of the kinetics is an accurate estimation of the particle temperature. It is necessary to know the rate of heating of the solid reactant in order to evaluate the mechanism and to estimate the chemical rate. For small particles (diameter < 1 mm) the particle temperature is similar to the bed temperature. In case of large particles it is necessary to determine or to calculate the particle temperature. To measure the temperature histories of large particles a thermocouple can be implanted inside the particle (refer to *Winter et al. 1995a)*. *Prins 1987* concluded that the differences in heat transfer between fixed and freely moving particles in a fluidized bed are only minor.

Disadvantages of the fluidized bed experiments are the difficulty to close the mass balances, variable and imprecise volatile matter residence times and the potential for significant secondary reactions of gas products. Particle residence times are also unknown under conditions when particles can be entrained from the bed.
Single particle conditions in fluidized beds will occur when the number of the particles is small enough so that the emissions from one particle will not interfere with the chemistry of the neighboring fuel particles. This number of particles dependent on the particle size and size of the reactor cross-section. For small particles it is not possible to make single particle tests because the amounts of the evolved gases would be lower than the analytical precisions.

Entrained Flow - Methods

Two different types of entrained flow methods can be found in research laboratories:

- In one type of reactors the flow of the solid reactant and the gas are in the same direction (co-current principle). This is the case when the solid reactant is fed from the same side of the reactor as the gas. This can be either from the top of the reactor or from the bottom. To obtain the co-current mode, specific reactant and operating conditions are required, e.g. particle size, gas velocity, etc. If the solid reactant is fed from the top of the reactor and falls downwards due to gravity and flow conditions, the reactor can be called drop-tube furnace. (This mode can also be obtained under counter-current conditions.)

- In the other type of reactors the flow of the solid reactant and the gas are in the opposite direction (counter-current principle). This is the case when the solid reactant and the gas are fed from different parts of the reactor and specific reactant and operating conditions are fulfilled, e.g. particle size, gas velocity, etc.

In principle the solid reactant is fed in a co- or counter-current mode to the reaction gas in a tube and reacts with the gas along its path through the tube under steady-state conditions. The gas flows are usually controlled by several mass-flow controllers. In Fig. 2.-9 a typical scheme of an entrained flow reactor is presented. In this example the solid reactant and the reaction gas is fed from the top of the reactor. The solid reactant and the reaction gas flow downwards to the quenching section of the reactor (drop-tube reactor). After a well-defined start of the reaction and a certain reaction time at a given temperature, a rapid quenching of the reaction is essential to derive reaction kinetics from the measurements. Conversions are usually obtained by discontinuous analyses of the solid reactant (e.g. ash) after it is removed from the reactor. Additional information is obtained by gas analysis. In Fig. 2.-10 an entrained flow reactor is presented, where the solid reactant is fed from the bottom and quenched at the top.

The reactor basically consists of a tube made of steel, alumina, quartz or special alloys (e.g. FeCrAl). The diameter of the reaction tube should be small, to minimize back-mixing and to obtain laminar flow-conditions. Back-mixing would lead to incorrect residence times in the tube. Usually flow straightener are used after the gas inlet. Radial concentration, temperature profiles should be as uniform as possible (plug-flow conditions). To obtain the optimal length of the reaction tube, the maximum conversions of the solid reactant should be estimated. If the conversion rates are low, long reaction tubes are necessary to obtain conversions which can be measured. Increasing the flow rates lead to shorter residence times but turbulence may increase, too. In addition, it has to be considered that the reaction tube usually accounts for only about 40 % of the total height of the unit. (If the reaction tube is 2 m in length the total height of the unit will be about 5 m.) If the conversion rates are expected as high, it will be difficult to measure fractions of conversions and differential analysis will not be possible. But differential analysis usually is essential to understand the reaction mechanism. If fast reaction rates are expected, especially good and fast mixing of the reactants has to be ensured because mixing must not be the limiting mechanism of the conversion reaction! Usual reaction tube lengths found in literature are in a range of 0.5 to 2.5 m.

Beside actual entrained flow reactors, premixed, laminar flat flame burners can be used where the fuel is suspended into the flame. No reactor walls exist and optical measurements are not hindered. The low but continuous fuel feed rates are difficult to obtain.

Entrained flow reactors (with upward and downward (drop tube) flow) are mainly used to simulate the high heating rates (10^5 K/s) of fine reacting particles (100 μm) existing in burners (Heat transfer by radiation). Because of the high flame temperatures with which pulverized fuel combustors operate, high temperatures in the laboratory-scale units should be obtained. The typical upper limit of the reactor temperature is between 1200 and 1700°C depending on material limitations of the reactor tube which usually consists of ceramic material or quartz. Steel tubes are not so frequently used. Usually single particle conditions are obtained with low but continuous feeding rates (lower limit about 3 mg/s). To change residence time the distance between solid reactant feeding and quenching is varied. The quenching is usually done with a water-cooled quenching probe (collector) supported by N_2 jets at the tip of the probe. Because of this configuration (moveable collector) the total height of the entrained flow reactor can be up to 4 or 6 m whereas the actual reaction zone length is much smaller (between 200 to 2000 mm). The typical range of particle residence time is 50 ms to 1 s. Gas velocities are kept low (0.02 to 2 m/s) to obtain laminar flow conditions. Tube diameters between 5 to 80 mm can be found. Usually tests are done at atmospheric pressure but recently elevated pressure units are used up to 20 bars. The reactor is put in a pressurized vessel.

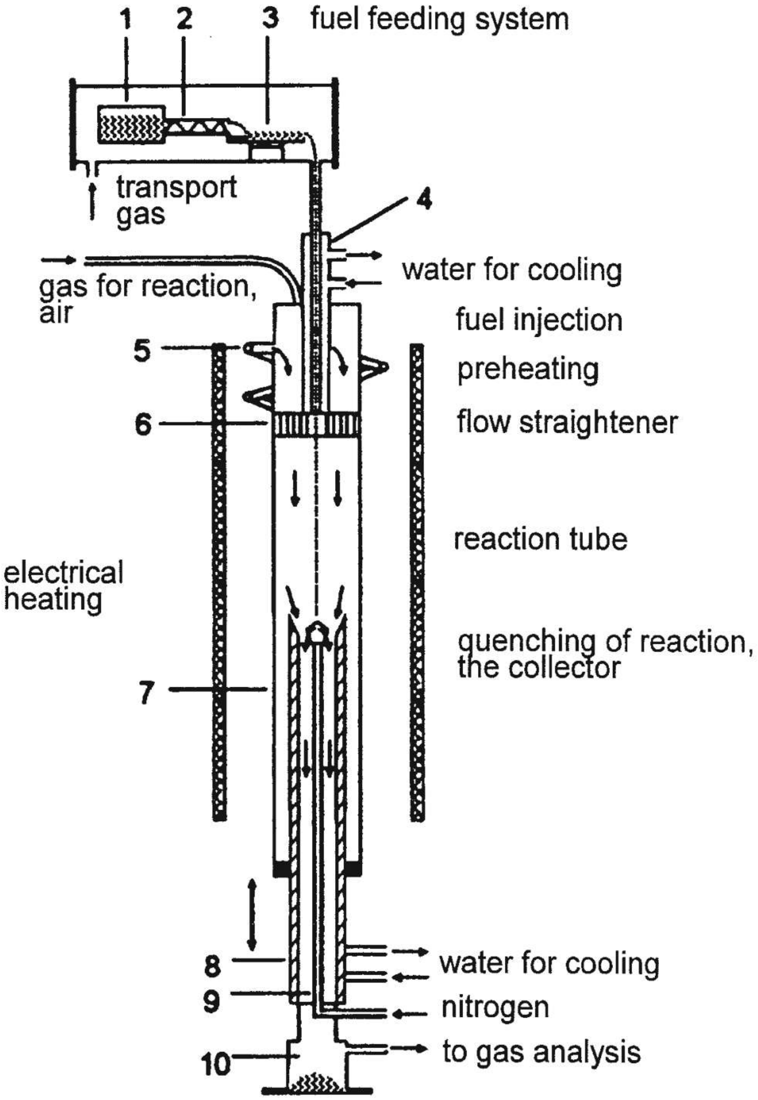

Figure 2.-9: A typical entrained flow reactor (drop-tube). The fuel or solid reactant and the reaction gas are fed at the top to the reactor. The bottom section is optimized for quenching the reaction. The internal diameter of the reaction tube is 56 mm, the height of the heated tube is 2.4 m. The reactor is electrically heated, each of the 4 sections is controlled by measuring the wall temperature of the reaction tube. The total height of the installation including fuel feeding system and quenching section is approx. 6 m. 1...storage bunker, 2...screw feeder, 3...vibration chute, 4...fuel injector, 5...helical tubes for preheating of reaction gas, 6...flow straigthener, 7...reaction tube, 8...collector, 9...nitrogen for quenching, 10...box for residues. (*Kleindienst et al. 1997*)

Problems and limitations

If measurements are done to obtain kinetic rate constants, activation energies, and frequency factors, care must be taken that correct residence times are used as well as conversions and reaction temperature which is the particle temperature. The main uncertainties are the particle temperature. The reacting particle is heated mainly by radiation and usually particle temperatures are assumed or calculated. Only few research groups measure the particle temperature (mainly with optical pyrometers). To obtain the correct conversions the reaction is quenched and the particles analyzed (usually weight, ultimate and proximate analyses). The enrichment of inerts in the solid reactant (e.g. ash, elements) is used as a tracer for conversion. The composition of the gas-phase is obtained by GC, NDIR, FTIR, MS techniques. To obtain correct residence times by changing the distance between solid reactant feeding and quenching, the particle velocity has to be known and constant (flow conditions).

Entrained flow reactors can be used to describe conversion kinetics of solid reactants under a wide range of operating conditions at atmospheric and elevated pressures. Especially high heating rates are obtained similar as in e.g. industrial pulverized fuel burners. Uncertainties in particle residence time, particle temperature and conversion exist.

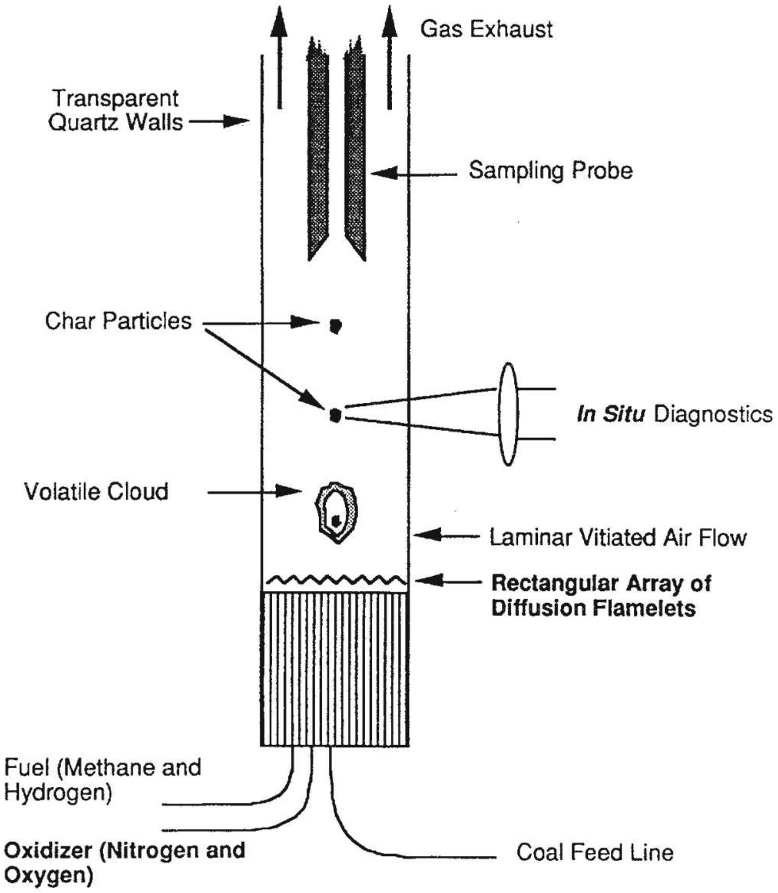

Figure 2.-10: An entrained flow reactor where the fuel (solid reactant) is fed from the bottom and quenched at the top (*Mitchell et al. 1992*). It is an quartz reactor, the cross section is 50 x 50 mm.

Summary

Characterizing an unknown solid reactant for a given process or designing a new process, its characteristics are very important. Without a detailed knowledge of how the solid reactant will behave under given operating conditions, the process may fail.

Beside the basic characteristics (type of the solid reactant, particle size, density, proximate and ultimate analysis, ash composition, ash melting, e.g. refer to *Reisinger and Hofbauer 1996*) its conversion reactivity is very important. This reactivity determines how fast the solid reactant will react under given conditions, e.g. how fast the reaction with O_2 (combustion) or H_2 (reduction) might be. Of course, its basic characteristics will allow to speculate about its reactivity but in literature only few and not very well tested correlations exist.

Additionally these correlations are not necessarily independent from the experimental set-up used. To minimize the risks for process optimization or process design the solid reactant should be tested at conditions as close to the actual conditions of the process as possible. Although chemical similarity can be obtained under certain conditions, in the case of studying heterogeneous reactions the chemical similarity rules have to be fulfilled (refer to Chapter 3).

Therefore TGA experiments with very low heating rates can not be used to describe the behavior of a fuel in a pulverized fuel flame or in a fluidized bed. If a pulverized fuel is burned in a flame the fuel undergoes high heating rates. Tests with small fuel particles typically for pulverized fuel flames and with high heating rates should be done (entrained flow reactors may be a good choice, but also burners, grid heaters and matrix reactors may be useful).
If the solid reactant will be used under fluidized bed conditions it should be tested in a laboratory-scale fluidized bed reactor, no matter if it undergoes oxidation, reduction or any other reaction.
If the fundamental behavior of the solid reactant should be tested or its composition studied, TGA tests with small particles may be appropriate. Mass and heat transfer restrictions can be almost excluded and the solid reactant itself studied. Also for grate combustor conditions TGA measurements with low heating rates may be applicable as well as fixed beds.

A comparison of typical operating conditions of the industrial-scale gas-solid processes studied in this work and laboratory-scale methods are presented in Table 2.-3.

Residence times in laboratory-scale units are relatively short and uncertainties in the time resolution are the consequence. Care has to be taken to close the mass balances and to optimize the sampling system. The low softening and melting temperatures of ashes have to be considered especially in fixed bed and fluidized bed reactor tests.

Beside the technical restrictions of the experimental set-up, it should be mentioned that the costs of the described laboratory-scale units differ significantly as well as the costs of the different analysis methods applied. Depending on the time and the experience of the researchers and technicians operating those units and deriving the information, the personal costs will vary significantly with the different techniques.

	COMBUSTION			IRON ORE REDUCTION	SINTER-PROCESS	DE-SULFURIZATION
technology	grate	fluidized bed	entrained	fluidized bed	grate	fluidized bed
gaseous reactants	O_2 (air)	O_2 (air)	O_2 (air)	H_2, CO, CH_4 (steam reformed natural gas)	O_2 (air)	SO_2, CO_2, HCl (flue gas from pulverized coal comb.)
chemical processes	thermal decomposition, carbon oxidation NO_x/N_2O formation	thermal decomposition, carbon oxidation NO_x/N_2O formation	thermal decomposition, carbon oxidation NO_x/N_2O formation	reduction of iron ore to iron	carbon oxidation, oxid. of metallurgical waste	$Ca(OH)_2$ forms $CaSO_3$, $CaSO_4$, $CaCO_3$, $CaCl_2$
temperature of the solid [°C]	400 - 1000	600 - 950	900 - 1700	600 - 900	800 - 1400	60 - 150
pressure [bar]	atmospheric	1 - 17	atmospheric	11	atmospheric	atmospheric
superficial gas velocity [m/s]	1 - 4	1 - 2.5 (bubbling) 3 - 8 (circulating)	5 - 10	~1 (bubbling)	1 (cold)	1 - 5 (circulating)
heating rates	low	medium - high	very high	medium - high	high	low
solid reactants	biomass, waste	coals, biomass, waste, sludge	coals, co-combustion with biomass	iron ore	cokes, alternative fuels: metallurgical waste	$Ca(OH)_2$
particle size [mm]	10 - 100	1 - 30 (bubbling) 0.5 - 10 (circulating)	0.010 - 0.100	0.05 - 6	0.2 - 5 (cokes)	0.001 - 0.01
laboratory-scale methods	• TGA (with low heating rates) • fixed bed	• fluidized bed (bubbling and circulating)	• entrained flow • burners • grid heaters • matrix reactors	• fluidized bed • fixed bed	• fixed bed • fluidized bed	• TGA • fluidized bed (circulating)

Table 2.-3: Comparison of typical operating conditions of the industrial-scale gas-solid processes studied and laboratory-scale methods.

Lots of kinetic data can be found in literature (mainly coals have been tested, biomass data and data of other solid reactants are rather rare) but often the rate constants differ in 2 orders of magnitude for the same solid reactant. For modeling purposes it is often very difficult to decide which data can be used for the conditions modeled. It should be possible to develop an international database where various different solid reactants are not only described by their basic characteristics (e.g. proximate and ultimate analysis) but also by their reactivities.

A drawback of this idea is that very different laboratory-scale units and different models are used to derive the kinetic parameters. But maybe in future it will be possible to standardize reactivity tests similar as the tests for calorific value or for proximate and ultimate analysis.

A different approach is to use well-characterized solid reactants for the calibration of the specific laboratory-scale units (e.g. graphite as been used in *Wartha et al. 1997* for the calibration of a laboratory-scale fluidized bed reactor for char combustion and 1,8-naphthalene-dicarboxylic acid anhydride for thermal decomposition). The measured reactivities will then be based relatively to the reactivity of the calibration reactant.

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3. THE CONCEPT OF CHEMICAL SIMILARITY

In designing a new process or optimizing an existing one for a new solid reactant it is very important that as much information as possible is available about the characteristics of the new solid reactant from the very beginning. Without a detailed knowledge about the solid reactant's behavior under operating conditions in the industrial-scale unit unexpected problems may arise, especially in the late stages of the project which may lead to process failures. Even if co-combustion of a fuel is considered in an existing plant (e.g. co-combustion of biomass with coal), the fuel's characteristics have to be known.

Laboratory-scale units offer substantial help in characterizing an unknown solid reactant. The advantages of these rather small units compared to the industrial-scale units are:

- laboratory-scale units are inexpensive
- their operation costs are very low
- their availability is very high, no restrictions exist due to production requirements (e.g. power production)
- changes in their set-up can be done quickly and cost effective
- operating conditions can usually be varied in a broad range, no restrictions exist to keep within the optimum range

But beside these advantages uncertainties exist. The laboratory-scale units are much smaller as the industrial-scale units. Refer to Fig. 3.-1, where a typical industrial-scale circulating fluidized bed boiler is compared to a laboratory-scale circulating fluidized bed combustor.

In the industrial process fluid dynamics and chemistry have to be considered. Fluid dynamics determine the stable operation range of the gas - solid process, gas and particles' residence time distribution, mixing, contact time and related features. But chemistry affects fluid dynamics and also determines the operation range (e.g. temperature, selectivity). Therefore detailed knowledge about fluid dynamic fundamentals as well as chemistry is essential.

Much effort has been put into developing correct scaling laws or similarity rules for fluid dynamics. Dimensionless groups have been derived describing the flow conditions under the boundary conditions used in the different regimes (viscous, intermediate or inertia regime, refer e.g. to *Glicksman 1988*). These scaling laws are used to design laboratory-scale units where the flow pattern obtained is similar to the flow pattern of industrial-scale units. Then, the flow pattern can be studied in detail in the laboratory-scale units (often made of plexiglass) and different designs of the industrial-scale unit can be tested. From these tests much knowledge can be gained about the optimal configuration of the industrial-scale unit. This is a very cost effective approach and minimizes the risks of process design (refer to *Steinrück et al. 1989*).

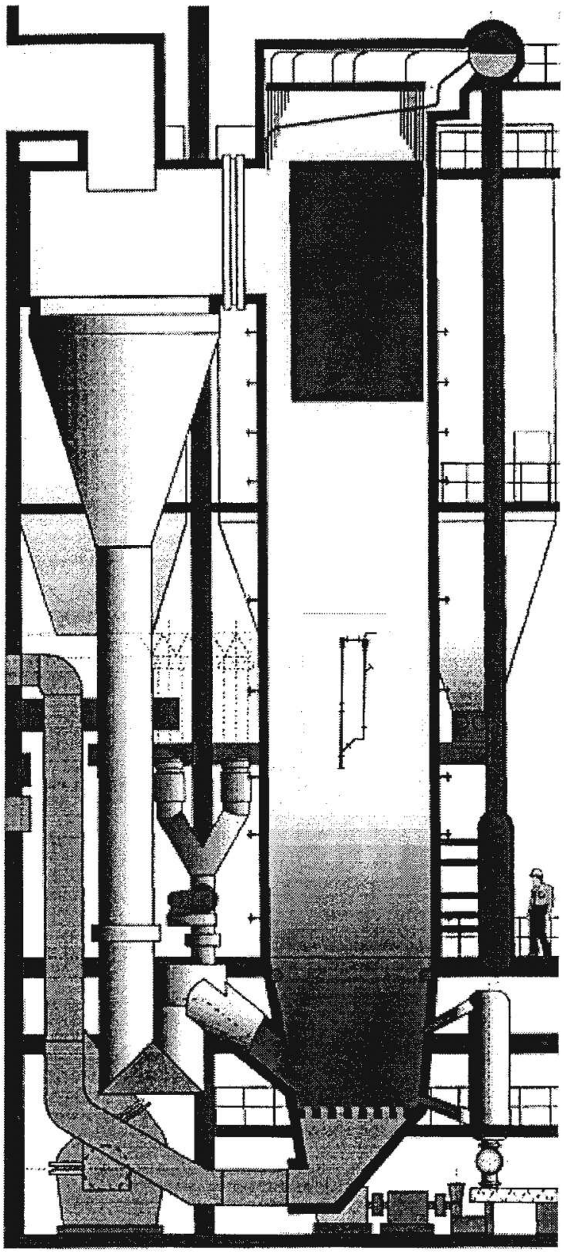

Figure 3.-1: Comparison of a typical industrial-scale circulating fluidized bed boiler with a typical laboratory-scale circulating fluidized bed combustor. The riser of the circulating fluidized bed boiler is 9.6 x 4.8 m in cross-section and 28 m tall. Its thermal power is 137 MW. The laboratory-scale circulating fluidized bed combustor is 35 mm in diameter and 2.4 m tall. For comparison it is put inside the riser of the industrial-scale unit.

The Traditional Approach

The basic idea of the traditional approach is to mirror the whole industrial process in the laboratory (refer to Fig. 3.-3), i.e. the laboratory-scale process is a "small" industrial-scale process. Then scale-up factors, usually dimensionless groups, or models are used to transfer the laboratory results to the industrial scale.

E.g. in *Werther 1978* this approach has been used successfully for a simple irreversible first order catalytic reaction. *Werther 1978* applied the two phase model for fluidized beds for heterogeneously catalyzed reactions (the Shell process for catalytic HCl oxidation) and found that high conversions can be achieved easily in laboratory-scale reactors. However, if the diameter of the unit increases the height of the reactor has to increase substantially to obtain similar conversions (refer to Table 3.-1). The reasons are the much lower mass transfer rates between bubble and emulsion phase in the large scale reactors.

	diameter	height	conversion
laboratory-scale	d = 0.10 m	h = 0.20 m	90 %
pilot-scale	d = 1.00 m	h = 2.00 m	90 %
laboratory-scale	d = 0.10 m	h = 0.10 m	99 %
pilot-scale	d = 1.00 m	h = 2.00 m	≈99 %

Table 3.-1: Comparison of the basic dimensions of a fluidized bed reactors of two sizes at constant conversion (example taken from *Werther 1978*, refer also to Fig. 3.-2).

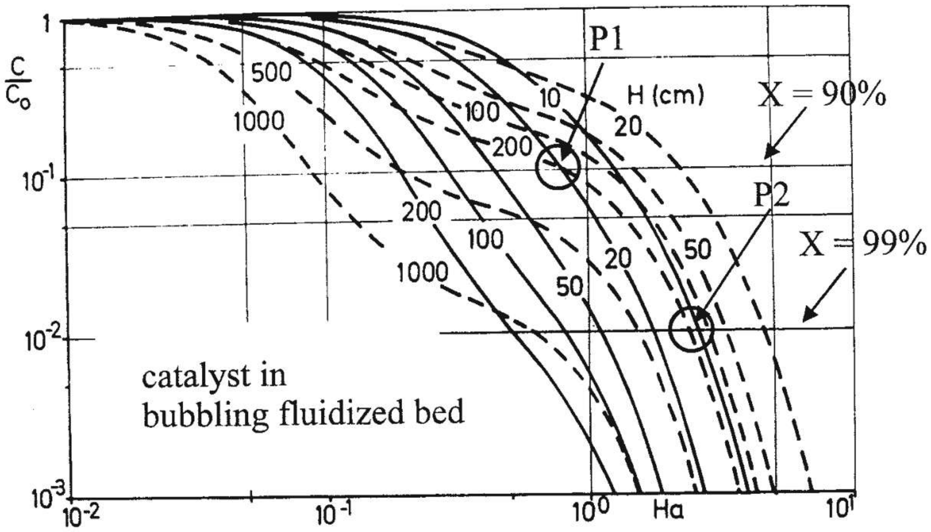

Figure 3.-2: Scale-up of a fluidized bed reactor with catalyst (example taken from *Werther 1978*). Solid lines indicate the results for the laboratory-scale reactor (d = 0.1 m), dashed lines indicate the results for the pilot-scale reactor (d = 1 m). X indicates conversion. P1 and P2 are used as examples for comparison with low and high Hatta (*Ha*) numbers, respectively.

The dimensionless groups, the Hatta number (*Ha*), the number of mass transfer units N_α and the ratio of film volume (cloud and wake) to the emulsion phase volume (Φ), characterize the conversion in the fluidized bed reactor. They were identified by applying the film theory and solving the governing differential equations, considering the boundary conditions. N_α and Φ depend on the reactor design, the bed material (the catalyst), the fluidizing gas and operating conditions and can be calculated. With this knowledge and with known chemical kinetics (considered in the *Ha* number) design diagrams can be developed (refer to Fig. 3.-2). These diagrams (for typical results refer also to Table 3.-1) confirm that if too small units are used in the laboratory-scale mass transfer and conversion will be high in the laboratory-scale but the conversions in the industrial-scale reactors are likely to be overestimated, especially in systems with fast chemistry, i.e. with high *Ha* numbers. This is in agreement with measurements and scale-up experience. In Fig. 3.-3 the traditional approach is illustrated.

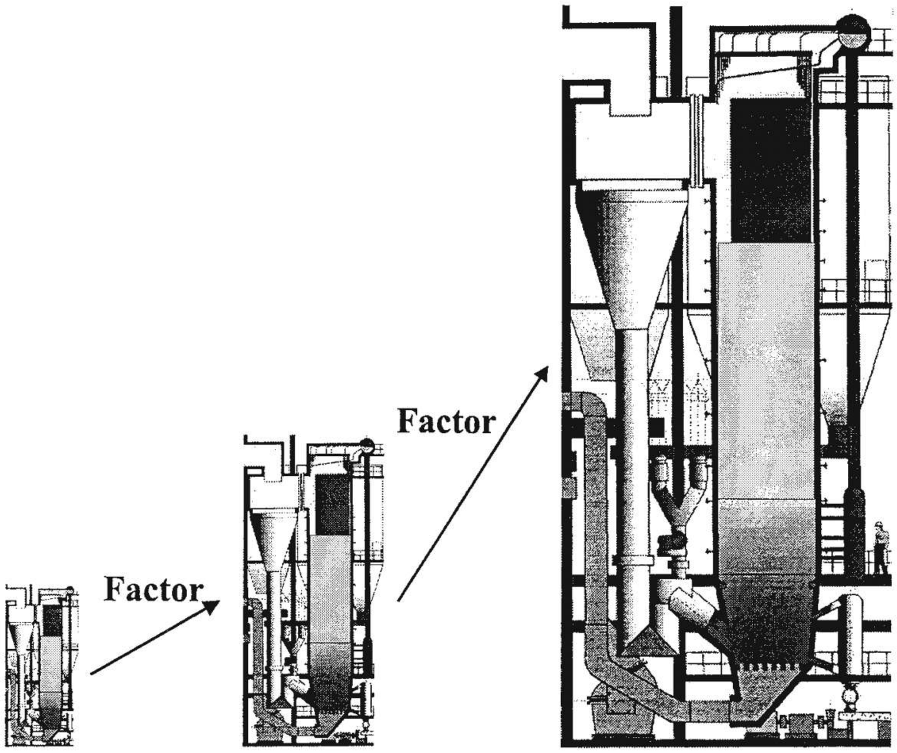

Fig. 3.-3: Illustration of the traditional approach for scale-up. Factor stands for a given set of dimensionless groups or models.

In Table 3.-2 an overview of dimensionless groups is given which are involved in characterizing processes of increasing complexity.

reactor/system	**characterizing dimensionless groups**
flow tube	Re, Eu, L/d
+ particles in flow tube (two phase flow)	+ Re_p, Fr_p, Ar, ρ/ρ_p, L/d_p, Ψ, ϕ_s
+ heat transfer to particles	+ Nu_p, Pr
+ mass transfer to particles	+ Sh, Sc
+ non-isothermal particles	+ Bi_h
+ concentration profiles in particles	+ Bi_m
+ chemical reactions in flow tube	+ DaI
+ mixing effects	+ Bo (Pe)
+ chemical reactions inside particles	+ $DaII$, ϕ
+ chemical reactions inside particles with heat generation during reaction	+ $DaIII$, $DaIV$

Table 3.-2: Examples of dimensionless groups involved in different processes with increasing complexity.

If a researcher wants to study the industrial process in a laboratory-scale unit, he or she has to consider the similarity rules for fluid dynamics and for the chemistry. Usually for the scaling of the two-phase flow occurring during the conversion of solid reactants several dimensionless numbers have to be fulfilled (particle Reynolds number, Froude number, ratio of gas to solids density, ratio of particle size to all lengths of the reactor, particle size distribution and shape, refer to Table 3.-2). Additionally, to these numbers the same temperature, pressure and species concentrations have to be used for reacting particles (Biot numbers, Damkohler numbers, Thiele modulus). If all these restrictions are considered the size of the laboratory-scale model will be exactly the same as the industrial-scale unit.

Scale-Up In Practice

In practice there are three main factors to consider in the development of a new process:

- On one hand it is important to minimize the risk of the new process. The start-up of the new unit should be done without major problems. And operating the new unit should be simple. This implies that the reactor has been tested extensively in the laboratory-scale and in the pilot-scale as well as its equipment and scale-up is done in small steps.
- On the other hand it is important to minimize the costs for the development of the new process. The more intermediate steps exist between laboratory-scale and industrial-scale the more expensive is the process development.
- In addition to the above mentioned, time is also of great importance. The time for the development of a new process should be as short as possible to compete with the constraints of a changing market.

Therefore experience and the development of reliable methods for scale-up and process development are necessary.

In the following examples from industry will be given showing how the problem of scale-up is approached:

One of the major advantages of circulating fluidized bed combustors is that low-rank fuels can be burned efficiently while allowing considerable variability in fuel characteristics and being environmentally friendly. CFBCs have proven its performance capability in the 250-300 MWe range. However, the next milestone in this field will be the step to 600 MWe and to demonstrate the competitivness of CFBCs in electricity generation in comparison with the well-known reference technology - pulverized fuel combustion (*Bursi et al. 1999*). The experience gained from two large French CFBCs - Emile Huchet 4 (125 MWe, ≈300 MW_{th}, 96 m^2 cross-section, 33 m in height) and Provence 4 (250 MWe, ≈600 MW_{th}, 170 m^2 cross-section, 37 m in height) are used to step towards the 600 MWe.
In Fig. 3.-4 the design concept of the Provence 4 250 MWe CFBC can be seen. The CFBC is divided in two main zones (two legs) (for details of the combustion chamber refer to Fig. 3.-5). It can be seen as two CFBCs attached to each other with two separate bottom zones but with one joint riser. Four cyclones are used for gas - solid separation and solids recirculation.

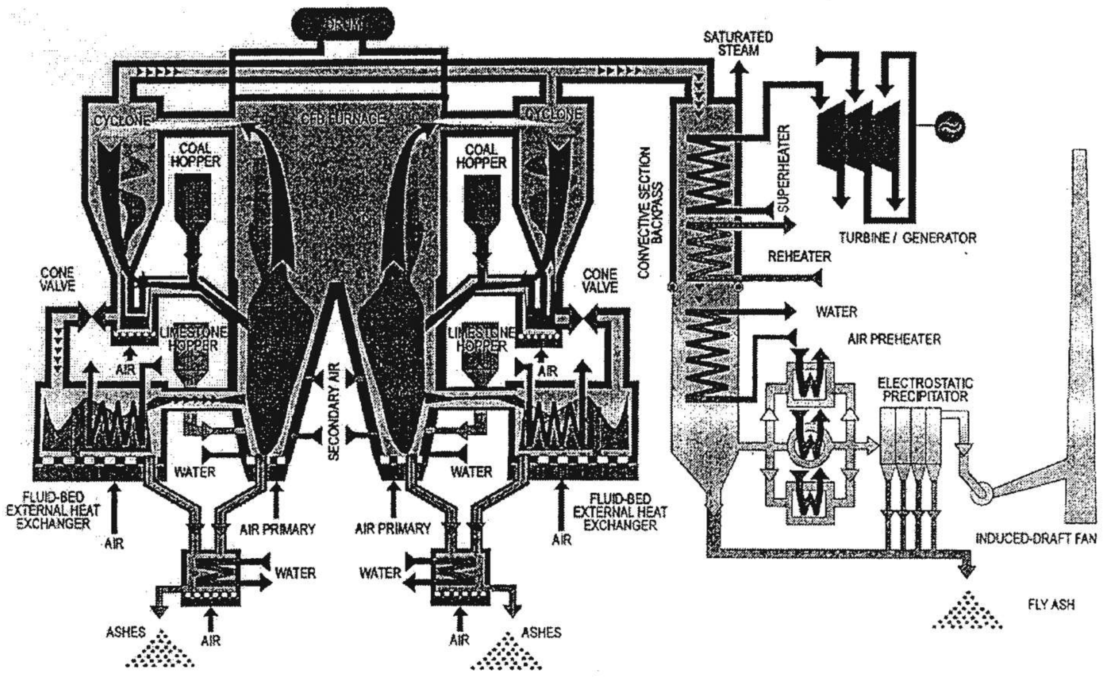

Fig. 3.-4: The Provence 250 MWe CFBC (*Jaud 1997*).

This scale-up concept to combine two units to one is frequently used in industry and reduces the risks significantly. The reactor dimensions (e.g. height) have not to be increased so much and scale-up factors based on these dimensions can be kept low (refer also to *Darling and Li 1997*, where the design of a 350 MWe CFBC is discussed).

It is also usual to build two units very close to each other using the same infrastructure (e.g. fuel handling, flue gas ducts, chimney). This concept is realized e.g. in the Tonghae thermal power plant (Korea) which consists of two separate 200 MWe CFBCs. The first unit is in operation since October 1998. The commercial operation of the second unit is expected in October 1999 (*Lee et al. 1999*).

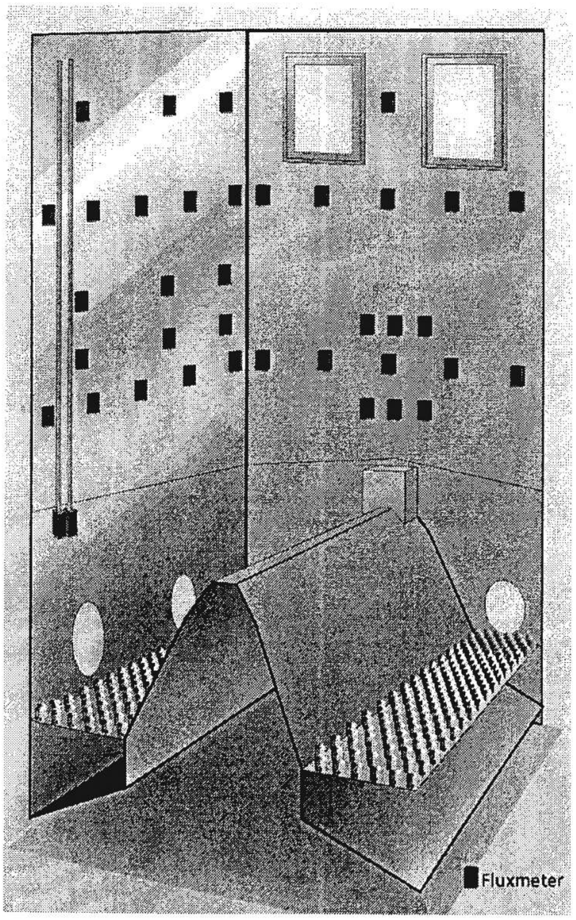

Figure 3.-5: The combustion chamber of the Provence 250 MWe CFBC (*EdF 1999*).

In *Schenk et al. 1998* a newly developed process for the reduction of fine iron ore is presented and discussed.

Most of the world's iron ore consists of fines (about 80 %) and therefore ecological and economical pressures require the development of new hot-metal production technologies on the basis of coal and fine iron ore.

For the development of this new process called FINEX the experience from the COREX and various fluidized bed processes were used. The COREX process uses coal and iron ore lumps (refer to Fig. 3.-6). The iron ore lumps are pre-reduced in a reduction shaft before transferred into the melter-gasifier reactor where the hot metal is produced. Because of the reduction shaft fine iron ore cannot be used directly in this process. The COREX process is a proven technology and industrial-scale units exist around the world. On the other hand fluidized bed processes have been developed and optimized to use fine iron ore which is reduced by reformed natural gas. Hot briquetted iron is the product (refer to Chapter 1). The reduction takes place in a series of fluidized bed reactors. Elements of this technology, the fluidized bed reactors, are used in the FINEX process to feed the fine iron ore into the melter-gasifier and for pre-reduction (refer to Fig. 3.-7). Obviously, the reducing gas differs in its composition in the FINEX process from the other processes. Therefore the reduction kinetics of the fine iron ore are different. However, this concept of scale-up reduces the risks in the development of the new process significantly.

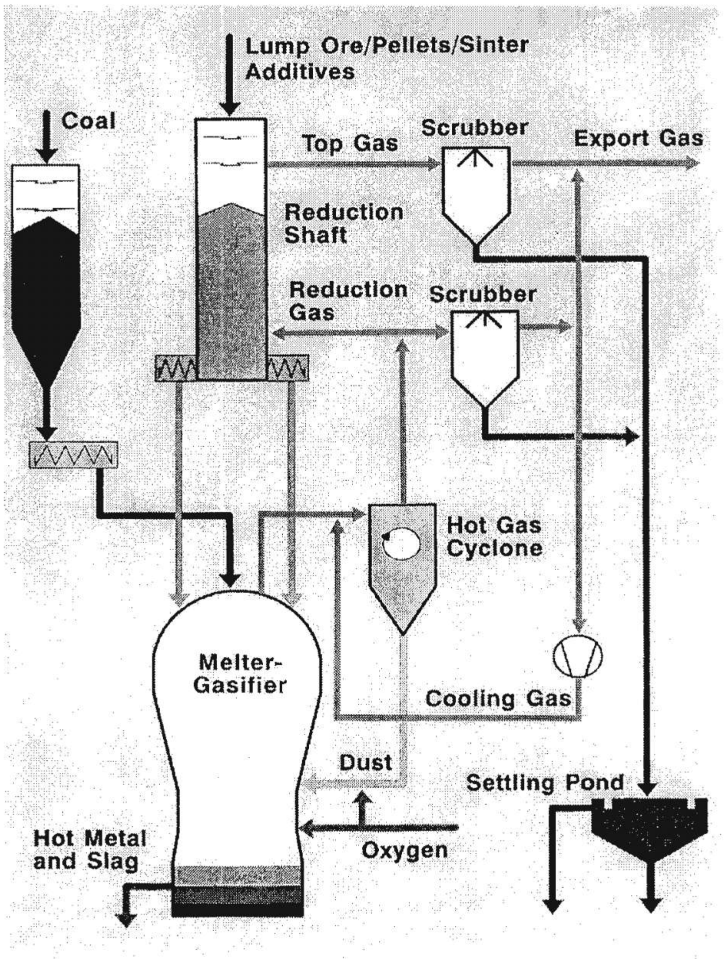

Figure 3.-6: The COREX process (*VAI 1997*).

In parallel this new process has been tested in laboratory-scale (15 t of fine ore/day). The laboratory-scale unit consists of one reactor in which the continuous operation of the FINEX process was tested by simulating each reactor individually. In addition tests were performed to study fluid dynamics and iron ore reduction kinetics.
In the pilot-scale unit the whole continuous process will be simulated in 1999 (150 t of fine ore/day). However, from an existing industrial-scale COREX unit the gas will be used (Pohang, Korea).
The capacity of the industrial plant will be approx. 3000 t / day.

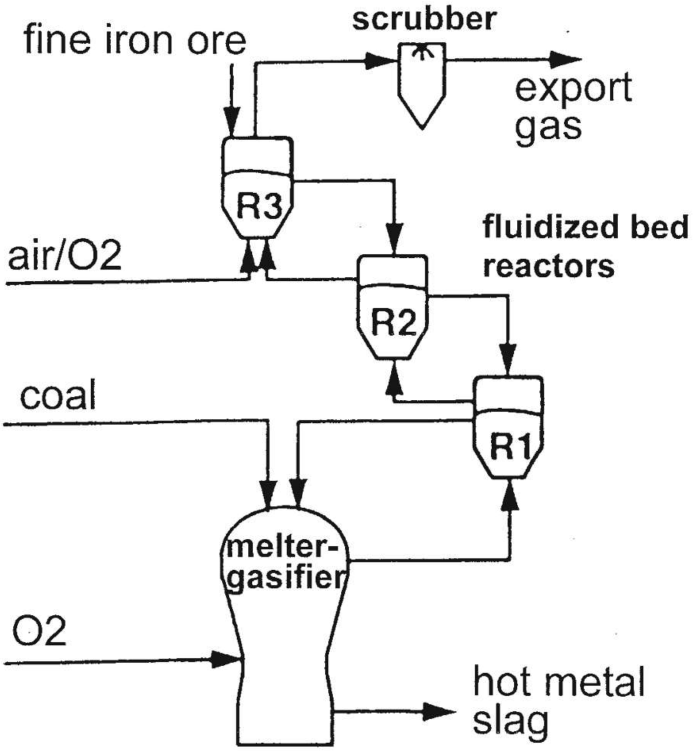

Figure 3.-7: The FINEX process (*Schenk et al. 1998*). R1, R2, R3 are fluidized bed reactors.

The Concept of Chemical Similarity

Temperature and species concentrations are the main influencing parameters of a homogeneous mechanism. But in a complex environment all species concentrations have to be considered, also the species concentrations of the intermediates even if they exist only for a very short time. At combustion temperatures these short-time living species are the radicals. They are highly reactive and control the mechanism. A high temperature does not only effect the rate constants (Arrhenius expression) but also effects the life-time of the radicals which are very important for the selectivity.

In Fig. 3.-8a and 3.-8b respectively, the nitrogen oxidation chemistry is given as an example demonstrating clearly the different reaction paths taken at different conditions. At the higher temperature (1200K) the selectivity for NO is much higher as at lower temperatures (1000K) where more N_2O is formed.

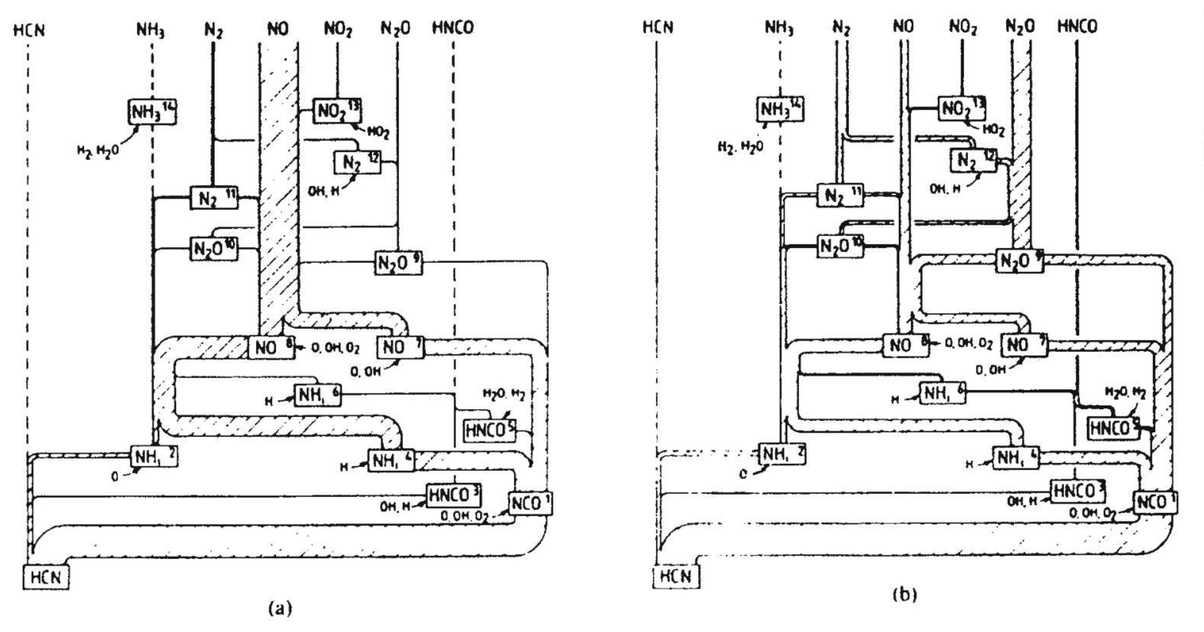

Figure 3.-8: Flow diagrams for fuel-lean oxidation of HCN at (a) high temperature (T=1200K) and (b) low temperature (T=1000K) based on integration of reaction rates of the Kilpinen/Hupa - Model (from *Kilpinen and Hupa 1991*). The thickness of the flows is proportional to the amount of nitrogen from initial HCN converted to the species shown in the box. (For NHi, i stands for i=0, 1, 2). Each box, called reaction box, represents a chemical reaction or a sequence of chemical reactions taking place when a nitrogen species coming into the box (from the left-hand side or right-hand side or from the bottom) is converted to the species written in the box. The small arrows near the box give the most important additional species needed in this reaction.

Not understanding the importance of the radicals, a researcher will look only at the stable species and follow their concentrations during the tests. If the researcher is doing the tests in a unit were the radicals are quenched (e.g. at walls or stable molecules), the radicals' concentrations will differ very much from the radicals' concentrations in the industrial-scale unit and a different mechanism will be studied in the laboratory-scale unit which may not be similar to the industrial process. The initiation step (e.g. ignition) will be delayed and different selectivities will occur (refer to Fig. 3.-8).
Besides temperature, species and intermediate species concentrations total pressure may change the on-going mechanism, too. This is especially a matter of interest in pressurized units (e.g. refer to pressurized fluidized bed combustion).

If the chemistry is studied in a laboratory-scale unit, the researcher has to insure that the conditions and equipment used correspond to the industrial process. Similar to the boundary conditions applied in scaling fluid dynamics, chemical boundary conditions exist.

Usually it is not possible to study all aspects at once in one laboratory-scale unit, but certain aspects (e.g. chemistry) can be studied, the characteristics of the solid reactants tested, if the chemical similarity rules are fulfilled.

Figure 3.-9 illustrates the idea of scaling of the chemistry for the riser of a circulating fluidized bed combustor. A finite volume of the riser (symbolized as cube, which is maybe 50 mm in length or whatever) is taken from the riser which might be 25 square meters in cross-section and 30 m tall. The surface areas of the cube symbolize the boundary conditions.

Without the correct boundary conditions the cube will not fit back into the riser. Inside the cube bed material (ash, silica sand) as well as solid fuel can be found in different sizes and shapes. The gas phase consists of various stable species (e.g. CO, CO_2, CH_4, NO, N_2O, HCN, NH_3, O_2, SO_2) as well as radicals (e.g. OH, H, HO_2, O, NCO, NH_2, NH, N) in different concentrations but at the same temperature and pressure. Then, this cube can be put into a laboratory-scale unit and studied there.

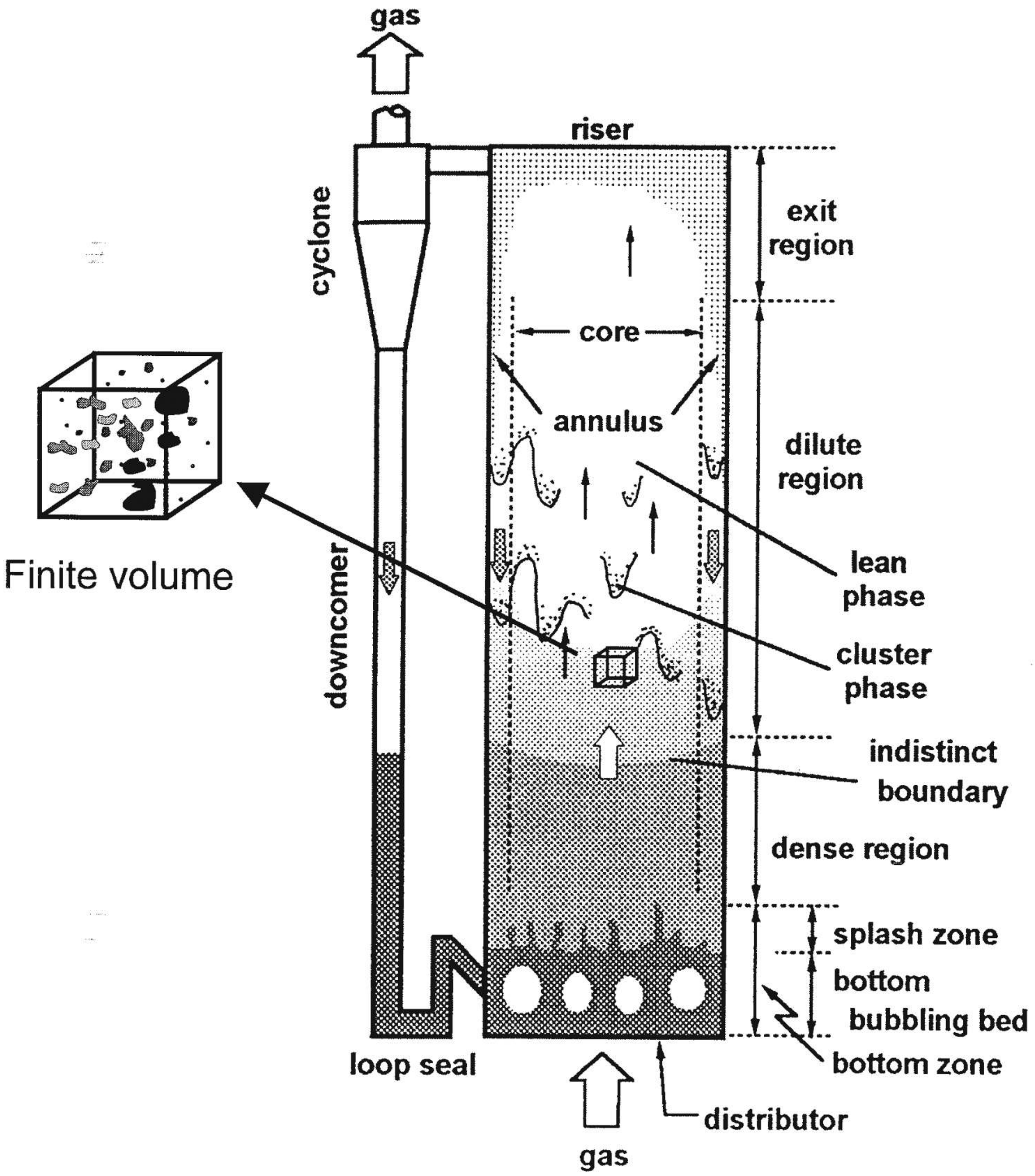

Figure 3.-9: The concept of chemical similarity is shown. A finite volume symbolized as a cube is taken from the riser of an industrial-scale unit. The surface areas of the cube symbolize the boundary conditions. Without the correct boundary conditions the cube will not fit back into the riser. Then the cube can be put into a laboratory-scale unit and studied there. If the chemical similarity rules are fulfilled, i.e. the correct boundary conditions are used, the results obtained in the laboratory-scale unit correspond to the industrial-scale unit. (The illustration of the typical flow structure in the circulating fluidized bed has been taken from *Horio 1997*).

Chemical Similarity Rules

To be able to put the cube back into the riser or - in other words - to obtain results in a laboratory-scale unit which correspond to the industrial-scale unit, it is necessary to fulfill the chemical similarity rules. But what are these chemical similarity rules?

The following analysis is based on a differential analysis. For given conditions small changes (e.g. concentration changes, conversions) will be obtained and the reaction rates will not be integrated with time. Therefore it is not necessary to have the same residence time in the laboratory-scale unit as in the industrial-scale unit, what would usually be very difficult (refer to Chapter 2). Furthermore, complex systems such as gas - solid reaction systems with intermediate species are usually not suitable for an integral analysis (*Baerns et al. 1987*).

In the case of a pure homogeneous reaction system it is not difficult to draw them:

At a given time, it is:

- gas temperature (T_g) and
- total pressure (P) and
- species concentration ($C_1,\dots C_i,\dots C_z$) where z is the maximum number of species in the system considering also intermediate species

or written as equation:

$$r_{hom,i} = \frac{dN_i}{dt}\cdot\frac{1}{V_R} = f_{hom,i}(T_g, P, C_1,\dots,C_i,\dots C_z)$$

where $r_{hom,i}$ is the homogeneous reaction rate of species i defined as the instantaneous change of moles of species i per time (dN_i/dt) based on the reaction volume (V_R) in which the reactions take place.

If the researcher performs tests in a laboratory-scale unit he or she has to provide the same species concentrations at the same gas temperature and total pressure. The conversions measured and kinetic constants obtained then correspond to the industrial process. Of course, mixing must be fast relative to the conversion rates otherwise conversion will depend on mixing, i.e. fluid dynamics and the results will not be independent from the unit used.

In gas - solid reaction systems additional similarity rules exist:

- the particle temperature (T_p) (for isothermal particles, small particles) or the temperature of a certain zone in the particle (for non-isothermal particles, large particles) it is the reaction temperature
- the gas temperature inside the pores of the particle ($T_{g,pore}$).

- the pressure inside the particle (P_p) which might differ from the bulk pressure (P), (e.g. during devolatilization)
- the species' concentrations inside the pores of the particle ($C_{1,p},...C_{i,p},...C_{z,p}$) to consider gas - phase reactions inside the pores and gas - solid reactions at the particle's internal surface
- the species' concentrations at the surface of the particle ($C_{1,s},...C_{i,s},...C_{z,s}$) to consider gas - solid reactions at the particle's external surface
- the physical properties of the solid reactant such as external/internal surface area (A_s), pore structure ($X_{p,pores}$) (size of the pores and distribution)
- the chemical composition of the solid reactant ($X_{p,chem}$) (care has to be taken to impurities which might be catalytic active)

or written as equation:

$$r_{het,i,A} = \frac{dN_i}{dt} \cdot \frac{1}{m_{p,A}} = f_{het,A}(T_{p,A}, T_{g,pore}, P_{p,A}, P, A_{s,A}, X_{p,pores,A}, X_{p,chem,A}, C_{1,p,A},.,C_{i,p,A},.,C_{z,p,A}, C_{1,s,A},.,C_{i,s,A},.,C_{z,s,A})$$

where $r_{het,i,A}$ is the heterogeneous reaction rate of species i defined as the instantaneous change of moles of species i per time (dN_i/dt) based on the actual mass of one type A particle ($m_{p,A}$) in which the reactions take place.

The total change of species i (dN_i/dt) in a finite volume as illustrated in Fig. 3.-9 can be obtained by considering the contributions of the homogeneous and heterogeneous reaction rates. Additionally, it has to be considered that there usually exists a particle size (mass) distribution for each type of particles (e.g. char particles, ash particles, limestone particles).

$$r_i = \frac{dN_i}{dt} = \int_{V_R} r_{hom,i}\, dV_R + \int_{m_{p,A}} r_{het,i,A}\, dm_{p,A} + \int_{m_{p,B}} r_{het,i,B}\, dm_{p,B} + \ldots$$

and for all species it is:

$$r_1 = \frac{dN_1}{dt} = \int_{V_R} r_{hom,1}\, dV_R + \int_{m_{p,A}} r_{het,1,A}\, dm_{p,A} + \int_{m_{p,B}} r_{het,1,B}\, dm_{p,B} + \ldots$$

....

$$r_i = \frac{dN_i}{dt} = \int_{V_R} r_{hom,i}\, dV_R + \int_{m_{p,A}} r_{het,i,A}\, dm_{p,A} + \int_{m_{p,B}} r_{het,i,B}\, dm_{p,B} + \ldots$$

....

$$r_z = \frac{dN_z}{dt} = \int_{V_R} r_{hom,z}\, dV_R + \int_{m_{p,A}} r_{het,z,A}\, dm_{p,A} + \int_{m_{p,B}} r_{het,z,B}\, dm_{p,B} + \ldots$$

leading to a very complex reaction system.

Because of the above mentioned similarity rules for gas - solid reaction systems, the actual fuel of the industrial-scale process has to be used in the laboratory-scale tests. Artificial fuels or solid reactants with well-known compositions (e.g. graphite or chemical substances) can be used as model fuels for calibration of test units (refer to *Wartha et. al. 1997*) or to study different aspects of the fuel type (e.g. *Hirama et al. 1994*). But even if the same solid reactant is used in laboratory-scale tests different results can be obtained, e.g. if the heating rates are different, the evolution of the pore size might be different as well as the decomposition reactions during devolatilization. For instance, to obtain isothermal particles the solid reactant is heated slowly in a thermogravimetric analyzer (TGA) under inert conditions (e.g. in nitrogen or argon) and different species will be released as if the tests were done in a fluidized bed reactor. Can the TGA results then used for designing a fluidized bed process? Therefore the

- heating rates of the solid reactant have to be considered. And this similarity rule affects the conditions in the laboratory-scale unit. (See also fluctuating conditions).

A similar problem which might be of importance for a proper scaling of the chemistry are fluctuations of the gaseous species and memory effects. For instance, in the riser of a circulating fluidized bed the conditions quickly change from oxidizing to reducing conditions and vice versa (*Leckner 1996*). If memory effects are dominant the application of kinetics obtained from tests where the concentration of e.g. oxygen was kept constant will fail.

- memory effects and fluctuations of conditions (e.g. gaseous species concentrations, surrounding temperature)

Also chemical and physical particle - particle interactions might be of importance. Particles of the same type and with the same or different size might interact via homogeneous or heterogeneous mechanism (e.g. ignition). Also particles of different types can interact (e.g. ash melting, sintering). Heterogeneous mechanism will be of major importance especially under fixed bed conditions.

- particle - particle interactions

It is often not possible to fulfill all those very stringent similarity rules to derive chemical kinetics in laboratory-scale units. However, useful information can be obtained, if the researcher is aware of the problems in designing laboratory-scale tests. He or she will know the limitations and will use the obtained results in a proper way depending on the aim of the work.

Nomenclature

a	thermal diffusivity	$[m^2.s^{-1}]$
ρ	density	$[kg.m^{-3}]$
ρ_p	particle density	$[kg.m^{-3}]$
λ	heat conductivity	$[W.m^{-1}.K^{-1}]$
λ_{eff}	effective heat conductivity	$[W.m^{-1}.K^{-1}]$
ν	kinematic viscosity	$[m^2.s^{-1}]$
τ	mean residence time in reactor	[s]
Ψ	particle size distribution	[1]
Φ	ratio of film volume to the emulsion phase volume	[1]
ϕ	Thiele modulus, $\phi = L_{pore} \cdot \sqrt{\frac{2 \cdot r_{het}}{r_{pore} \cdot D_{eff} \cdot C}}$	[1]
ϕ_S	sphericity of particles	[1]
ΔH	reaction enthalpy	[J/mol]
A_S, $A_{S,A}$	external or internal surface area, and of particle type A	$[m^2]$
Ar	Archimedes number, $Ar = \frac{g \cdot d_p^{\ 3}}{\nu^2} \cdot \frac{\rho_p - \rho}{\rho}$	[1]
Bi_h	Biot number for heat transfer, $Bi_h = \frac{k_h \cdot r_p}{\lambda_{eff}}$	[1]
Bi_m	Biot number for mass transfer, $Bi_m = \frac{k_m \cdot r_p}{D_{eff}}$	[1]
Bo	Bodenstein number, $Bo = \frac{u \cdot L}{D_{ax}}$	[1]
C	concentration at outlet of reactor	$[mol.m^{-3}]$
C_0	concentration at inlet of reactor	$[mol.m^{-3}]$
C_i	concentration of species i, i is running from 1 to z	$[mol.m^{-3}]$
$C_{i,p}$	concentration of species i, i is running from 1 to z, inside particle	$[mol.m^{-3}]$
$C_{i,p,A}$	concentration of species i, inside particle type A	$[mol.m^{-3}]$
$C_{i,s}$	concentration of species i, at particle's external surface	$[mol.m^{-3}]$
$C_{i,s,A}$	concentration of species i, at particle A's external surface	$[mol.m^{-3}]$
d	diameter of reactor	[m]
DaI	Damkohler number I, $DaI = \frac{r \cdot \tau}{C}$	[1]
$DaII$	Damkohler number II, $DaII = \frac{r_{het}}{k_m \cdot C}$	[1]
$DaIII$	Damkohler number III, $DaIII = \left\lvert \frac{\Delta H \cdot r \cdot d_p}{k_h \cdot T_g} \right\rvert$	[1]
$DaIV$	Damkohler number IV, $DaIV = \left\lvert \frac{\Delta H \cdot r \cdot d_p^{\ 2}}{\lambda_{eff} \cdot T_p} \right\rvert$	[1]
D_{ax}	axial dispersion coefficient	$[m^2.s^{-1}]$
D_{eff}	effective diffusion coefficient	$[m^2.s^{-1}]$
D_g	diffusion coefficient	$[m^2.s^{-1}]$
d_p	diameter of particle	[m]
Eu	Euler number, $Eu = \frac{p}{\rho \cdot u^2}$	[1]
$f_{hom,i}$	function for homogeneous reactions for species i	$[mol.m^{-3}.s^{-1}]$
$f_{het,i}$	function for heterogeneous reactions for species i	$[mol.kg^{-1}.s^{-1}]$

Fr_p	particle Froud number, $Fr_p = \frac{u^2}{g \cdot d_p}$	[1]
g	acceleration due to gravity	[m.s^{-2}]
h, H	height of reactor	[m] or [cm]
Ha	Hatta number, $Ha^2 = \frac{k \cdot D_{eff}}{k_m^{\ 2}}$	[1]
k	first order irreversible reaction rate constant	[s^{-1}]
k_h	heat transfer coefficient	[W.m^{-2}.K^{-1}]
k_m	mass transfer coefficient	[m.s^{-1}]
L	length of reactor	[m]
L_{pore}	pore length	[m]
$m_{p,A}$, $m_{p,B}$	mass of particle type A, type B	[kg]
N_α	number of mass transfer units	[1]
N_i	number of moles of species i	[mol]
Nu_p	particle Nusselt number, $Nu_p = \frac{k_h \cdot d_p}{\lambda}$	[1]
p, P	pressure	[Pa]
P_p, $P_{p,A}$	pressure inside the pores of the particle, and particle type A	[Pa]
Pe	Peclet number, $Pe = \frac{u \cdot d}{D_{ax}}$	[1]
Pr	Prandtl number, $\mathrm{Pr} = \frac{\nu}{a}$	[1]
r	reaction rate	[mol.m^{-3}.s^{-1}]
r_i	extensive reaction rate of species i	[mol. s^{-1}]
$r_{hom,i}$	homogeneous reaction rate of species i	[mol.m^{-3}.s^{-1}]
r_{het}	heterogeneous reaction rate	[mol.m^{-2}.s^{-1}]
$r_{het,i,A}$, $r_{het,i,B}$	heterogeneous reaction rate with particle type A, type B	[mol.kg^{-1}.s^{-1}]
r_p	radius of particle	[m]
r_{pore}	pore radius	[m]
Re	Reynolds number, $Re = \frac{u \cdot d}{\nu}$	[1]
Re_p	particle Reynolds number, $Re_p = \frac{u \cdot d_p}{\nu}$	[1]
Sc	Schmidt number, $Sc = \frac{\nu}{D_g}$	[1]
Sh	Sherwood number, $Sh = \frac{k_m \cdot d_p}{D_g}$	[1]
t	time	[s]
T_g	gas temperature	[K]
$T_{g,pore}$	gas temperature in the pores of the particle	[K]
$T_{p,}$, $T_{p,A}$	particle temperature, temperature of particle type A	[K]
u	velocity	[m.s^{-1}]
V_R	reaction volume	[m^3]
X	conversion, $X = (1 - \frac{C}{C_0}) \cdot 100$	[%]
$X_{p,chem}$, $X_{p,chem,A}$	chemical composition of particle (function), and particle type A	[1]
$X_{p,pores}$, $X_{p,pores,A}$	pore structure (function), and particle type A	[1]
z	maximum number of species	[1]

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4. METHODOLOGY USED

4.1. EXPERIMENTAL

4.1.1. The Laboratory-Scale Units

In the following the laboratory-scale units used in this work will be presented and shortly described. For further details it will be referred to the corresponding papers.

The formation rate unit (FRU)

The formation rate unit (FRU, see Fig. 4.1.-1) was designed to obtain the formation rates of CO_2, CO, CH_4, SO_2, NO, NO_2, N_2O, HCN, NH_3 and other species generated during single fuel particle combustion. The gas residence times are low (usually < 140 ms) in the hot reaction zone and the composition of the gas is analyzed shortly after the burning fuel particle usually with FT-IR.

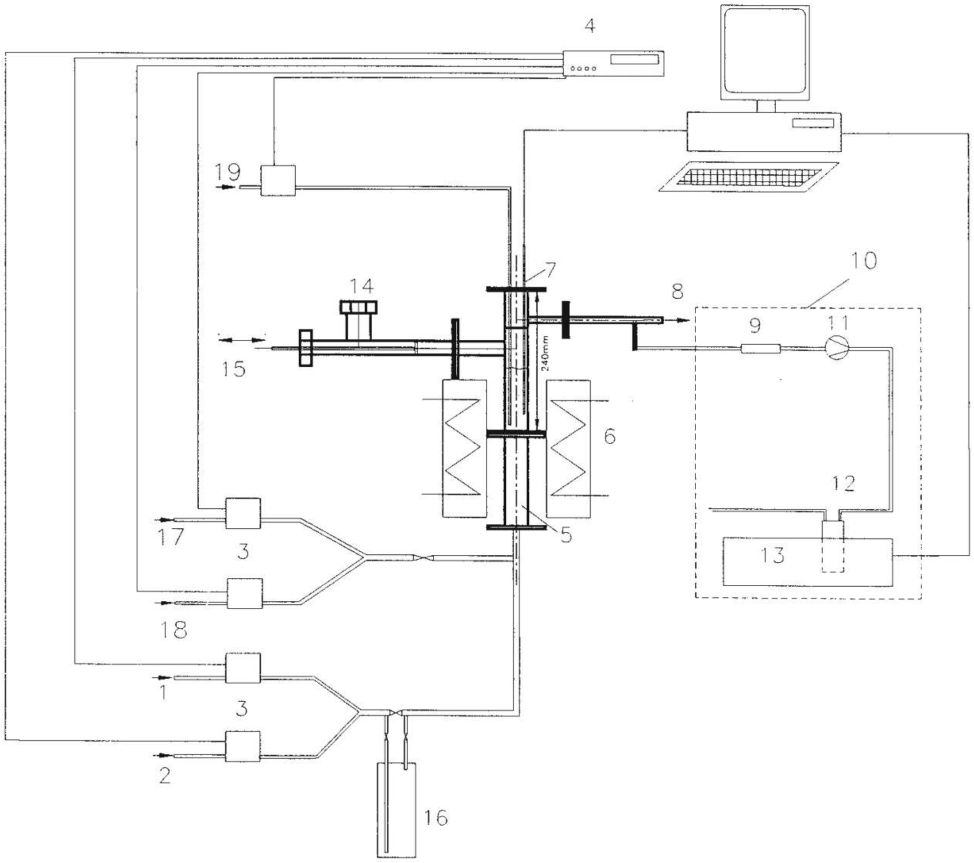

Figure 4.1.-1: The formation rate unit (FRU): 1,2...inlet of fluidizing gas, 3...mass-flow controllers, 4...display for the mass-flows, 5...preheating zone, 6...heating shells, 7...thermocouple, 8...to the chimney, 9...heated filter, 10...heated sample lines, 11...heated pump, 12...heated gas cell, 13...FTIR spectrometer, 14,15...fuel inlet, 16...flask for iodine addition in a water-bath, 17,18...inlet of reaction gas (NH_3, HCN, NO, N_2O)

The FRU (internal diameter 35 mm, height 250 mm) is made of quartz glass to minimize possible catalytic effects of the reactor wall and to allow visual observation. The distributor is a quartz glass frit. A fluidized bed of silica sand was used to minimize temperature gradients around the fuel particle. The FRU is electrically heated by heating shells producing a uniform temperature around the fuel particle (2 to 20 mm in diameter), which was varied between 600 and 900°C. Air/nitrogen mixtures were used to change the oxygen partial pressure of the fluidizing gas between 0.05 and 21 kPa. The superficial velocity was varied between 0.2 and 1 m/s. Additional gases can be added.

Results of the measurements can be found in *Wartha et al. 1996, 1997a,b, 1999* and *Winter et al. 1996a,b,c, 1997a,b, 1999a,b.*

The high-temperature combustor (HTC)

The high-temperature combustor (HTC, refer to Fig. 4.1.-2) was designed for combustion tests of batches of small fuel particles (100 - 5000 μm) at high temperatures (up to 1100°C).

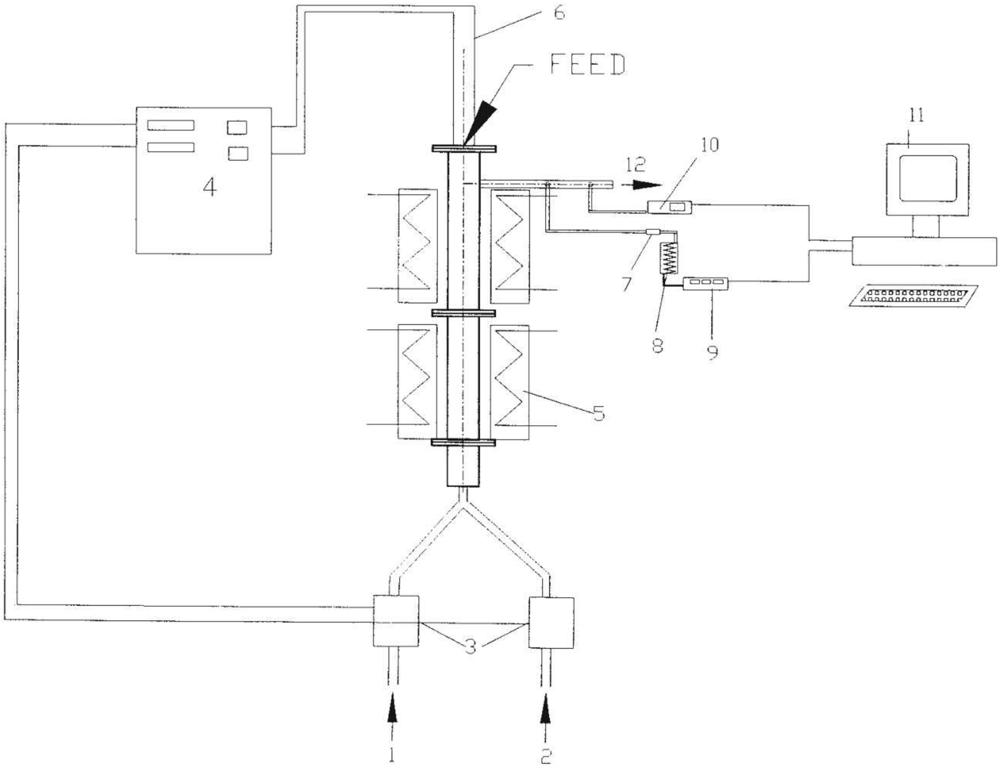

Figure 4.1.-2: The high-temperature combustor (HTC): 1,2...inlet of gas (air/nitrogen, air/oxygen), 3...mass-flow controller, 4...display for the mass-flows, 5...heating system, 6...thermocouple, 7...gas filter, 8...gas-cooler, 9...O2/CO2/CO - analyzer (paramagnetic, NDIR), 10...flame ionization detector, 11...data acquisition, 12...to the chimney

The reactor is made of stainless steel. The HTC is electrically heated with heating shells producing a uniform bed temperature around the fuel particles, which was varied between 700 and 1100°C. Air/nitrogen and air/oxygen mixtures were used to change the oxygen partial pressure of the fluidizing gas between 10 and 50 kPa. The superficial gas velocity was kept constant at 0.3 m/s for all operating conditions, controlled by two mass-flow controllers.

A batch of fuel particles was fed with a nitrogen gas pulse into the HTC. In the flue gas CO_2, CO, THC, and O_2 were measured continuously with NDIR, flame ionization detector, and paramagnetic techniques. The emissions from the fuel particles are quantified and a carbon mass balance is performed (refer to *Winter et al. 1999c*).

The quartz circulating fluidized bed combustor (q-CFBC)

The quartz circulating fluidized bed combustor (q-CFBC, refer to Fig. 4.1.-3) was designed to perform continuous combustion tests under CFBC conditions. During the combustion of the solid fuel concentrations of CO_2, CO, CH_4, NO, N_2O, and HCN were measured along the height of the riser.

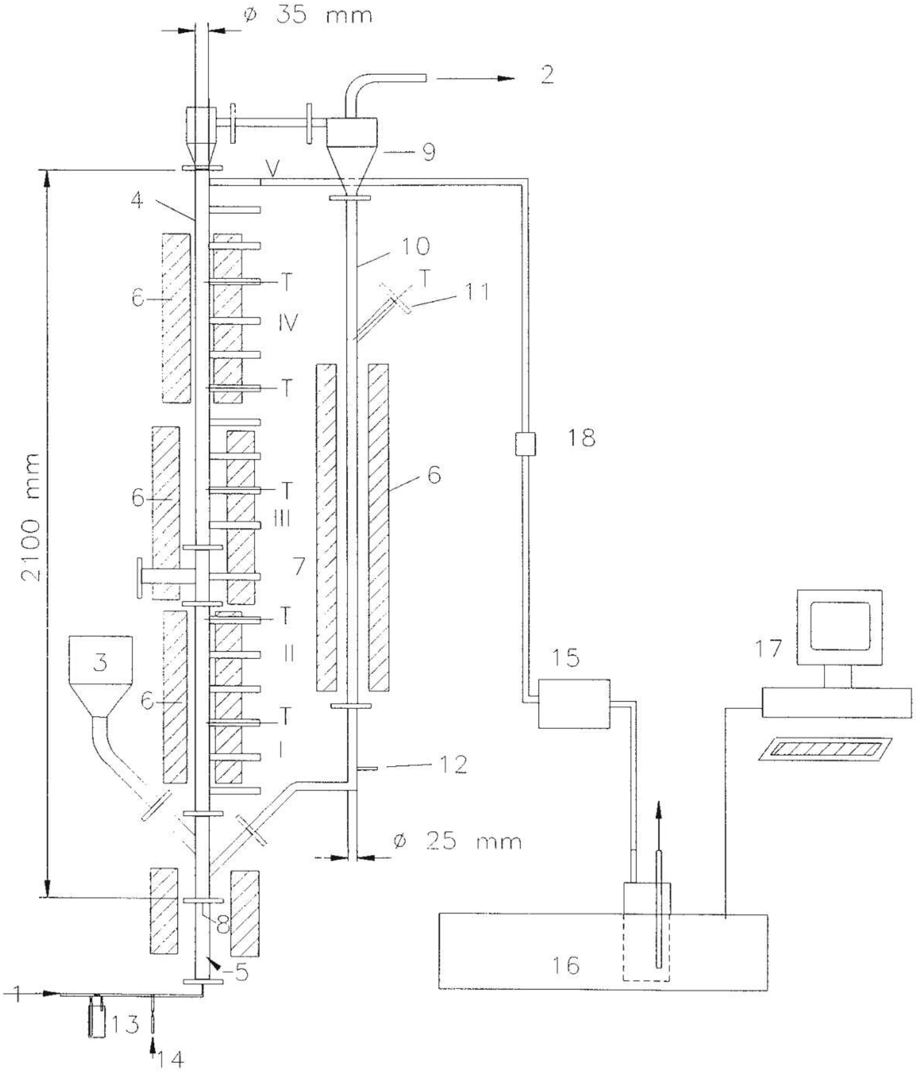

Figure 4.1.-3: The quartz circulating fluidized bed combustor (q-CFBC):

1...gas inlet,
2...exhaust pipe,
3...fuel inlet,
4...riser,
5...preheating zone,
6...heating system,
7...multipurpose tap,
I-V gas sampling,
II gas injection, pressure, temperature,
8...gas distribution plate,
9...cyclone,
10...return leg,
11...particle feed,
12...control air,
13...flask for iodine addition or water addition,
14...N_2O addition,
15...filter,
16...FTIR with gas cell,
17...data acquisition,
18...filter.

The laboratory-scale q-CFBC has an electrically heated quartz-glass riser (35 mm internal diameter and 2100 mm in height). Gas samples and temperature measurements were taken from various positions of the riser. The gas samples were continuously analyzed for CO_2, CO, NO, N_2O, and HCN. The bed material was silica sand with a mean diameter of 125 µm, the superficial velocity was varied between 0.1 to 5 m/s, the temperature was varied between 600 to 900 °C. In the fluidizing air iodine was added by sublimation of solid iodine in a flask warmed in a water bath, refer *Winter et al. 1996d, 1997c, 1999d.* Also N_2O gas was added to the fluidizing air. The solid fuel (450 to 2000 μm) was fed to the bottom bed zone with a feed-rate of 100 g/h.

The circulating fluidized bed combustor (CFBC)

In Fig. 2.-8 the laboratory-scale circulating fluidized bed combustor (CFBC) for single fuel particle studies is presented.
The unit is made of stainless steel and is electrically heated by heating shells changing the temperature in a range from 700 to 950°C. At a given height of the riser (internal diameter of 51.2 mm, 3.7 m tall) a special measurement pipe with a quartz glass window was inserted between two flanges. The fuel particle (8 to 17 mm in diameter) fixed on a thermocouple was inserted from the back into the measurement pipe, i.e. into to riser. From the front a video camera recorded the changes of the reacting fuel particle (particle size and shape, flame ignition and extinction). With a pyrometer the particle's surface temperature was obtained. Shortly above the fuel particle (gas residence times < 0.01 s) the concentrations of CO and CO_2 were measured on-line with ND-IR analyzers. Superficial gas velocities up to 9.5 m/s were obtained and the oxygen partial pressure was varied between 13 and 21 kPa (for further details refer to *Winter et al. 1995*).

The reaction rate unit (RRU)

The reaction rate unit (RRU, refer to Fig. 4.1.-4) is designed to study a given mechanism at well defined conditions.

The flow tube reactor made of quartz glass was designed to obtain the flexibility in changing residence time independently from temperature and flow-rate by changing the length of reaction zone. The reactor consists of three separately in height adjustable reactant tubes and an adjustable carrier gas tube in the preheating zone, a reactor tube and an adjustable sampling probe. The length of the reaction zone can be set by adjusting the position of reactant tubes and the sampling probe.
The reactant gases and the carrier gas, flowing inside the reactant tubes and the carrier gas tube respectively, go downwards through the preheating zone. The flow-rate is controlled by mass-flow controllers. Additional components can be added into the carrier gas line. All the inlet gases are well mixed before entering the reaction zone. This is mainly achieved by the small holes on the tip of the reactant tubes.

The internal diameter of the reaction zone is 12 mm. A length of 310 mm of the reaction zone is chosen usually. The reactor was designed to attain plug-flow conditions.

The reactor is heated by electrical heating shells with three temperature controllers. The temperature is measured with thermocouples, 0.5 mm in diameter, positioned on the outer wall of the reactor. A uniform temperature profile can be maintained within ± 8°C along the reaction zone and almost isothermal conditions can be achieved. One removable thermocouple was placed inside the reactor to measure the temperature inside the reactor.

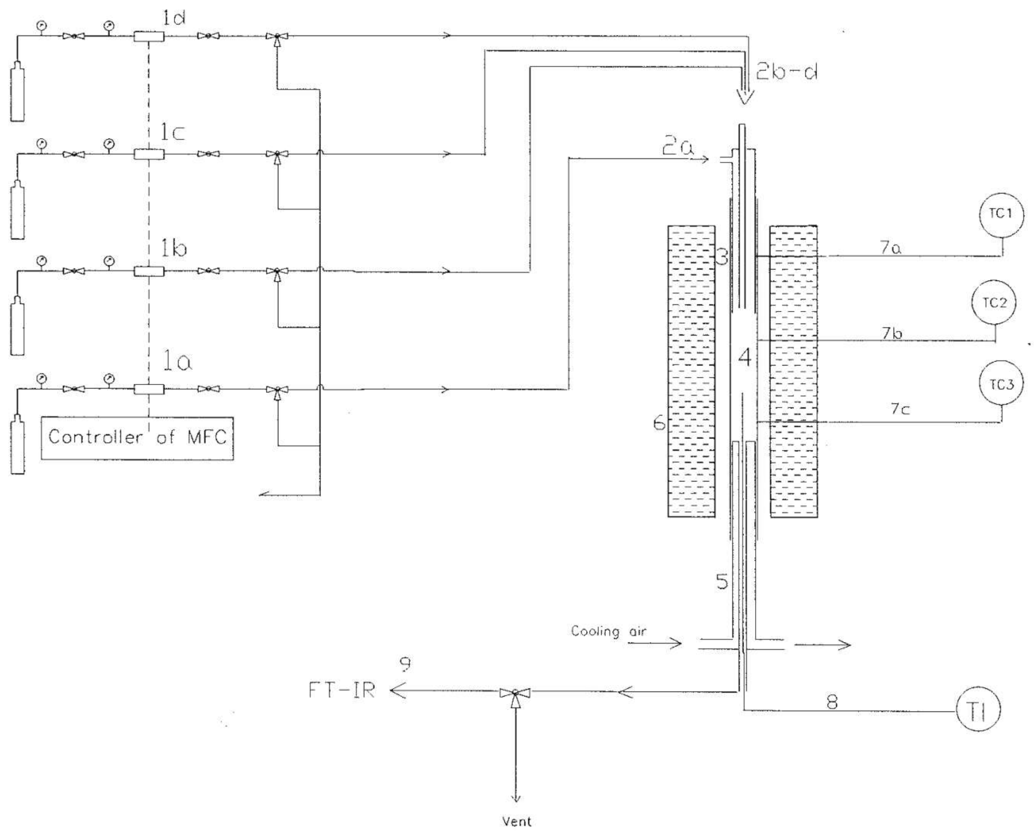

Figure 4.1.-4: The reaction rate unit (RRU): 1a-d...mass-flow controllers, 2a...flow inlet for carrier gas and additional component, 2b-d...flow inlet for reactant gases, 3...preheating zone, 4...reaction zone, 5...sampling probe, 6...heating shells, 7a-c...thermocouples connected to controllers, 8...removable thermocouple, 9...sampling line to the FT-IR spectrometer.

The outlet gases from the reaction zone are quenched in a narrow air cooled tube in the sampling probe. The gas analysis focused on the following species : N_2O, NO, SO_2, CO, CH_4, CO_2, HCN and NH_3 which were analyzed with a high performance FT-IR spectrometer. Iodine was added into the reaction system by generating iodine vapor through sublimation of solid iodine in a flask warmed up in a water-bath which then enriched the carrier gas. The iodine concentration was kept between 250 and 270 ppm in all tests. The tests were performed at atmospheric pressure in a temperature range between 700°C to 1000°C with residence times between 0.2 s to 0.3 s at 900°C. For further details refer to *Löffler et al. 1999*.

The pressurized and the continuous iron ore reduction units

In a pressurized batch (Fig. 4.1-5) and in an atmospheric continuous (Fig. 4.1-6) fluidized bed reactor iron ore reduction has been studied. The effect of the operating conditions (temperature, pressure, gas composition (H_2, CO, CH_4, CO_2, H_2O, N_2)) on the reduction kinetics were tested for different iron ores and evaluated.

In the atmospheric continuous fluidized bed reactor a tracer method based on the magnetic properties of magnetite was developed to obtain the residence time distribution of the iron ore (*Habermann et al. 1998*).

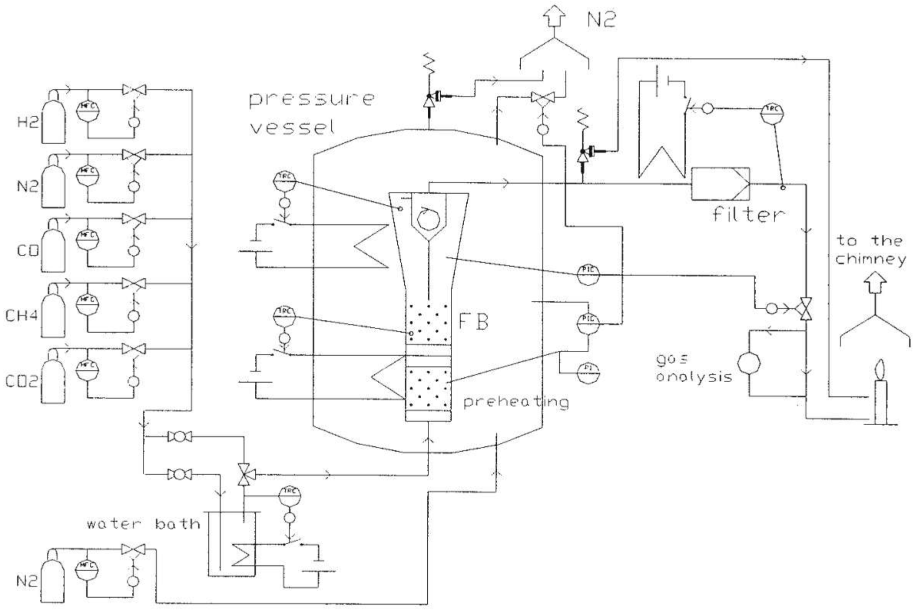

Figure 4.1.-5: The pressurized iron ore reduction unit (p-IRU).

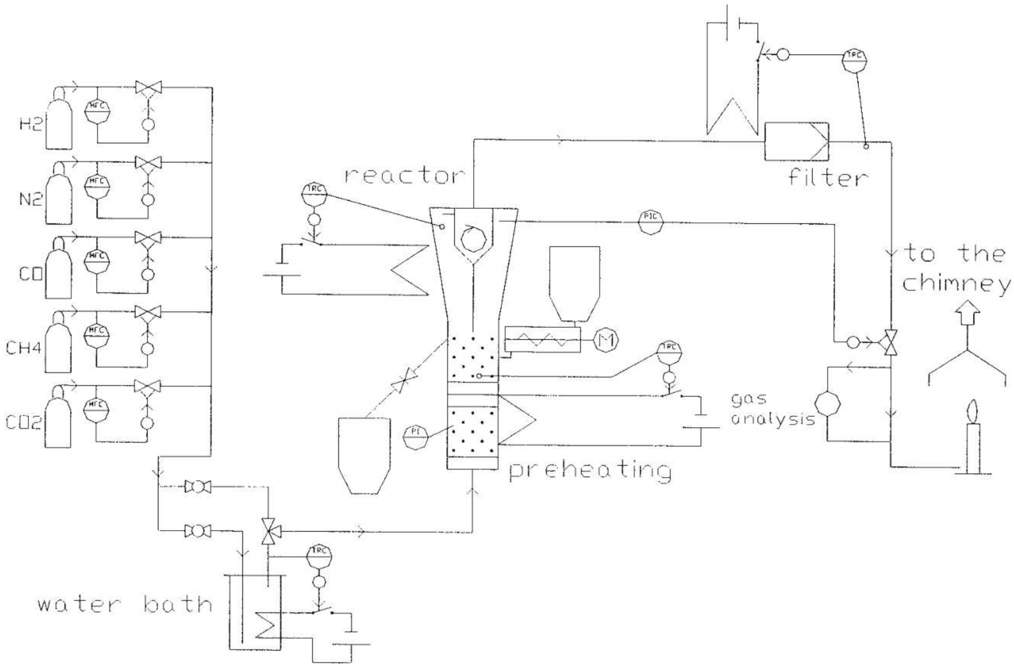

Figure 4.1.-6: The continuous iron ore reduction unit (c-IRU).

In addition to the gas analysis the iron ore has been taken out of the reactor after certain time intervals and analyzed for Fe^{2+}, Fe^{3+}, Fe^{0}, and total Fe by a wet chemistry technique. Furthermore the distribution of Fe and oxygen in the partly reduced iron ore particles was analyzed as well as its pore structure and porosity.

Plexiglass units

Various different units made of plexiglass were designed to study fluid-dynamical aspects (e.g. particle mixing, particle residence time distribution, segregation, entrainment, optimal geometry of the reactor, the cyclone) of the gas - solid processes.

These units have been scaled using similarity rules which allow to study the fluid-dynamics of a high temperature process at room temperatures. Additionally, the plexiglass allows visual observation of the flow pattern.

A tracer method based on the magnetic properties of some iron compounds has been developed to measure the residence time distribution of bed particles and is presented in *Habermann et al. 1998.*

The pilot-scale desulfurization unit

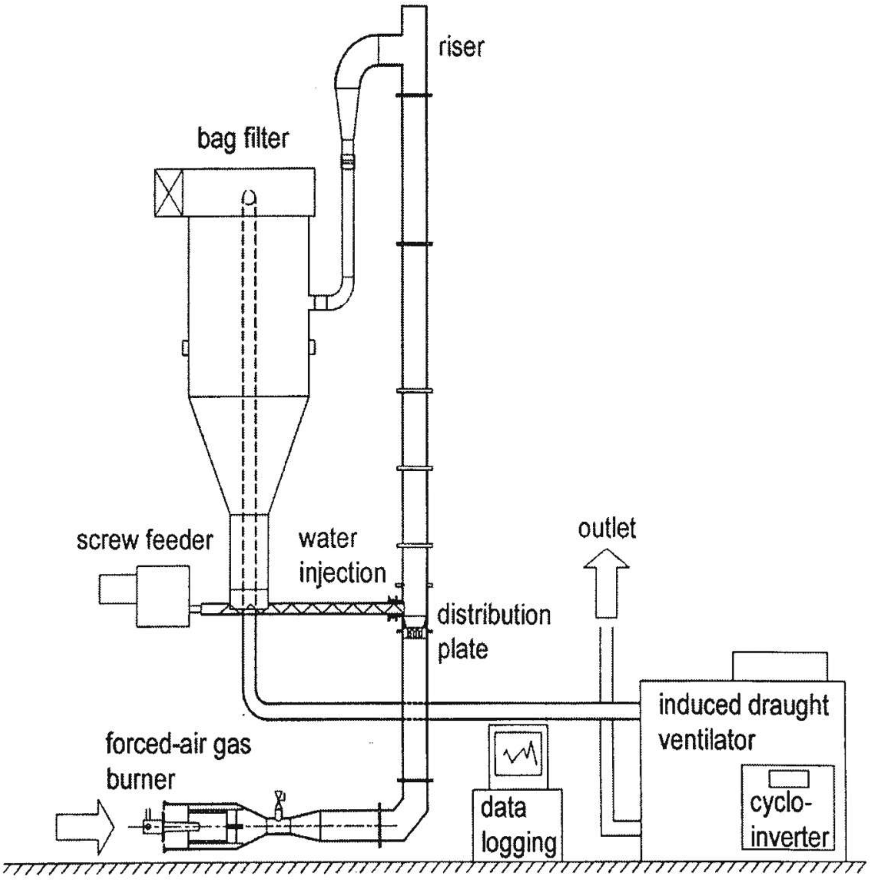

Figure 4.1.-7: The pilot-scale desulfurization unit.

To study the flow structure of group C particles for scale-up, a laboratory-scale CFB unit with a riser made of glass (internal diameter 200 mm, 5500 mm in height) was used (Fig. 4.1-7). Air was heated up to the operating temperatures by a gas burner before being accelerated through the nozzle plate distributor. The solids were fed into the riser directly above the conical section of the nozzle plate and were entrained upwards by gas jets. The air was separated from the solids in the bag filter before leaving the system through the outlet of the ventilator. The precipitated solids were collected in the conical section of the bag filter and were recirculated into the riser by the screw feeder. The riser consisted of eight glass sections connected by Teflon rings with fixed temperature and pressure measuring devices. The air flow was controlled by a cyclo-inverter unit connected with a PC, which was used for the data logging of the operating parameters. Axial and radial temperature profiles as well as axial pressure profiles were obtained in this laboratory-scale CFB unit. The flow structure was studied by visual observation and with video techniques (refer to *Winter et al. 1999e*).

In-situ laser diagnostic tool

High-speed continuous-wave cavity ring down (CW-CRD) measurements of multiple trace gases have been achieved using two multiplexed distributed feedback (DFB) diode-lasers operating near 1391 nm and 1402 nm (refer to Fig. 4.1-8). Measurements at rates of up to 800 ring down events per second were performed. The shot-to-shot fluctuations of the exponential decay time constant was typically 0.6%. The achieved minimal detectable absorbance with CRD mirrors of 99,95% reflectivity was approximately 1.9x10^{-9} cm^{-1} and corresponds to a detection limit (S/N=1) of 1.5 ppb of H_2O (for the absorption line near 7181.17 cm^{-1}, at room temperature, and 1-atm pressure).

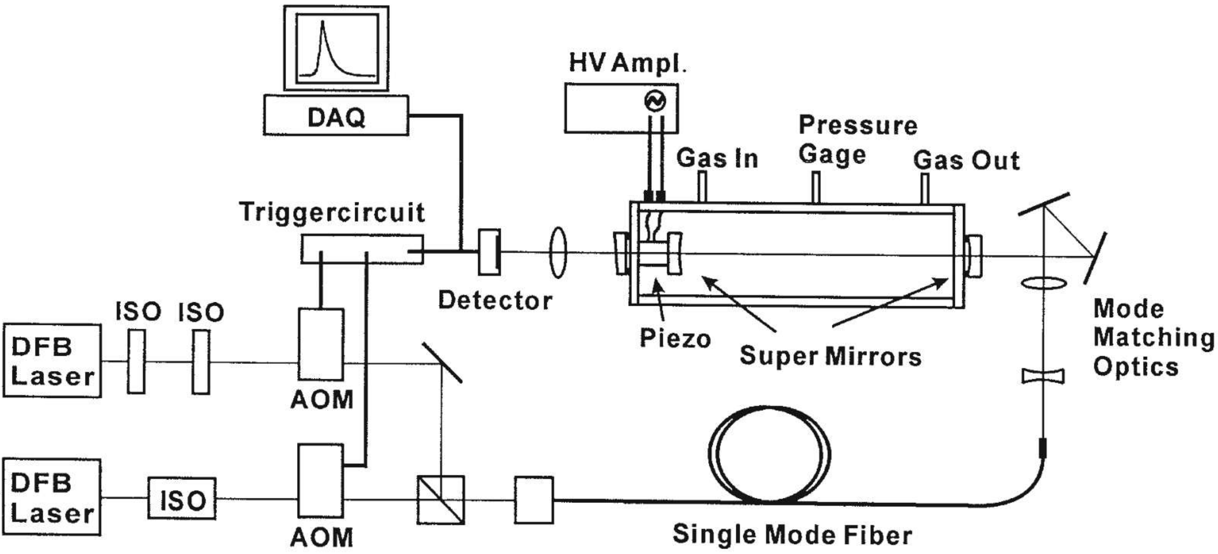

Figure 4.1.-8: Schematic of the high-speed CW cavity ring down setup (DFB ... distributed feedback, AOM ... acoustic-optic modulator).

The two DFB diode lasers are coupled into one single mode fiber with a polarizing beam splitter. The output of the fiber is mode matched into the cavity. For multiple species measurements of narrow and broad band absorbing molecules, time division multiplexing is applied. The cavity is a stable optical resonator with 39.51-cm length. The two supermirrors have 1-m radius of curvature and 99.95% reflectivity. A piezoelectric transducer sinusoidally varied the cavity length by about 900 nm at a 1.5-kHz rate. Two times each period the laser is in resonance with the cavity and a build up of laser energy in the cavity occurs. As the trigger circuit detects a certain energy build up level, the laser radiation is switched off by the acoustic-optic modulator (AOM). The resulting exponential decay (ring down) of optical power in the cavity is recorded by a 12-bit 20-MS/s data acquisition board, evaluated and stored in the computer at a repetition rate of up to 800 Hz. This repetition rate was limited by the optical power of the lasers and the laser line widths (>10MHz). A repetition rate of 3-5 kHz would be achievable with stronger lasers and more narrow linewidth. The absorption of the trace gas at the laser wavelength is calculated from the decay time constant. With this setup the concentrations of two broadband absorbing species (methanol, isopropanol) and some narrowband absorbing molecules can be simultaneously determined. For further details refer to *Totschnig et al. 1998a, b*.

4.1.2. The Conditions Tested

In Table 4.1.-1 an overview about the solid reactants and conditions used as well as the methods used is presented.

Parameter	**Variation**
Solid reactants	bituminous coals, subbituminous coals, petroleum coke, cokes, graphite, peat, spruce wood, alder wood, beech wood, bark, waste wood, wooden pressboard, wooden hardboard, paper, malt waste, other biomass-waste, straw, plastics, polyethylene, polypropylene, tires, 1,8-naphtalene-dicarboxylic acid, sewage sludge, oxidation catalyst, iron ores, fine iron, metallurgical waste, $Ca(OH)_2$, iodine
Particle size	1 µm to 20 mm
Particle shape	spheres, chips, foils, irregularly shaped particles
Temperature	70 to 1150°C
Oxygen	0 to 50 vol.-%
Gas Velocity	0.1 to 9.5 m/s
Gas residence time	10 ms to 2 s
Pressure	1 to 7 bar
Fluidization regimes	fixed bed, bubbling and circulating fluidized bed, entrained flow
Species quantified	CO, CO_2, CH_4, O_2, H_2O, NO, N_2O, NO_2, SO_2, HCN, NH_3, CH_3OH, i-C_3H_7OH
Lab-scale units	formation rate unit (FRU), high-temperature combustor (HTC), quartz circulating fluidized bed combustor (q-CFBC), circulating fluidized bed combustor (CFBC), reaction rate unit (RRU), pressurized iron ore reduction unit (p-IRU), continuous iron ore reduction unit (c-IRU), different plexiglass units, pilot-scale desulfurization unit
Analytical methods	gas: non dispersive infrared (ND-IR), fourier transform infrared (FT-IR), gaschromatography with electron capture detector (GC-ECD), mass-spectrometry with chemical ionization (CI-MS), flame ionization detector (FID), paramagnetic, chemi-luminescence, diode lasers with cavity ring-down (CRD). solids: porosity, elemental distribution in particles, wet chemistry methods, electron microscopy, microscopy, particle size, video imaging, proximate and ultimate analyses temperature of gas & solids: pyrometry, thermocouples additional: mass-flow controllers, pressure controllers, balances

Table 4.1.-1: Overview about the conditions tested and methods used in this work.

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4.2. MODELING

In the following the different calculation models developed and used in this work will be presented and shortly described. For further details it will be referred to the corresponding papers.

4.2.1. Devolatilization and Char Combustion Models

In *Winter et al. 1995* an integral and a differential analysis of the devolatilization process under fluidized bed combustor conditions was performed for various different fuels. In Fig. 4.2.-1 the developed shrinking core extended model is shown. The carbon release rate limiting steps for devolatilization are chemical reaction and heat transfer. The evolution of the volatile matter increases the pressure in the pores of the particles and generates a fast convective flow to the particle surface and into the bulk stream. Devolatilization is defined by the following reaction:

Fuel ===> Volatiles + Solid Residue

The shrinking core extended model divides the reactive spherical core in spherical shells. The decrease of carbon mass in each spherical shell is proportional to the chemical rate constant ($k_{vm,j}$) and the content of mass of volatile carbon (dm_{vm}) in each spherical shell.

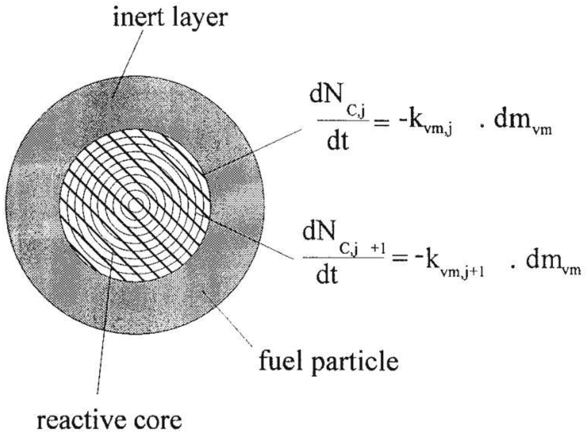

Figure 4.2.-1: Shrinking core extended model

$$\frac{dN_{C,j}}{dt} = -k_{vm,j} . dm_{vm}$$

The chemical rate constant ($k_{vm,j}$) is described by the Arrhenius expression and the differential amount of the mass of volatile carbon can be described with the following equation:

$$dm_{vm} = \rho_{vm} . 4 . r^2 . \pi . dr$$

where (ρ_{vm}) is the density of the volatile matter in the reactive core and ($4r^2 \pi dr$) is the spherical shell volume. The rate for the devolatilization of the spherical fuel is obtained by integrating from the center ($r=0$) to the shrinking core ($r=r_c$):

$$\frac{dN_C}{dt} = -A.4.\pi.\rho_{vm}.\int_0^{r_C(t)} e^{\frac{-E}{RT_j(r,t)}}.r^2.dr$$

The density ρ_{vm} is constant in the shrinking core of unreacted volatile carbon. To integrate the equation the temperature profile inside the reactive core must be known. According to the implanted thermocouple measurements the intraparticle temperatures can be taken. The frequency factor (A) and the activation energy (E) were fitted to the measured data.

Additionally the shrinking core model as well as the shrinking particle model were used to describe char combustion.

In *Winter et al. 1997a* a detailed analysis of the devolatilization process and the char combustion process under fluidized bed combustor conditions is provided considering instantaneous changes of the fuel properties inside the fuel particle and studying the effect of fuel particle size, bed temperature, oxygen concentration, superficial gas velocity, moisture content of the fuel, bed voidage, size of bed material, effect of the flame of the volatile matter, type of fuel. The aim to produce a modern (object oriented) program (refer to Fig. 4.2.-2) which runs on most machines of our university led to the program development system C++ with the Microsoft™ Foundation Classes under Windows™ 3.1. The object oriented approach enabled the development of a framework that can be used with various submodels e.g. models for convective and radiative heat transfer, devolatilization models, flame distance models, etc. Using the unified model-object, all these models (operands) can be individually changed and easily combined.

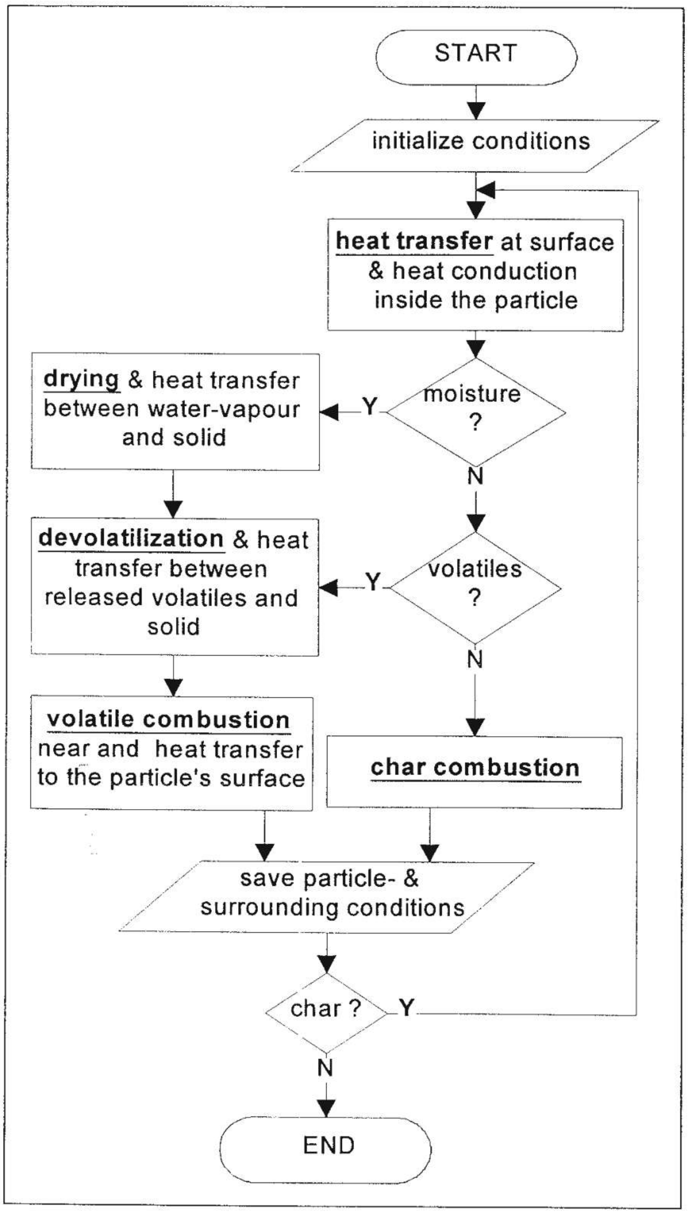

Figure 4.2.-2: The flow chart describing the calculation process of the program.

4.2.2. The Single Particle NO/N_2O Formation Model

In *Winter et al. 1996* a single particle NO/N_2O formation model was developed. With this model NO and N_2O formation was studied during devolatilization and char combustion in a fluidized bed. The nitrogen chemistry was decoupled from the carbon oxidation chemistry by estimating the concentration of the radicals (OH, HO_2, O, H). 18 reactions with nitrogen containing species were considered including homogeneous and heterogeneously catalyzed reactions. The main reaction paths used in the model are given in Fig. 4.2.-3.

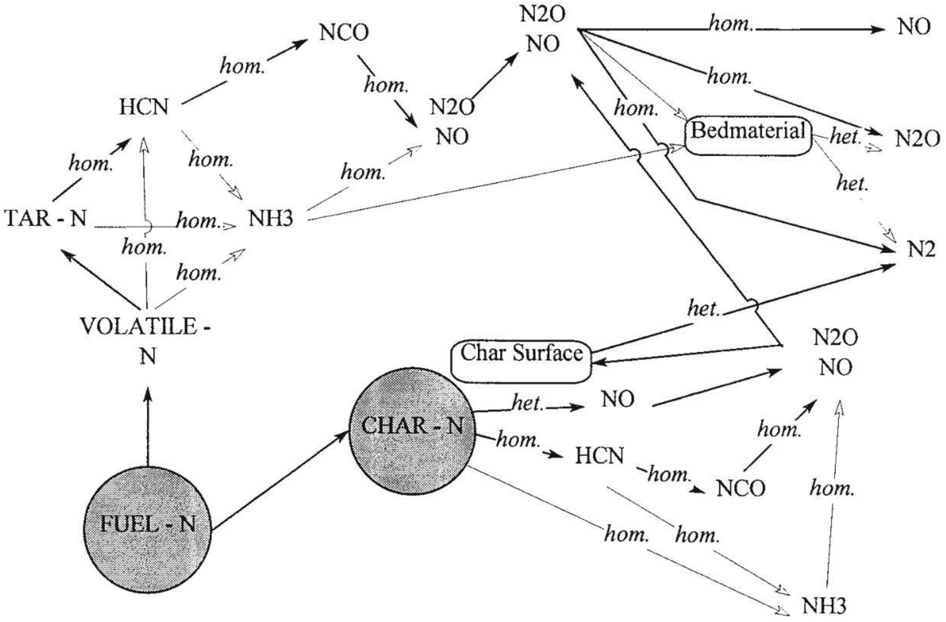

Figure 4.2.-3: The reaction paths of fuel nitrogen to NO and N_2O. Bold arrows indicate the main reaction paths evaluated from the model for bituminous coal.

This model has been further developed and applied in *Winter et al. 1997b* and *Winter et al. 1999*. In *Winter et al. 1999* the model consists of 72 homogeneous (elementary) and 13 heterogeneous and heterogeneously catalyzed reactions where either the bed material or the char is the solid reactant or catalyst. 13 nitrogen containing species are considered in the complex reaction network, viz. CN, HCN, HNCO, HNO, NO, N_2O, NCO, N, NH, NH_2, NH_3, NNH, N_2. For further details refer also to *Löffler et al. 1999a*.

4.2.4. The NO/N_2O Model for CFBC

In *Schweinberger et al. 1994* a model was developed to calculate the NO and N_2O concentration profiles in an industrial-scale circulating fluidized bed combustor depending on fuel and operating conditions. It was the first type of model which combined heterogeneously catalyzed reactions (13 reactions) with homogeneous radical reactions (20 reactions). An extensive parameter study was performed with this new type of CFBC model where the effect of species' concentrations as well as the temperature, voidage and the composition of the bed material was obtained. The concentration profiles for NO and N_2O were calculated for an Ahlström type CFBC (Wachtberg in Germany, 147 MW_{th}, 9.0 x 5.7 m in cross-section, 34 m in height) burning brown coal, the input data (voidage, oxygen concentration and release of the volatiles) was obtained from the CFBC-simulation model of *Haider 1993*.

The NO/N_2O model has been further developed and used as a submodel in the global CFBC simulation model of *Werner et al. 1996* (refer to Fig. 4.2.-4), to calculate industrial-scale CFBC. After testing its capability in the laboratory-scale quartz CFBC and further development (refer to Chapter 4.1, *Löffler et al. 1998*) it was included in *Werner et al. 1999*.

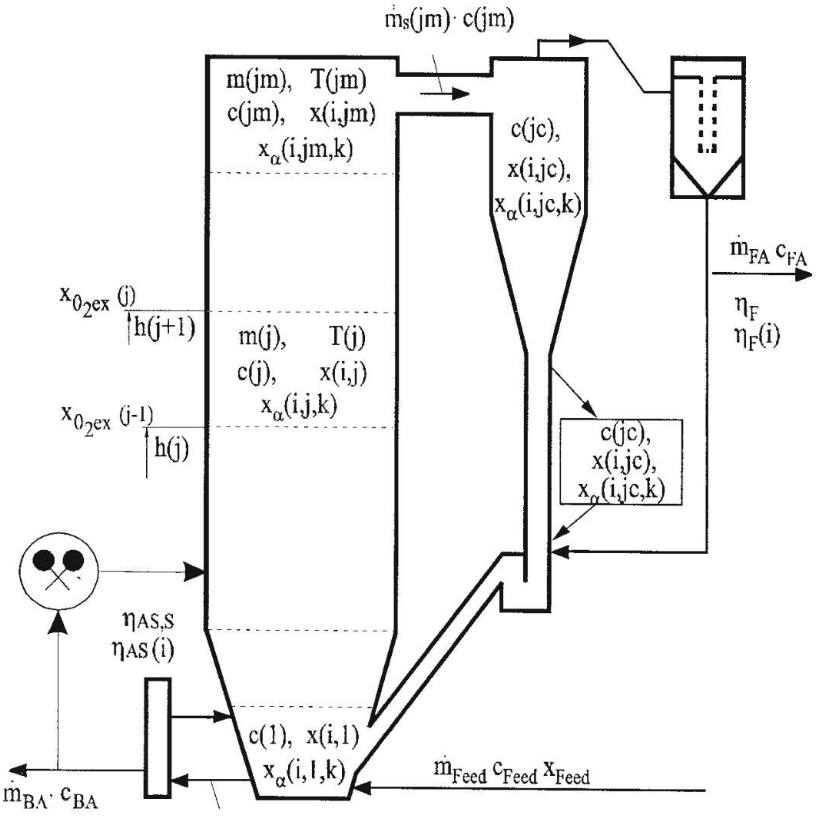

Fig. 4.2.-4: The division of the CFBC into the balance cells as a basis for the formulation of the fractional mass balances.

The model is a post processor of the overall combustion model. It is divided into three modules: the reactor, the fuel particle and the kinetic chemistry model.

The reactor: It is assumed that the species, the solids and the temperature are evenly distributed over the cross section. The reactions are modeled by dividing the riser into different plug flow reactors (PFR), in which the temperature and the solids concentration are constant.

The fuel particle: The fuel particle model is used to calculate the release of nitrogen containing species during devolatilization and char combustion. Therefore it is assumed that during devolatilization nitrogen is released as HCN and NH_3, respectively. These are released proportional to the carbon release at a ratio of 95 to 5, since it was found that HCN is the dominating nitrogen containing product of devolatilization from coals. During char combustion nitrogen is released as HCN, NO and N_2. NO is formed in heterogeneous oxidation, when oxygen breaks up the heterogeneous rings on the char surface. Part of the NO is reduced to N_2 on the char surface. HCN is a primary gaseous product of char combustion.

20 mol-% of the char nitrogen is released as N_2 and 45 mol-% is released as NO. The rest of 35 mol-% is released as HCN.

The kinetic chemistry model: The kinetic model consists of 78 homogeneous and 17 heterogeneous reactions catalyzed by char, bedmaterial and CaO. These reactions deal with 13 nitrogen containing species, i.e. CN, HCN, HNCO, HNO, N, NO, N_2O, NCO, NH, NH_2, NH_3, NNH and N_2. To decouple the carbon from the nitrogen chemistry the concentrations of O_2, CO, CO_2 and H_2O are taken from the overall combustion model. The concentrations of H, O, OH and HO_2, which are the main links between carbon and nitrogen chemistry, are calculated similar to a method of Bulewicz et al. (1989). Under FBC conditions the main route for CO oxidation is following reaction: $CO + OH \rightarrow CO_2 + H$. The concentration of the OH radicals can be estimated using the concentration profiles of CO and CO_2 and the kinetics of this reaction. The concentration of the other radicals is estimated to be equal to OH.

In *Winter et al. 1999a* the CFBC NO/N_2O model was combined with the single particle NO/N_2O formation model similar as described above to predict the concentration profiles of NO, N_2O and HCN as well as the iodine addition tests in the laboratory-scale quartz CFBC (refer to Chapter 4.1).

4.2.5. Modeling of Homogeneous Reaction Systems

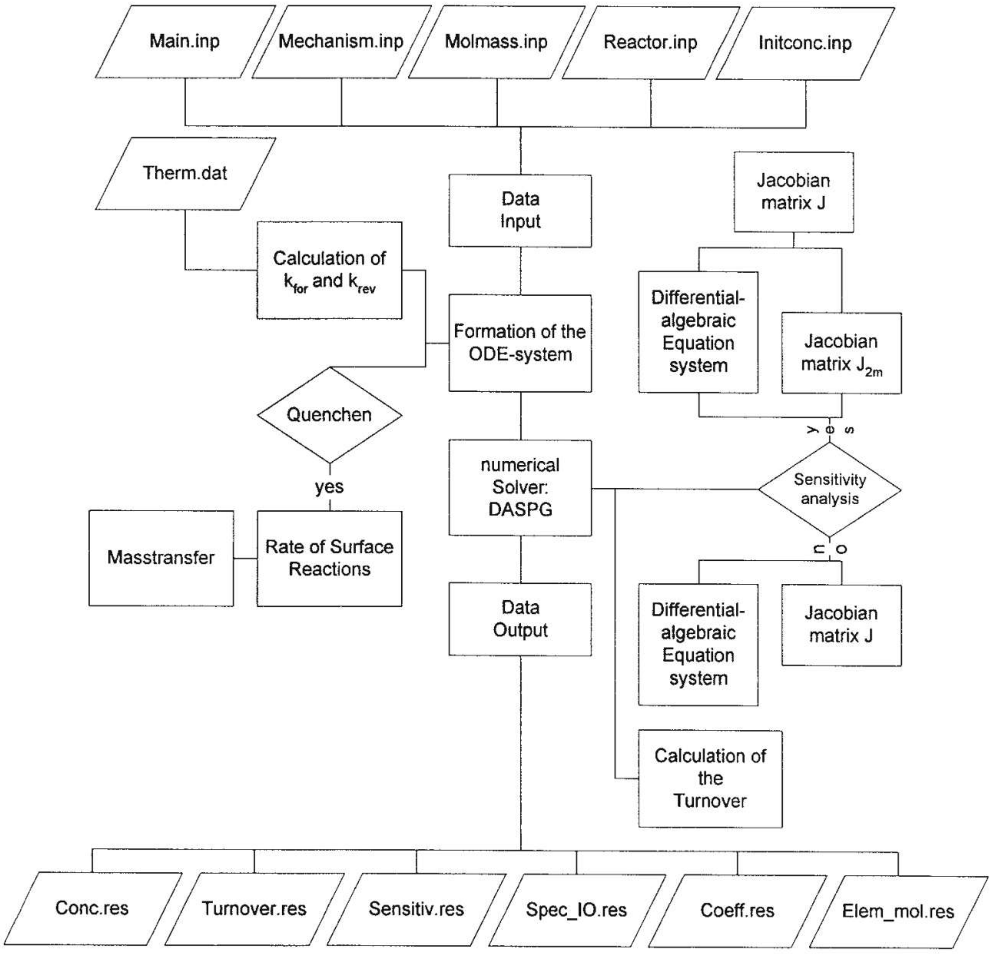

Figure 4.2.-5: The program structure of PFRCalc V 2.0.

The program PFRCalc V 2.0 (*Löffler et al. 1999b*) was developed to simulate homogeneous reactions in a plug–flow reactor with a given temperature profile. A system of any number of elementary and global reactions can be calculated including three body and pressure dependent reactions. As results the concentrations profiles of each species and the turnover of each reaction versus residence time can be obtained. Further it is possible to get residence time dependent the linear sensitivity coefficients with respect to the reaction rate constant of the single reactions and the inlet concentrations of a specified species, respectively. For reactors with a high surface-to-volume ratio the quenching of the radicals (i.e. O, H, OH, and HO_2) on the reactor surface can be taken into account.
The program is implemented in a Fortran code (Fortran 90), that is written in a modular structure, so that submodels can be changed easily or used in other models.
In *Löffler et al. 1999b* the model and its governing equations are explained and a short manual for its usage is given.

In *Löffler et al. 1999c* the model was used to study the effect of SO_2 on NO and N_2O formation from HCN oxidation. The mechanism used is based on the GRIMECH 2.11 mechanism (*Bowman et al. 1996*) consisting of 277 elementary reactions involving 49 species, describing H/N/C/O systems. This base reaction mechanism has been updated and optimized and enlarged (e.g. addition of sulfur chemistry: 67 reactions dealing with 15 sulfur species).

4.2.6. The NO Formation Model under Grate Furnace Conditions

A simple model for the conversion of biomass nitrogen to NO has been developed in *Wartha et al. 1997*, as shown schematically in Fig. 4.2.-6. The nitrogen in the fuel splits between the char and volatiles. A fixed fraction of the char-nitrogen is converted to NO. All volatile nitrogen is released as NH_3. The gases from char combustion, including NO, feed into the volatiles combustion zone. There NH_3 is oxidized to NO and also reduces NO according to the global reactions:

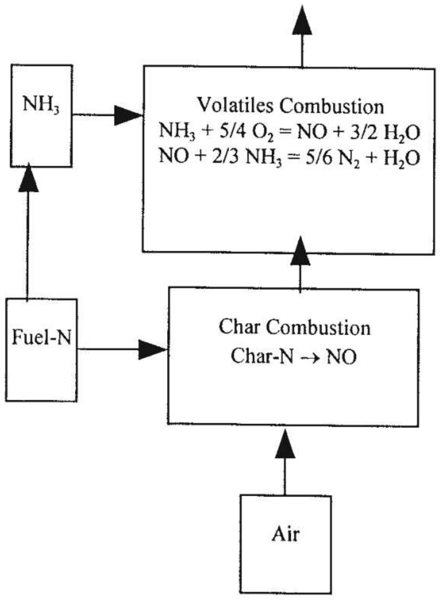

Figure 4.2.-6: The reaction paths to NO and N_2 used in the model.

This simple model could surprisingly well capture the experimental results of fuel nitrogen conversion to NO of biomass burning under grate and fluidized bed combustor conditions.

4.2.7. Reactor Model to Evaluate the RTD of Particles

A simple reactor model has been developed (*Habermann et al. 1998*) to evaluate the effect of fluiddynamics on the residence time distribution (RTD) of particles under cold and hot conditions in a fluidized bed reactor.

The model divides the fluidized bed reactor into two zones (refer to Fig. 4.2.-7): One zone which is perfectly mixed and modeled as a continuously stirred tank reactor (CSTR) and a dead-zone which is not participating. There are two parameters associated with this model: Γ ($=M_1/M$), the fraction of the bed mass in the well-mixed zone and λ ($=q/Q$), the ratio of mass exchange rate to feed rate. Fitting this model to the data from the scaled cold test gave $\Gamma = 0.88$ and $\lambda < 0.01$. Such a low exchange rate is indistinguishable from that for a simple CSTR with mass ΓM, i.e. the dead-zone is stagnant.

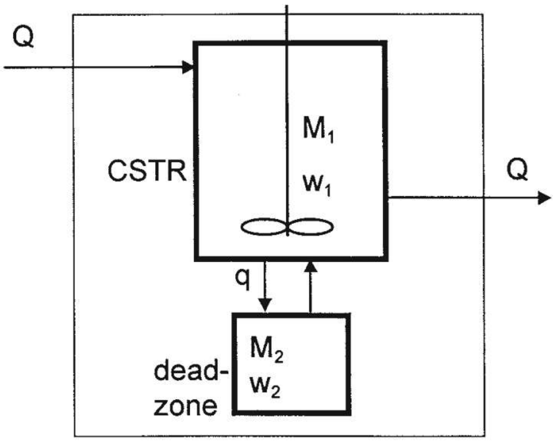

Figure 4.2.-7: Flow diagram of a CSTR with dead-zone (M_1 ... mass of particles in CSTR, M_2 ... mass of particles in dead-zone, $M = M_1 + M_2$, w_1 ... mass fraction of tracer in CSTR, w_2 ... mass fraction of tracer in dead-zone, Q ... mass flow rate of particles to bed, q ... mass flow rate of particle exchange between CSTR and dead-zone).

4.2.8. Model to Calculate CFB-Fluiddynamics for Group C Particles

Describing the fluidization of group C particles in CFB units led to a model, which connects the flow structure with the operating conditions and design (*Winter et al. 1999b*). Special geometries of the units had to be considered, e.g. the position of the solids feed, the distribution plate and the position of the water inlet. To predict the effect of these devices on the flow structure, the CFB unit was divided into 5 zones (refer to Fig. 4.2.-8). Representing the solid-gas-mixing area, the bottom of the unit was split into a solid feed / recirculation-, a gas distribution / jet- and a water injection-zone. The upper flow area consisted of a transport zone and an exit zone. Each zone can be calculated separately describing the flow structure fast and accurately. The relevant flow parameters had to be defined well at the boundaries of each single zone. Contact points were calculated to ensure correct data exchange. Inside the zones smooth transitions were defined. A sudden transition between the gas-solid-mixing area and the transport zone was intended.

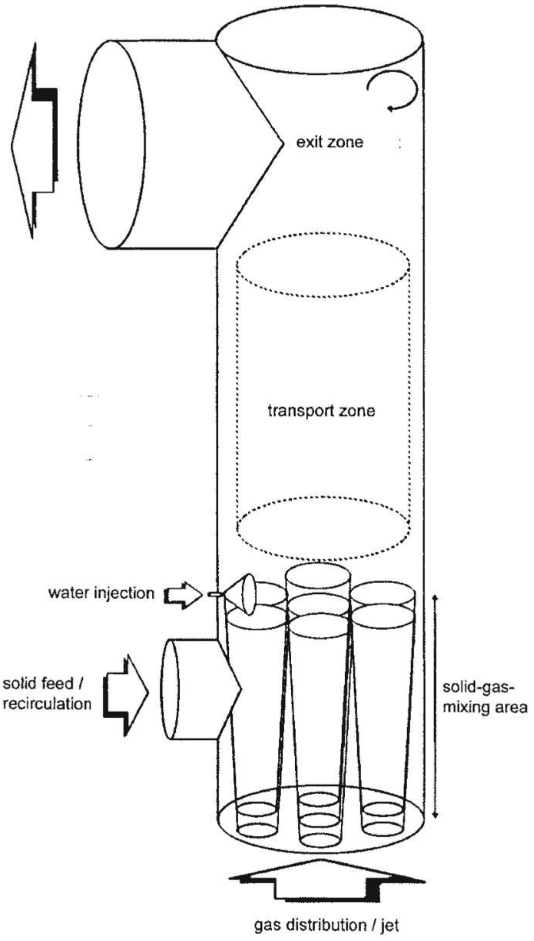

Figure 4.2.-8: The principal divisions of the CFB model.

The fluidizing gas was split into 7 jets. The initial velocity u_{jet} of a jet depended on the specific nozzle geometry. *Roach (1993)* correlated penetration length data for single jets in the so called jetting regime. Following his investigations, the penetration length H_{jet} for a single jet can be calculated as:

$$H_{jet} = D_{jet} K_{jet} \left[\left(\frac{u_{jet}}{\sqrt{g d_p}} \right) \left(\frac{\rho_g}{\rho_p} \right) \left(\frac{d_p}{D_{jet}} \right)^{\alpha} \right]$$

K_{jet} is a factor including geometric and fluid parameters like the outlet angle of the jet, the drag coefficient as well as experimental founded constants. Roach defined the dependencies of H_{jet} more detailed, but considering our state of modeling it was sufficient to adapt the parameter mathematically to the experimental results. The coefficient α, which is also an experimental founded constant, was set to a value of 0.25 according to Roach.

The incoming particles were distributed to the nearest jets in radial position causing a non-uniform particle distribution over the cross-section of the riser. The height of the solid-gas mixing area was equivalent to the penetration length of the jets. At the end of the jets, an unique solid fraction over the cross-section was defined. The exchange of the entrained solids started when the single jets overlapped.

Above the solids feed port, water was injected through a nozzle with a wide angle of approx. 60° - 150°. On the one hand the water cooled the gas and on the other it was moistening the fine particles for the absorption process. The fine water droplets were not supposed to penetrate deeply into the gas-solid flow, because that would cause an undesirable formation of large agglomerates over the cross-section of the unit.

To calculate the flow structure of the transport zone, the core - annulus approach was made. Models using this approach are based on the assumption, that the solids in the annular layer are distributed evenly. The thickness of the layer decreases in the upward direction to zero at the riser exit. Additionally to that theory in the prevailed model a non-uniform annulus was predicted depending on the radial position of the exit.

A gas-solid separation takes place in the exit zone. That caused an increase in the suspension density at the top mainly depending on the size of the particles and the superficial velocity. An 'exit-reflection-coefficient' was defined as the fraction of solids which are sent downwards vertically in the annulus. This coefficient is clearly a function of particle and gas density, particle size, gas velocity and solid flux.

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5. RESULTS AND DISCUSSION

In the following examples will be given to demonstrate the importance of chemical similarity for the optimization and design of gas - solid processes.

5.1. THE IMPORTANCE OF RADICALS

5.1.1. From the Single Particle to the Pilot-Scale - An Experimental Approach

In the following an example is given where scaling of chemistry has been done successfully. Tests with a petroleum coke were performed in the CANMET pilot-scale circulating fluidized bed combustor (CFBC) which is 0.45 m in diameter and 7 m high (refer to *Winter et al. 1999a*). The aim of the tests was to improve the understanding of the N_2O formation mechanism under CFBC conditions. Petroleum coke was fed continuously into the pilot-plant. Then, to study the effect of the homogeneous chemistry, iodine was added to suppress the radicals. It was found that if iodine is added, the concentrations of CO and NO increase, whereas N_2O decreases (refer to Tab. 5.1.-1). The increase of CO could be explained: Iodine suppresses the concentrations of the radicals by catalytic cycles, thus inhibits the oxidation of CO with the OH radical to CO_2. Also the hydrocarbons followed this trend. But - at that time - it was not clear why N_2O decreased and NO increased. However, the strong response of both species to the addition of iodine revealed that radicals are very important under those conditions affecting NO and N_2O.

	before cyclone				after cyclone			
Run	CO (%)	NO (ppm)	N_2O (ppm)	HC (ppm)	CO (%)	NO (ppm)	N_2O (ppm)	HC (ppm)
15	0.40	93	na	2730	0.05	72	134.5	0
15I	1.93 ↑	442 ↑	16.5	8310	1.59 ↑	295 ↑	26.5 ↓	7400

Table 5.1.-1: Gas concentrations were measured before and after the cyclone in the CANMET pilot-scale CFBC (0.45 m in diameter, 7 m high) burning petroleum coke (*Winter et al. 1999a*). Run 15I is with, run 15 without iodine addition. (HC is hydrocarbons).

Additional tests were performed with the petroleum coke in the laboratory-scale quartz CFBC (35 mm in diameter, approx. 2.4 m high) at TU-Vienna (refer to Chapter 4.1.1). The coke was fed continuously into the unit and at a given time iodine was added. The results are given in Fig. 5.1.-1. It can be seen that a similar behavior to the pilot-scale CFBC was found: An increase of CO, the hydrocarbons (e.g. CH_4) and NO, whereas N_2O completely disappeared. (Additionally, N_2O was added to the fluidizing gas to study if N_2O addition affects the other species, but obviously it did not.) Both units give a very similar response to the same stimulus, viz. the addition of iodine. They show the same trends which are based - with a very high likelihood - on the same mechanism. Chemical similarity was achieved. It could also be explained why the N_2O completely disappeared in the laboratory-scale CFBC: In these tests iodine was added to the fluidizing gas by sublimation of solid iodine in a flask warmed in a water bath. Therefore its concentration was almost uniform in the unit. In the pilot-scale tests solid iodine was added directly into the CFBC and might vaporize as it mixed, producing a plume and was likely absent from regions at the bottom of the combustor. Mixing problems occur in larger units.

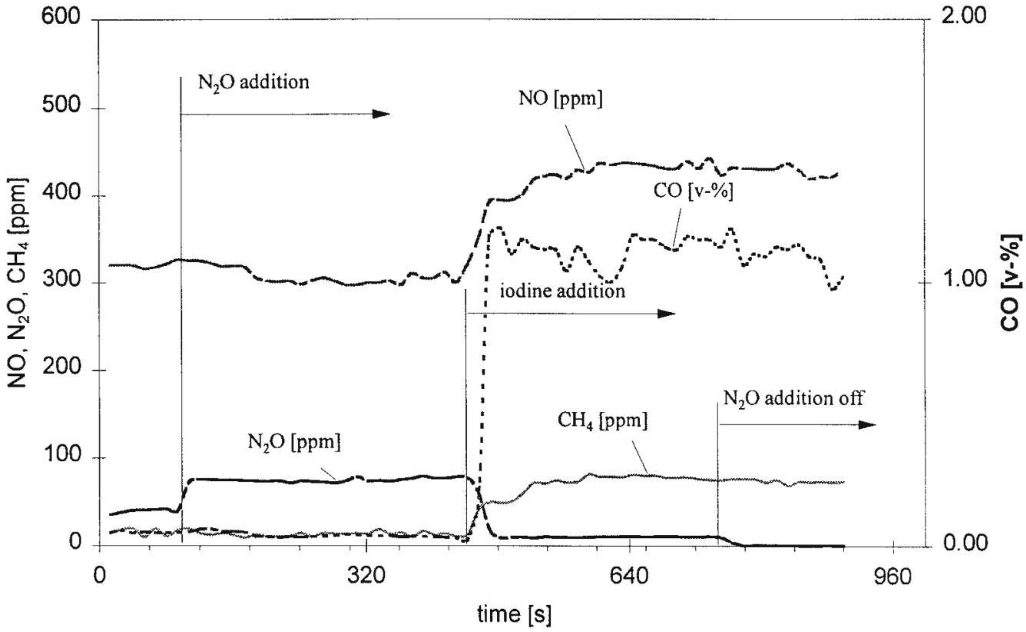

Figure 5.1.-1: Concentration histories in the laboratory-scale quartz CFBC (35 mm in diameter, approx. 2.4 m high) burning petroleum coke (from *Winter et al. 1996a*) with and without iodine and N_2O addition.

After those tests were finished we knew that the pilot-scale and the laboratory-scale CFBC show chemical similarity. This is a very important fact because tests performed in the laboratory-scale unit are much cheaper and cost effective. But still we did not completely understand why N_2O decreased and NO increased. Therefore additional tests were performed in the formation rate unit (FRU) at TU-Vienna which can be operated as a bubbling fluidized bed and is made of quartz glass (35 mm in diameter, static bed height is about 40 mm, refer to Chapter 4.1.1. and *Winter et al. 1996b*). The FRU is designed in that way that the gas residence time is very short (typically below 140 ms) and the gas composition can be measured shortly after the burning fuel. In Fig. 5.1.-2 iodine was added to a batch of petroleum coke particles whereas in Fig. 5.1.-3 the results for a single petroleum coke particle are presented.

Those tests performed in the FRU show that chemical similarity between the pilot-scale CFBC, the laboratory-scale CFBC, the single particle and batch tests in the laboratory-scale FRU exists because the same trends were found as iodine was added (*Winter et al. 1999a*). Additional to the N_2O and NO measurements in the CFBC units HCN was measured giving additional information about the on-going N_2O and NO formation mechanism. These results are also in excellent agreement with previous findings in *Winter et al. 1996b* where iodine was added during char combustion of a bituminous coal particle in the FRU. There it was concluded that NO is primarily heterogeneously formed by char-nitrogen oxidation. But a volatile species, which has been identified as HCN, is simultaneously released. This species is homogeneously oxidized to NCO which further reacts with NO to form N_2O. If iodine is added the radicals are suppressed and N_2O can not be formed. HCN will increase as well as NO.

The knowledge of the dependencies and on-going NO and N_2O formation mechanisms is very important for the reduction of pollutants (optimization) of industrial-scale CFBCs. The trends obtained from the laboratory-scale unit which corresponds to the industrial-scale unit will be used as guidelines for optimizing the operating conditions (e.g. compare also the temperature dependence of N_2O).

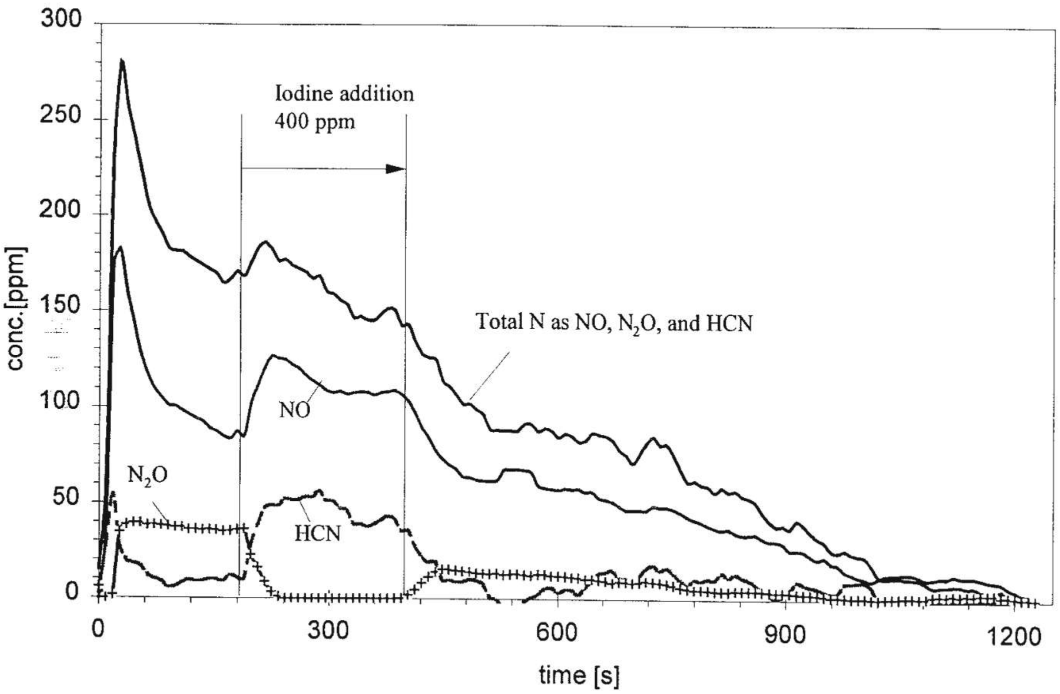

Figure 5.1.-2: Concentration histories of a batch of petroleum coke particles (initial mass about 2 g) in the quartz formation rate unit (FRU, 35 mm in diameter, static bed height is about 40 mm). Additionally to N_2O and NO HCN was measured. Iodine was added during the char combustion period (at 180 s).

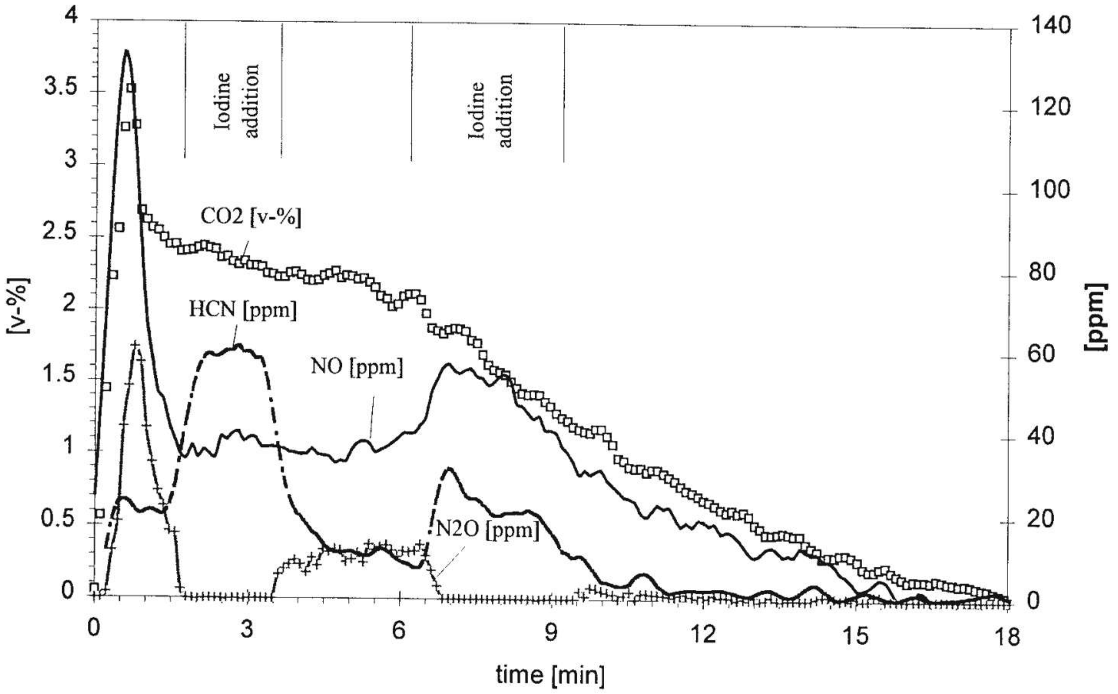

Figure 5.1.-3: Concentration histories of a single petroleum coke particle (initial mass about 1 g) in the quartz formation rate unit (FRU, 35 mm in diameter, static bed height is about 40 mm). Additionally to N_2O and NO HCN was measured. Iodine was added two times during the char combustion period.

5.1.2. From the Single Particle to the Industrial-Scale - A Modeling Approach

In Chapter 5.1.1 an experimental method (iodine addition) was applied to test if chemical similarity exists between laboratory-scale units and a pilot-scale unit. This method was used to study the NO and N_2O formation paths.

Parallel to the experimental work modeling work was performed to simulate and discuss the experimental results on a quantitative basis (*Winter et al. 1999a*). A detailed single particle NO/N_2O formation model was developed (refer to Chapter 4.2.2.). This formation model was tested well in the formation rate unit (FRU) (refer to Chapter 4.1.1). Then the single particle formation model was incorporated into the CFBC NO/N_2O model (refer to Chapter 4.2.4) and tested in the laboratory-scale CFBC (refer to Chapter 4.1.1.) under well-defined operating conditions (e.g. also the HCN profiles and concentration changes were measured).
Finally the CFBC NO/N_2O model was incorporated as a submodel into the global CFBC simulation model of *Werner et al. 1996, 1999*. With this global CFBC simulation model the NO, N_2O emissions of an industrial-scale CFBC can be calculated (e.g. a 147 MW_{th} CFBC in Germany). In Fig. 5.1.-4 typical modeling results are given.

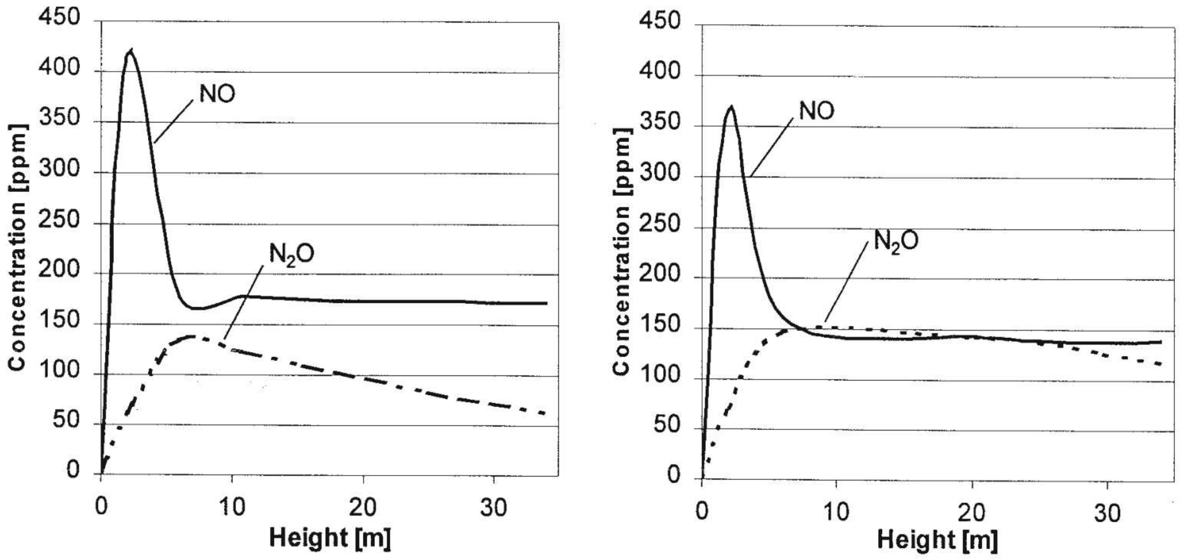

Figure 5.1.-4: Typical modeling results of NO and N_2O in a 147 MW_{th} CFBC for full (left) and partial load (right) conditions with secondary air injection at 3 m.

5.1.3. Importance of Radicals for the Destruction of N_2O

Another example which demonstrates the importance of radicals (reactive intermediate species) clearly is given in *Winter et al. 1999b*. In this work the destruction of N_2O was investigated in the laboratory-scale CFBC (refer to Chapter 4.1.1). It was demonstrated by applying the iodine addition method that the direct homogeneous reaction of N_2O with CO is negligible. However, CO addition effects N_2O indirectly via its radicals (H, OH) generated during the oxidation of CO to CO_2. The radicals (especially the H-radical) destroy N_2O not the CO.

5.1.4. Interaction between Nitrogen Chemistry and SO_2

In *Löffler et al. 1999* the interaction between the nitrogen chemistry and SO_2 was studied because SO_2 has been found affecting NO and N_2O emissions in laboratory-scale (e.g. *Anthony and Lu 1998*), pilot-scale (e.g. *Leckner and Amand 1987,*) and industrial-scale (e.g. *Bencteux et al. 1999*) fluidized bed combustors. Some studies suggest that the radical recombination reactions of SO_2 are responsible for this effect.

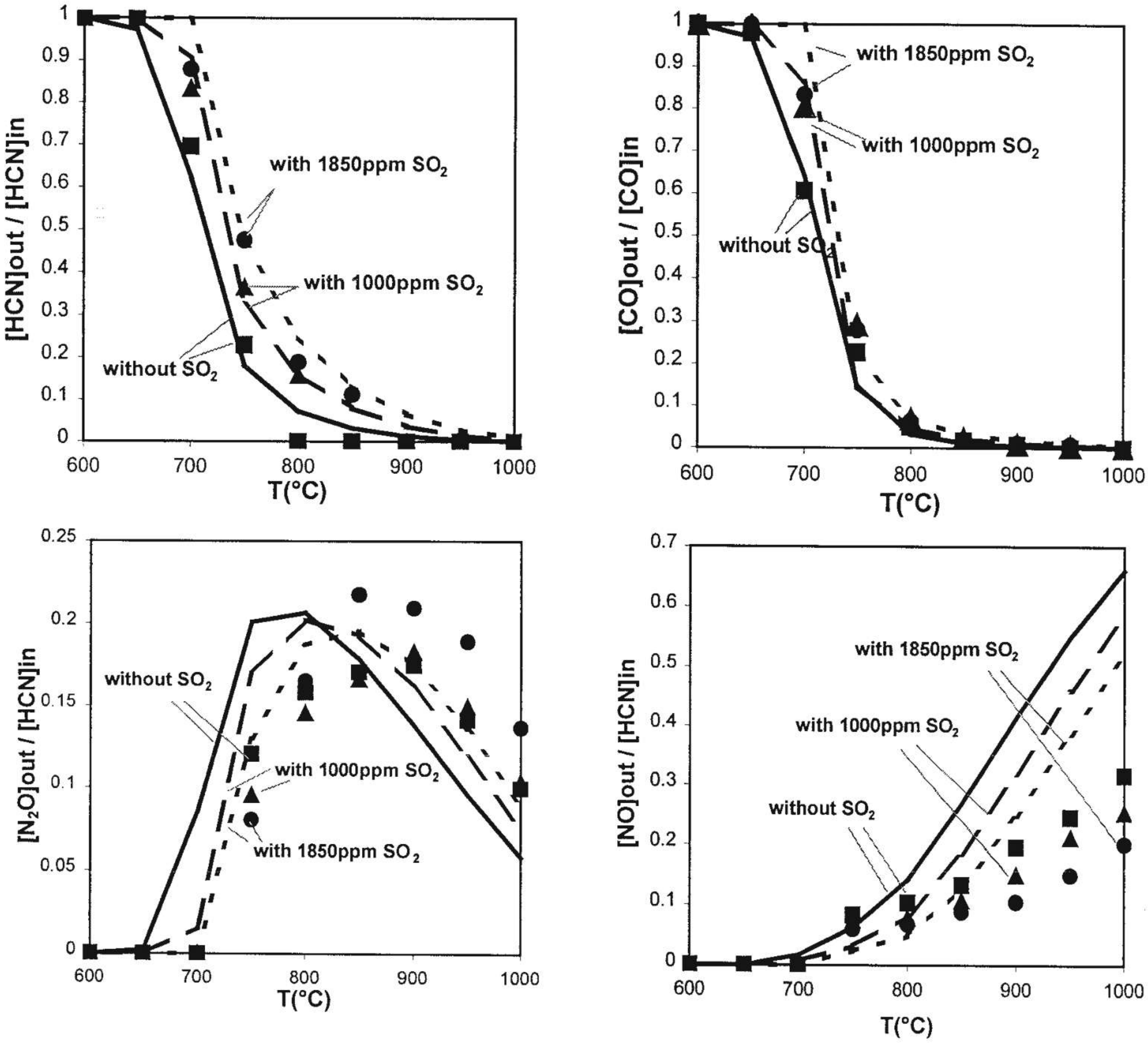

Figure 5.1.-5: Comparison with the model for the effect of SO_2 on NO and N_2O formation in the $HCN/CO/H_2O/O_2$ system. Lines show the modeling results, symbols show the experimental data. (a) HCN conversion, (b) CO conversion, (c) N_2O yield (d) NO yield. (■): the $HCN/CO/H_2O/O_2$ system, inlet conc. [240ppm/1180ppm/3000ppm/10%], $\tau=0.289$ s (at 900°C). (▲):the $HCN/CO/H_2O/O_2/SO_2$ system, inlet conc. [240ppm/1200ppm/3000ppm/10%/1000ppm], $\tau = 0.289$ s (at 900°C). (●):the $HCN/CO/H_2O/O_2$/SO2 system, inlet conc. [240ppm/1200ppm/3000ppm/10%/1850ppm], $\tau = 0.289$ s (at 900°C).

In this work the effect of SO_2 on NO and N_2O formation was investigated through HCN oxidation since HCN is known as important precursor for NO and N_2O. The tests were performed in a quartz flow reactor (RRU, refer to Chapter 4.1.1) in the temperature range from 600 to 1000°C. H_2, CO and CH_4 were added to simulate the combustion of volatiles. A detailed chemical kinetic model (refer to Chapter 4.2.5) was used to analyze the experimental data. The homogeneous tests showed significant inhibition by SO_2 on the oxidation of the reactants (refer to Fig. 5.1.-5). SO_2 enhanced radical recombination. Due to the lower concentration of radicals, the CO and HCN oxidation rates decreased and higher concentrations of CO and HCN were found leaving the RRU. In consequence NO decreased because of the reduced oxidation of HCN. N_2O showed an ambivalent behavior. In the lower temperature range (below 800°C) it decreased because formation is inhibited whereas in the high temperature range N_2O increased because the radical destruction reactions were strongly inhibited.

In this study the importance of the homogeneous interaction of the HCN oxidation chemistry with SO_2 was demonstrated. The SO_2 concentration level in an industrial-scale CFBC depends mainly on the sulfur content of the actual coal burned as well as the efficiency of sulfur capture in the fluidized bed. Therefore homogeneous as well as heterogeneous effects have to be considered to explain the changes in NO and N_2O emissions of an industrial-scale CFBC. Each mechanism has to be studied separatly to obtain its relative importance.

5.2. FUEL-NITROGEN CONVERSION TO NO

The conversion of the fuel nitrogen to NO was studied in different units of different scales. A range of various fuels was burned in the formation rate unit (FRU, refer to Chapter 4.1.1) as single particles and under continuous operation in a 50 kW_{th} bubbling fluidized bed combustor (*Wartha et al. 1997*) and in a 200 kW_{th} grate furnace (*Wartha et al. 1997*). Additionally those results were compared to data from literature (refer to Fig. 5.2.-1).

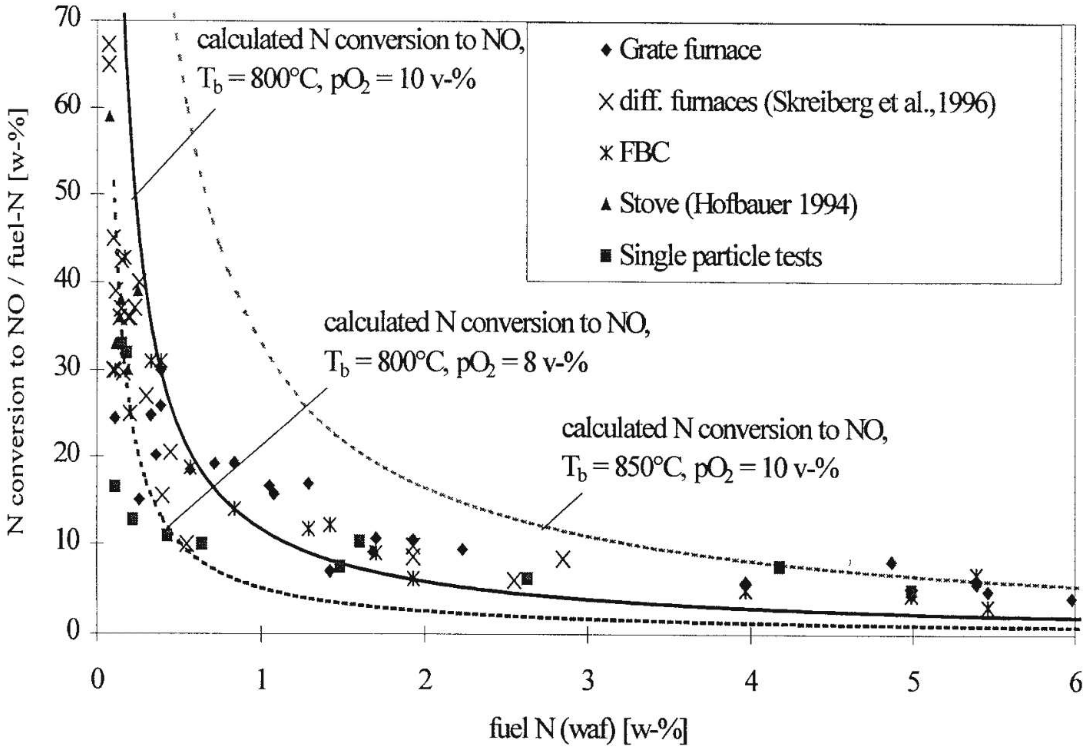

Figure 5.2.-1: The effect of the nitrogen content of the fuel on its conversion to NO (*Winter et al. 1999c*). Data include measurements from the 200 kW grate furnace, the single particle tests, a 50 MW_{th} bubbling fluidized bed combustor (FBC), a stove and other furnaces. Lines refer to modeling work (*Wartha et al. 1997*).

It was found that during the combustion of fuels with higher nitrogen contents more NO was formed but the conversion of fuel-nitrogen to NO decreased. This behavior could be explained with the increased presence of nitrogenous species (e.g. NH_3, HCN) which reduced the NO generated by oxidation of these same species. This behavior can be compared with the thermal DeNOx or SNR process where NH_3 is added to the exhaust gas after the combustion chamber reducing NO to N_2.

5.3. THE EFFECT OF FUEL TYPE

5.3.1. The Conversion of Carbon

In the formation rate unit (FRU, refer to Chapter 4.1.1.) various different fuels were burned as single particles under well-defined conditions. The concentrations of CO, CO_2, CH_4, SO_2, NO, NO_2, N_2O, NH_3, and HCN were measured shortly after the particle. In Fig. 5.3.-1 a typical measurement run of a burning wood particle is given (not all concentration histories are shown).

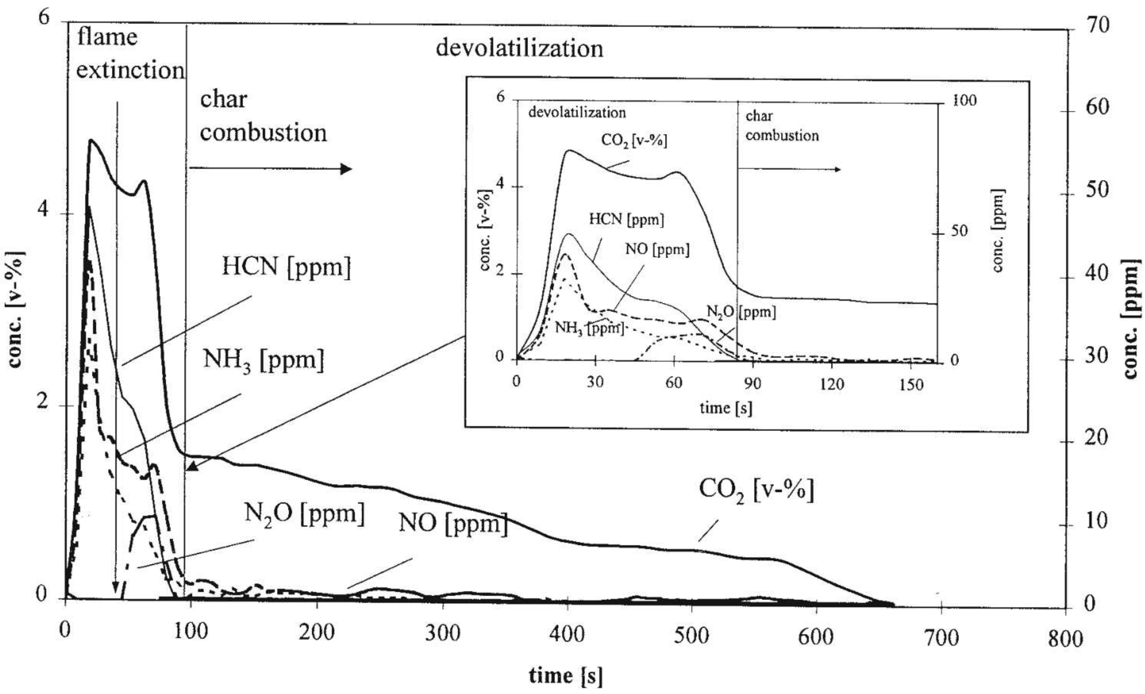

Figure 5.3.-1: CO_2, NO, N_2O, HCN, and NH_3 concentration changes of a burning single beech wood particle in the FRU at 800°C and 10 kPa oxygen.

Analyzing the carbon containing species (CO, CO_2, CH_4, other hydrocarbons) in the gas-phase, the conversion of the fuel carbon was obtained during devolatilization and char combustion and kinetic data derived.

In Figs. 5.3.-2 and 5.3.-3 the integral analyses (the fuel classification systems) of devolatilization and char combustion are shown. The amount of carbon released during devolatilization respectively during char combustion was integrated with time. Mean carbon release rates with devolatilization time resp. char combustion time were obtained. Standard fuels were defined and the mean carbon release rates were based on the mean carbon release rates of the standards (viz. the relative mean carbon release rates) to compare the different fuels. These standards can also be used to compare different laboratory-scale units and experimental test procedures.

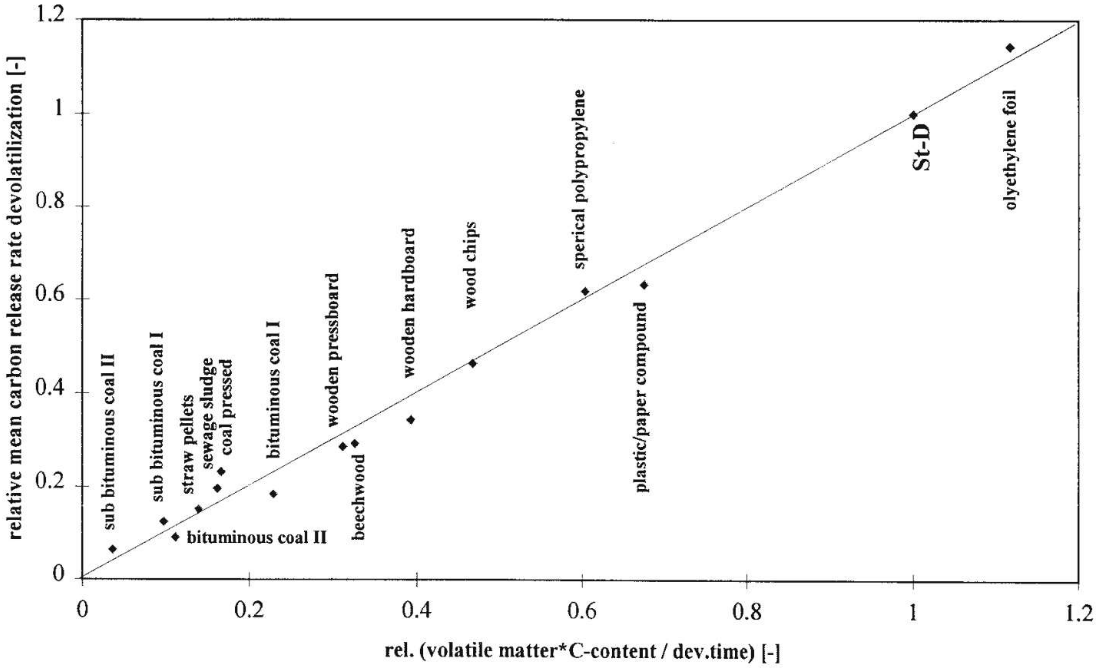

Figure 5.3.-2: Fuel classification for devolatilization: relative mean carbon release rate devolatilization from measurements versus relative mean carbon release rate devolatilization from classification system. St-D is the calibration standard for devolatilization. 1,8-naphthalene-dicarboxylic acid anhydride is used as calibration standard for devolatilization (for further details refer to *Wartha et al. 1998*).

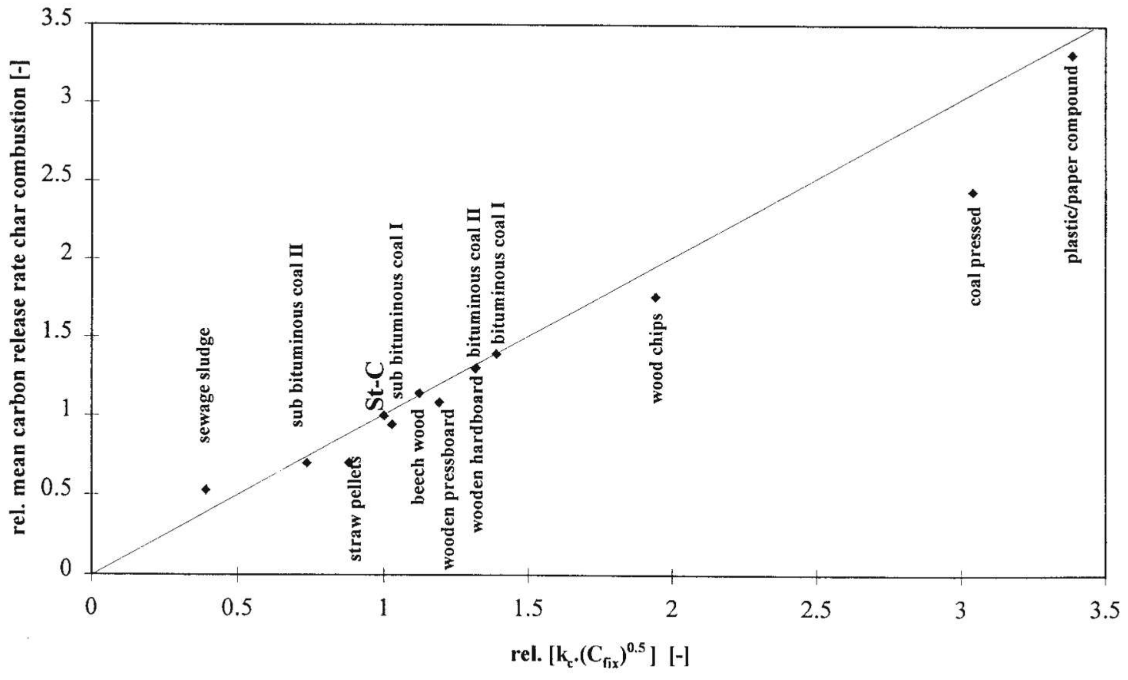

Figure 5.3.-3: Fuel classification for char combustion: relative mean carbon release rate char combustion from measurements versus relative mean carbon release rate char combustion from classification system. St-C is the calibration standard for char combustion. Graphite is used as calibration standard for char combustion (for further details refer to *Wartha et al. 1998*).

In *Winter et al. 1997* a full differential analysis of the devolatilization and char combustion of five different fuels was performed (refer also to Chapter 4.2.1). The effects of fuel particle size, bed temperature, oxygen concentration, superficial gas velocity, moisture content of the fuel, bed voidage, size of bed material, effect of the flame of the volatile matter, and type of fuel were studied by experimental and modeling work. Figure 5.3.-4 shows the changes of the carbon release rates (C-loss) and the particles' center temperatures of different fuels with time.

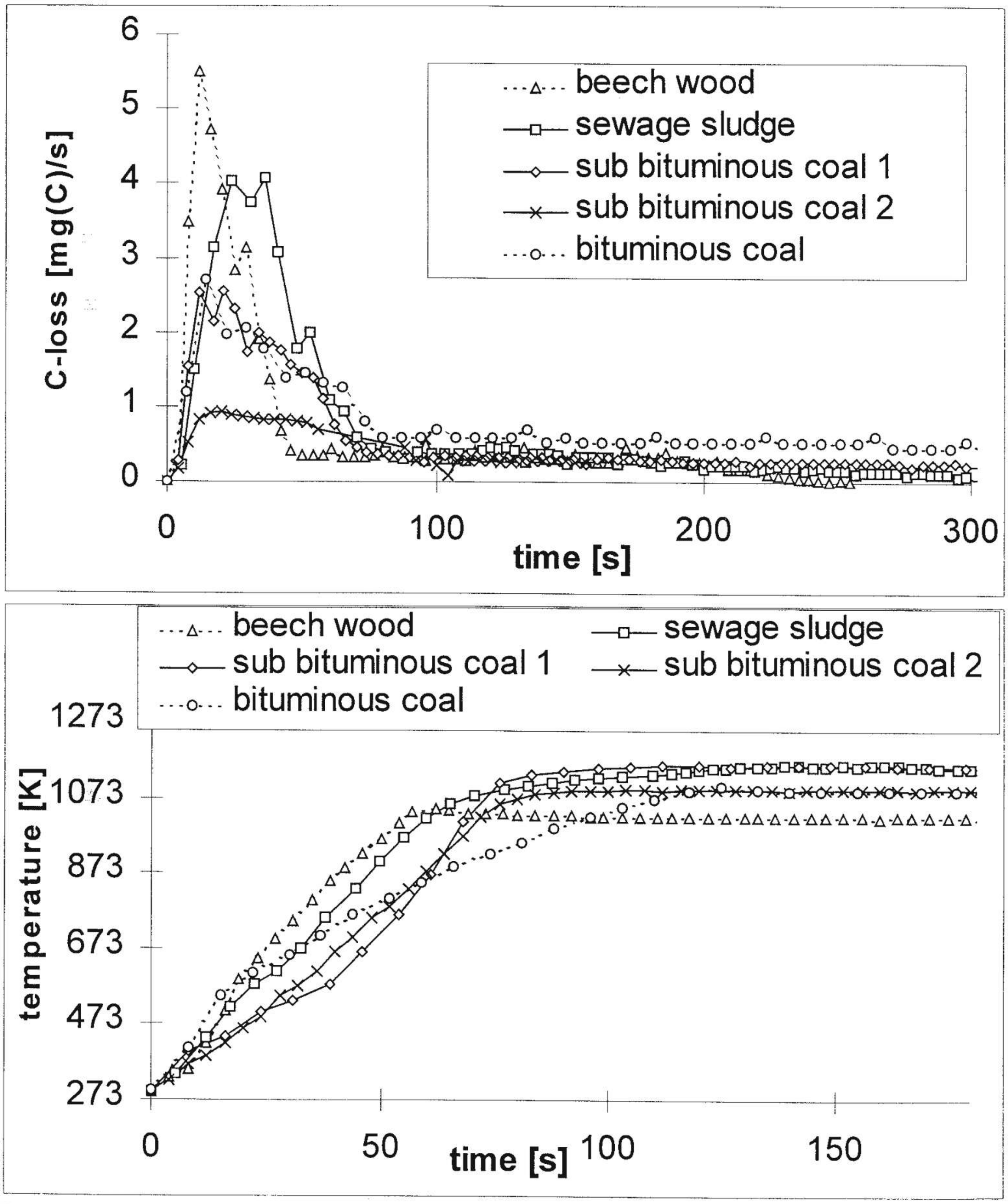

Figure 5.3.-4: Carbon-loss resp. carbon release rates (top) and center temperatures (below) of particles of different fuel types in the FRU (initial size of the fuel particle = 10 mm, bed temperature = 800°C, oxygen partial pressure = 10 kPa, superficial gas velocity = 0.675 m/s).

From Fig. 5.3.-4 it can clearly be seen that the fuels (starting with the same initial diameter) have very different reaction rates due to the wide range of the physical and chemical properties of the fuels. One of the most important parameters is the volatile yield. The carbon release rates of the volatile-rich beech wood particles are about three times higher than the release rates of the sub-bituminous coal 1. The bituminous coal shows carbon release rates during devolatilization comparable to those of sub-bituminous coal 1, but the char combustion rates of the bituminous coal are about twice as high. Due to the low carbon release rates of the particles with low densities the char burnout times are not as different as they could be. The devolatilization times increase with increasing density. The center temperatures follow a similar rule. Fuels with higher volatile matter and lower density heat-up faster.

The engineer has to be careful to generalize these conclusions drawn above. These results were obtained under certain experimental conditions which might not be similar to his/her application of interest. In literature a wide range of different laboratory-scale units exists (refer to Chapter 2) and rate constants of carbon conversion even for the same fuel can differ in their order of magnitude. Therefore the engineer who wants to use these results should check carefully the similarity rules if he or she can transfer these results to his/her application.

However, in the field of solid fuel combustion the importance of fuel reactivity is well known for the optimization of the combustor design. If the fuel is very reactive producing high amounts of volatiles then the combustion in the gas-phase gains importance. The characteristics of gas-phase combustion have to be considered in the design and operation of the combustor. The location of the combustion will shift to upper parts of the combustor changing the temperature distribution and heat transfer. Plumes of unburned volatiles might even reach the top (emissions!) when the mixing is poor and strong fluctuations in the oxygen concentration will be found locally. Especially care has to be taken to the feeding sections of very reactive fuels. The char content within the combustor will be low (e.g. *Amand et al. 1997*).
If the fuel is unreactive and low in volatiles, char combustion will gain importance. The location of combustion is closely connected to the location of the char particles. If those are large, combustion will take place mainly in the bottom part of the combustor changing the temperature distribution and heat transfer. With decreasing reactivity the time for complete conversion increases and more time for better mixing is available.

5.3.2. The Conversion of Fuel-Nitrogen

Strongly connected to the conversion of carbon is the conversion of fuel-nitrogen. Due to the wide range of fuels used (e.g. coals, biomass) different precursors (e.g. HCN, NH_3) are released as intermediates which undergo different reaction paths, e.g. it is well known that HCN is a strong precursor for N_2O whereas NH_3 is not. However, not only the amount of the different precursors formed is of importance, but also the time when they are formed. Fuel-nitrogen released during devolatilization undergoes different reaction paths as char nitrogen.

In Fig. 5.3.-1 a typical measurement run of a burning wood particle in the formation rate unit (FRU, refer to Chapter 4.1.1.) is given. The different formation characteristics of NO, N_2O, NH_3, and HCN can be seen as well as the CO_2 indicating the instantaneous carbon conversion rates. In Figs. 5.3.-5 to 5.3.-7 the amount of NO, N_2O, NH_3, and HCN formed is based on the conversion of the fuel-nitrogen and for a better comparison of the different fuels combustion time was converted to the degree of carbon conversion.

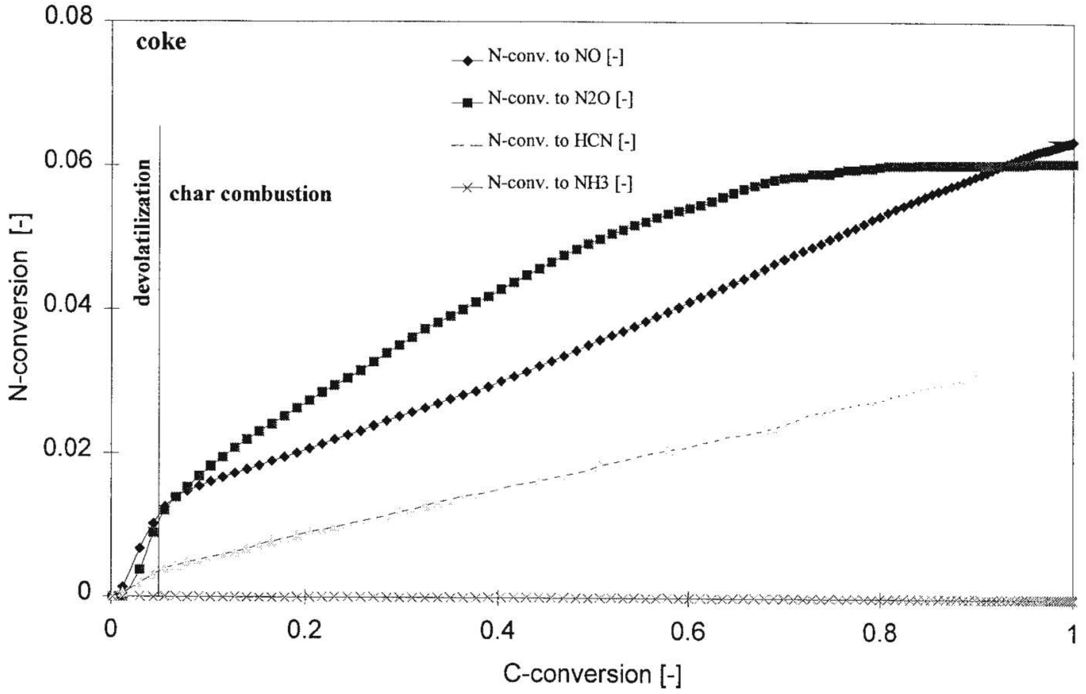

Figure 5.3.-5: Fuel-nitrogen conversion to NO, N_2O, HCN, and NH_3 versus carbon-conversion from petroleum coke, single particle experiment in the FRU at 800°C and 10kPa oxygen.

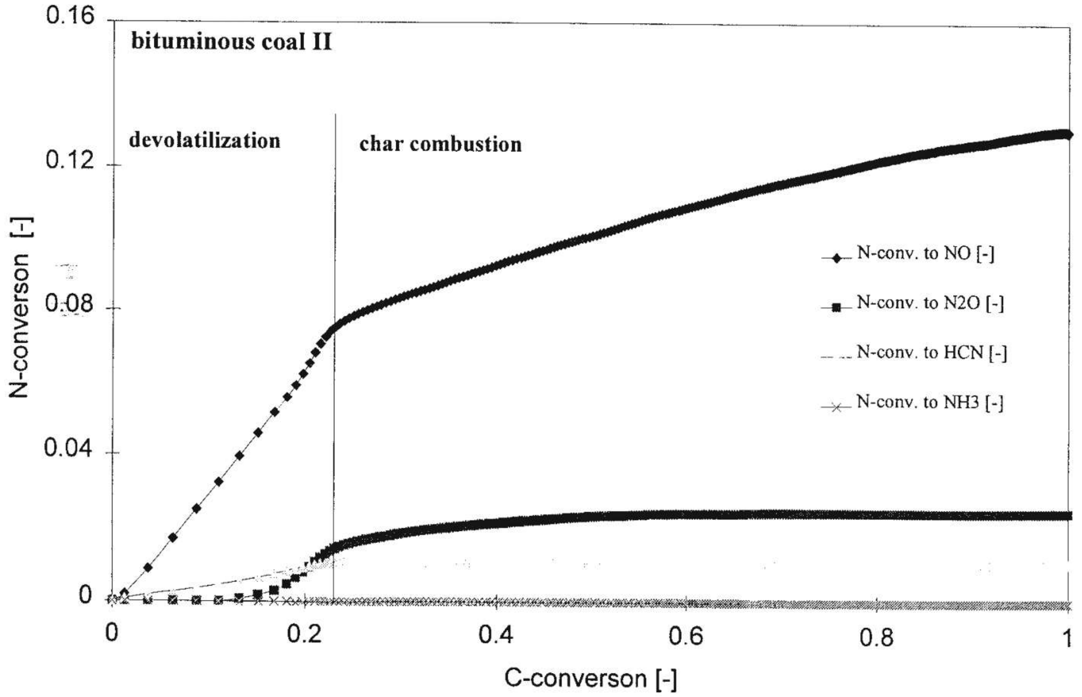

Figure 5.3.-6: Fuel-nitrogen conversion to NO, N_2O, HCN, and NH_3 versus carbon-conversion from bituminous coal, single particle experiment in the FRU at 800°C and 10kPa oxygen.

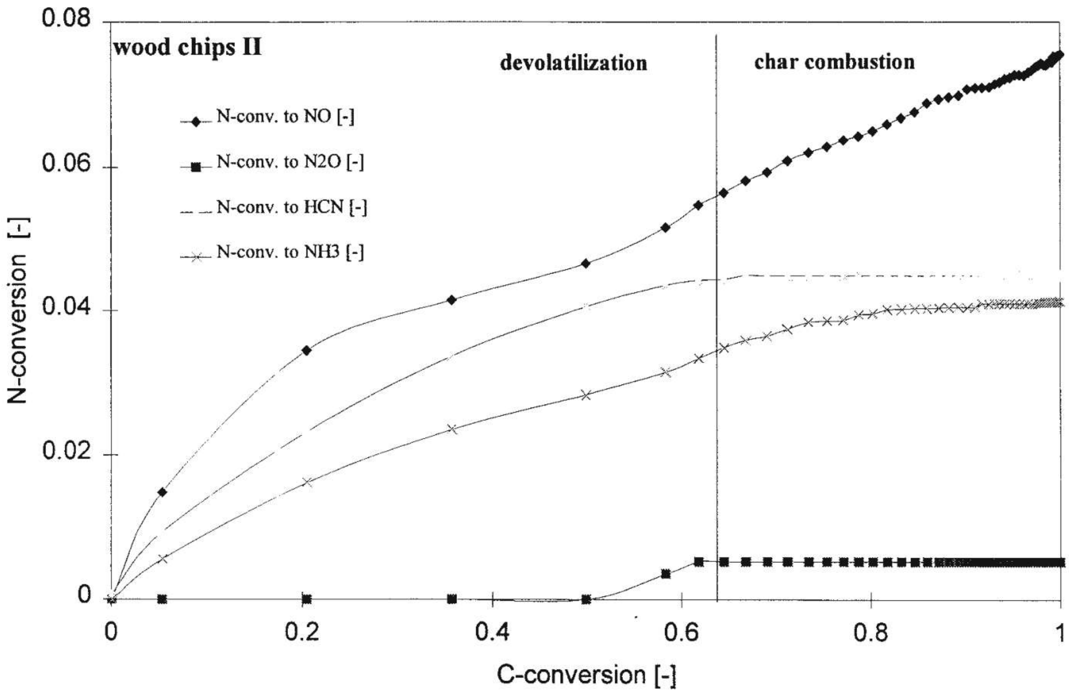

Figure 5.3.-7: Fuel-nitrogen conversion to NO, N_2O, HCN, and NH_3 versus carbon-conversion from wood chips, single particle experiment in the FRU at 800°C and 10kPa oxygen (refer also to *Winter et al. 1999d*).

In Figs. 5.3.-5 to 5.3.-7 the different characteristics of the fuels can be seen obtained in the FRU at 800°C and 10kPa oxygen partial pressure. The coke shows the lowest content of volatiles and devolatilization is of minor importance. During char combustion mostly NO and also high amounts of N_2O are formed. HCN is high as well and almost no NH_3 is formed. In the case of the bituminous coal, devolatilization gains importance and about half of its NO formed is during devolatilization. For N_2O formation devolatilization is more important than char combustion. Almost no NH_3 is formed. In wood combustion devolatilization is the major pollutant formation period. High conversions to NO can be found. Only few N_2O is formed at the end of devolatilization. High conversions to NH_3 can be found which are close to HCN.

Generally, these characteristics can be found in pilot-scale and industrial-scale combustors, altered by destruction reactions. However, formation is always of great importance because the level for destruction starts from the level of formation.
In wood combustion it is well known that high amounts of volatiles will be generated. The conversions to NO are relatively high and almost no N_2O can be found. (e.g. *Leckner and Karlsson 1993, Liu et al. 1999*) The char concentration in the combustor is usually very low because of the fuel's high reactivity and high content of volatile matter. High amounts of NH_3 are detected during wood combustion (*Amand et al. 1999*). During coal combustion the picture is different. N_2O increases significantly and can be a major drawback. HCN is the major precursor, NH_3 is usually of minor importance. The concentration of char in the combustor rises significantly and has a beneficial effect on the NO emissions (NO is partly destroyed on the char surface). Burning petroleum coke, high levels of N_2O can be reached (refer to Table 5.1.1 showing the concentration measurements in the CANMET pilot-scale CFBC, *Winter et al. 1999a*).

5.4. FUELS IN THE SINTER-PROCESS

In *Winter et al. 1999e* the reactivities of alternative fuels (e.g. dust from blast furnace, recycling material, fine metal, sinter coke, petroleum coke, anthracite) were studied in the laboratory-scale for the sinter process and a classification system was derived. In Fig. 5.4.-1 some typical results are given. The steepness of the lines corresponds to the reaction rate constant (*kg*) which is the descriptive parameter (refer to Table 5.4.-1).

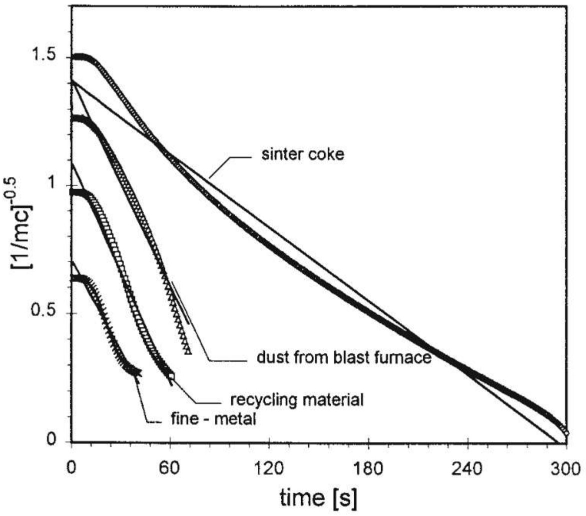

Figure 5.4.-1: The figure shows the results of the reaction rate measurements of selected sinter fuels. The steepness of the lines corresponds to the to the reaction rate constant (*kg*).

Fuel	k_g $[g^{0.5}.s^{-1}]$
sinter coke I	-0.0096
sinter coke II	-0.0061
sinter coke powder	-0.0284
petroleum coke	-0.0096
Anthracite	-0.0110
dust from blast furnace	-0.0268
recycling material	-0.0284
fine – metal	-0.0232

Table 5.4.-1: Comparison of reaction rate constants (*kg*) of selected sinter fuels.

The reaction rate constants (*kg*) were then correlated with results from the sinter-pot which corresponds to pilot-scale measurements. It is a well-proven method. Design equations for the sinter process were derived. In Fig. 5.4.-2 the correlation of the mass of return of fines directly with *kg* is shown. The mass of return of fines is an important criterion for the sinter process.

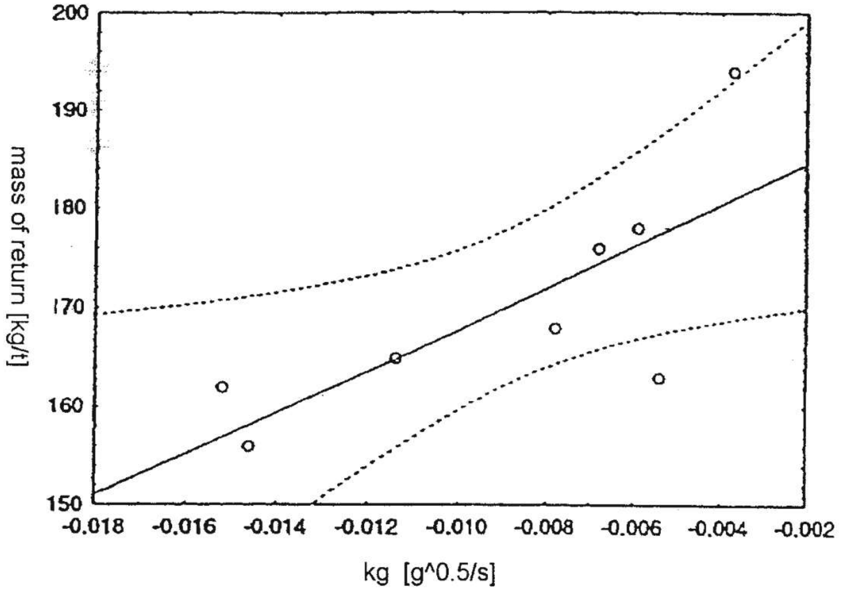

Figure 5.4.-2: Reaction rate constant versus mass of return fines. The dotted lines show the statistical confidence interval.

It was also possible to calculate the productivity of the sinter process which is the main design equation. The sinter productivity (in tons of sinter per m^2 and per day) is a function of the reaction rate constant (*kg*) and the diameter of the fuel. In Fig. 5.4.-3 the calculated results are compared to measurements.

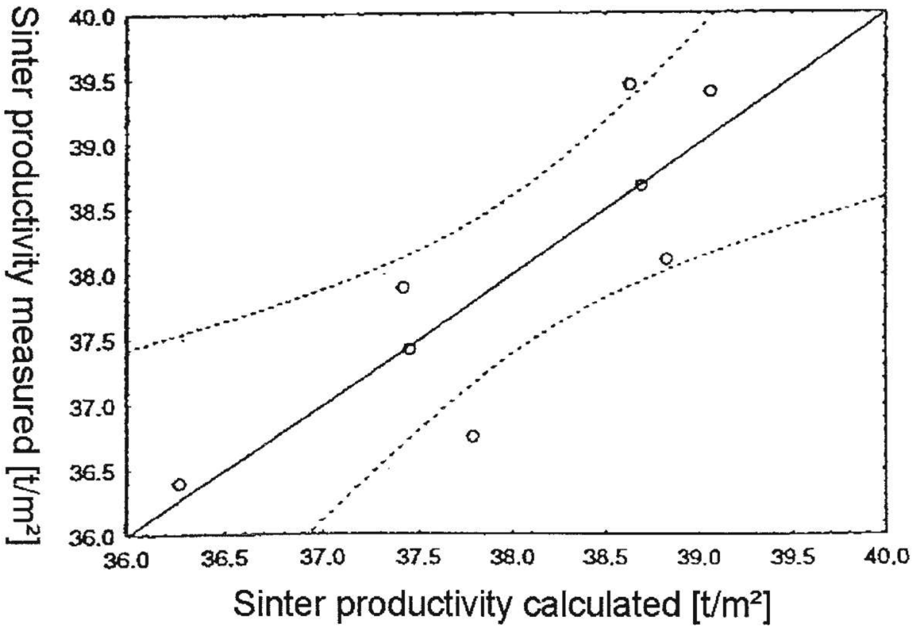

Figure 5.4.-3: Sinter productivity calculated versus measured. The dotted lines show the statistical confidence interval (t is tons per day).

5.5. IRON ORE REDUCTION

In this study the reduction kinetics of iron ore fines was tested in the laboratory-scale. Care was taken to design and to operate the laboratory-scale unit under conditions which are similar to the industrial-scale (refer also to Chapter 1, the FINMET process). The reducing gas, produced by steam reformed natural gas, was simulated with gas mixtures of H_2, H_2O, CO, CO_2 in nitrogen. This gas was the fluidizing gas and used for the reduction of fine iron ore in a fluidized bed reactor (refer also to Chapter 4.1.1), which operated under elevated pressures similar as the industrial-scale process. To operate the laboratory-scale reactor as a differential reactor (low conversions, uniform conditions) mixtures of silica sand and iron ore were used as the bed material.

The reduction kinetics were obtained by measuring H_2O, CO, CH_4, CO_2 in the flue gas of the laboratory-scale unit (by FT-IR spectroscopy) and by applying a balance of oxygen and carbon. In Figure 5.5.-1 a typical measurement run is shown. The instantaneous reduction rates can be seen by following the formation of the reduction products H_2O and CO_2. The effects of temperature, gas composition, pressure, and iron ore particle size were investigated and quantified.

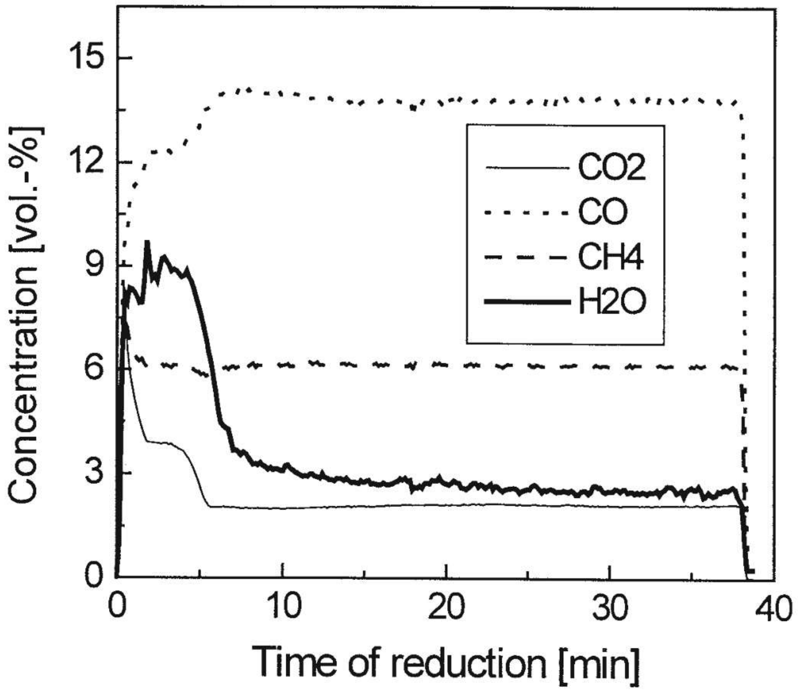

Figure 5.5.-1: A typical measurement run during the reduction of iron ore fines in the fluidized bed reactor.

In Fig. 5.5.-2 the reduction rates are plotted versus the degree of reduction (fractional reduction), the effect of temperature is shown. It can be seen that with increasing temperature the reduction rates increase. At the highest temperature (1113K) the reduction rates continue to stay on a high level even at high reduction degrees. Decreasing the temperature to 823K the typical reduction characteristics will change qualitatively and the rates are at their lowest level.

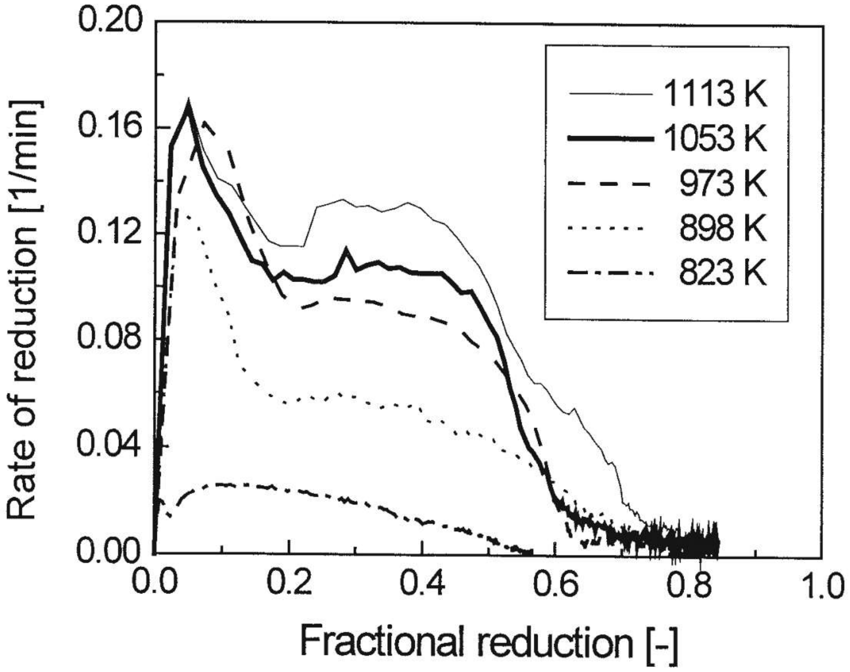

Figure 5.5.-2: The effect of temperature during the reduction of iron ore fines.

The kinetic data were used to calculate the degrees of reduction for continuous operation of a laboratory-scale unit (refer to Chapter 4.1.1). Generally, good agreement was obtained.

5.6. FLUID DYNAMICS OF COHESIVE PARTICLES

In the field of desulfurization, modeling and experimental work was carried out to optimize existing desulfurization reactors and to design new and improved ones. It was necessary to understand and to describe the fluid dynamics of fine particles ($Ca(OH)_2$, mean particle size 5µm, refer also to Chapter 1) which are strongly cohesive (Geldart Group C particles). With a newly developed model (refer to Chapter 4.2.8) the effect of reactor design, water injection and operating conditions on fluid dynamics were studied. Laboratory-scale and pilot-scale results were used for comparison, and the model applied for industrial-scale (refer to *Winter et al. 1999f*).

One of the major difficulties in modeling processes where very fine and therefore strongly cohesive particles are involved is to know the actual particle size distribution in the reactor. Due to the strong interparticle forces agglomerates are formed *in-situ* which can be 2 orders of magnitude larger (e.g. 300 µm) than the initial particle size. These agglomerates significantly affect fluid dynamics because the mean diameter "seen" from the fluid is much larger than the particle diameter. However, these agglomerates are rather loose and can be rapidly destroyed by high momentum forces which might occur in the reactor under normal operating conditions.

To consider the strong interparticle forces and agglomerates' formation and destruction, a similar approach has been used as described in the concept of chemical similarity. The design principles of the laboratory-scale unit were not based on the traditional approach where the fluid dynamics of the whole industrial process is mirrored in the laboratory-scale unit and the laboratory-scale process is a "small" industrial-scale process (refer to Chapter 3). In literature no reliable scaling criteria can be found for the fluid dynamics of cohesive particles. Usually interparticle forces are neglected while deriving such scaling criteria (refer e.g. to *Glicksman 1988*).

In this study the same principles were used which are the basis for the concept of chemical similarity: A finite volume from the industrial-scale unit was mirrored in the laboratory-scale unit (refer to Chapter 3). However, here it was not focused on chemistry but on fluid dynamics and forces. Care was taken to have similar conditions in the laboratory-scale unit from the fluid dynamical point of view. The same sorbent was used with its actual chemical and physical composition and size distribution as in the industrial-scale process to ensure that the same interparticle forces will exist in the laboratory-scale unit. The same temperatures as well as the same gas velocities were used as in the industrial-scale process.

However, not all similarity rules could have been fulfilled. The pulverized coal boiler was not simulated. Air was used and only little natural gas was burned to preheat the gas up to its desired inlet temperature (high excess air ratios). Therefore the chemical composition of the gas differed (e.g. low in CO_2) from an actual composition of a pulverized coal boiler's flue gas. Also the fly ash which is formed in a pulverized coal boiler was not simulated. Since it was not intended to study the on-going chemical processes it was assumed that these violations from the similarity rules were of minor importance and chemistry was not significantly affecting fluid dynamics. Therefore fluid dynamics was studied separately from chemistry. Although the gas was different in its chemical composition, the physical differences (e.g. gas density, gas temperature, gas viscosity) were small. The utilization of an actual sorbent ensured that the most important similarity rules were fulfilled. The formation and destruction of agglomerates was analyzed by visual and optical methods (video camera) and used for the development of the model (*Winter et al. 1999f*).

In Table 5.6.1 typical modeling results are presented. For further details refer to *Winter et al. 1999f.*

	symbol	unit	laboratory	medium	industrial	pilot
mean particle diameter	d_0	[μm]	15	20	40	20
superficial velocity	u_0	[m/s]	4.9	4.6	4.5	2.6
max. jet velocity	u_{jet}	[m/s]	56,9	53,4	52,2	44,7
jet constant	K_{jet}	-	150	150	150	150
jet penetration length (Eq.3)	H_{jet}	[m]	1.4	3.1	14.5	3.9
single jet length	$H_{single\ jet}$	[m]	0.65	1.46	6.9	3.9
height of jets exchange	$H_{exchange}$	[m]	0.75	1.55	7.6	-
height of transport zone	$H_{transport}$	[m]	2,6	5.9	6.5	5.1

Table 5.6.-1: Modeling results of the distribution/jet zones of different scales (refer to *Winter et al. 1999f*).

However, to generalize the concept of similarity to design and optimize processes utilizing cohesive particles further work will be needed.

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6. SUMMARY AND CONCLUSIONS

The optimization and design of processes is one of the most important areas of process engineering. In practice the aims in the development of a new process are to minimize the risk of the new process, to minimize the costs for its development and to minimize the time for its development to compete with the constraints of a changing market.

Therefore experience and the development of reliable experimental and theoretical methods for scale-up and process design are necessary. Laboratory-scale units offer substantial information and are inexpensive, low in their operation costs, high in their availability, changes can be done quickly and at low costs and the operating conditions can be varied in a broad range. However, uncertainties exist and the results can be used incorrectly.

In this thesis the concept of chemical similarity between industrial-scale, pilot-scale and laboratory-scale units was introduced and demonstrated with examples from different gas - solid processes (the combustion of solid fuels, iron ore reduction, the sinter process and flue gas desulfurization). This concept was used to get important and reliable information from laboratory-scale units which can be used to optimize and design industrial-scale processes.

The basic principle of the concept of chemical similarity is that a finite volume of the industrial-scale reactor is mirrored in the laboratory-scale unit. To do this correctly certain similarity rules have to be fulfilled. For a pure homogeneous system these are at a given time: Gas temperature, total pressure, and species concentration, considering also the intermediate species.
In gas - solid reaction systems additional similarity rules exist:

- the particle temperature or the temperature of a certain zone in the particle
- the gas temperature inside the pores of the particle
- the pressure inside the particle which might differ from the bulk pressure
- the species' concentrations inside the pores of the particle to consider gas - phase reactions inside the pores and gas - solid reactions at the particle's internal surface
- the species' concentrations at the surface of the particle to consider gas - solid reactions at the particle's external surface
- the physical properties of the solid reactant such as external/internal surface area, pore structure (size of the pores and distribution)
- the chemical composition of the solid reactant (care has to be taken to impurities which might be catalytic active)

Because of the above mentioned similarity rules for gas - solid reaction systems, the actual solid reactant of the industrial-scale process has to be used in the laboratory-scale tests. Difficulties may arise in practice because the heating rates of the solid reactant have to be considered affecting the operating conditions in the laboratory-scale unit.

A similar problem which might be of importance for a proper scaling of the chemistry are fluctuations of the gaseous species and memory effects. If memory effects are dominant the application of kinetic data obtained from laboratory tests where the species' concentrations were kept constant will fail.

Also chemical and physical particle - particle interactions might be of importance. Particles of the same type and with the same or different size might interact via homogeneous or heterogeneous mechanism. Also particles of different types can interact. Heterogeneous mechanism will be of major importance especially under fixed bed conditions.

The concept of chemical similarity was demonstrated successfully in the following research areas:

The importance of radicals for CO and hydrocarbon oxidation and NO/N_2O formation was confirmed starting from the single burning particle, to burning batches of particles, further to combustion tests in a laboratory-scale CFBC up to a pilot-scale CFBC. A newly developed method was used, the method of iodine addition which enhances radical recombination reactions. Simultaneously it was shown that chemical similarity was obtained between the different test units.

In parallel, modeling work was done and a single particle model was developed and well tested in the formation rate unit. Then this model was incorporated into the CFBC NO/N_2O model which was also carefully tested in the laboratory-scale. Finally, this model was used successfully as a submodel in a global CFBC simulation model predicting NO and N_2O concentration profiles in an industrial-scale unit.

Additionally, the importance of the radicals as reactive intermediates was shown for the destruction of N_2O during CO oxidation in the laboratory-scale CFBC.

Similar trends as during the addition of iodine were found on CO, NO, and N_2O when SO_2 was added during the homogeneous oxidation of HCN studied in a laboratory-scale flow reactor. SO_2 also enhances radical recombination. This study was an important contribution to improve the understanding of trends observed from pilot-scale and industrial-scale units burning coals with different sulfur contents.

It was found that during the combustion of fuels with higher nitrogen contents more NO was formed but the conversion of fuel-nitrogen to NO decreased. This behavior was found in single particle combustion tests, during the combustion in a laboratory-scale fluidized bed combustor, and in a pilot-scale grate combustor. This behavior could be explained with the increased presence of nitrogenous species (e.g. NH_3, HCN) which reduced the NO generated by the oxidation of these same species.

The reactivities for devolatilization and char combustion of various different fuels ranging from coals to biomass to plastics and waste were determined in the laboratory-scale by integral and differential analysis. A classification system for the reactivities was established and calibrated with selected well-defined materials (graphite for char combustion and naphthalene-dicarboxylic acid anhydride for devolatilization). These standards can also be used to calibrate laboratory-scale units and procedures. The results were compared to experience well-known from industrial-scale units.

The propensity of a wide range of fuels (from petroleum coke to coals and biomass) for NO and N_2O formation was studied considering also the intermediates HCN and NH_3. Their NO and N_2O formation characteristics was obtained from transient concentration measurements during devolatilization and char combustion in a laboratory-scale unit. Generally, these characteristics can be found in pilot-scale and industrial-scale combustors, altered by destruction reactions.

In the laboratory-scale the reactivities of alternative fuels (dust from blast furnace, recycling material, fine metal, sinter coke, petroleum coke, anthracite) were studied for the sinter process and a classification system was derived. The reaction rate constants correlated well with sinter-pot results which corresponds to pilot-scale measurements. Design equations for the sinter process were derived, e.g. for the process productivity.

The reduction kinetics of iron ore fines with gas mixtures of H_2, H_2O, CO, CO_2 in nitrogen were studied in a laboratory-scale fluidized bed reactor at atmospheric and elevated pressures. The effects of temperature, gas composition, pressure, and iron ore particle size were investigated and quantified. The kinetic data were used to calculate the degrees of reduction for continuous operation of a laboratory-scale unit. Generally, good agreement was obtained.

To study fluid dynamics of fine particles which are strongly cohesive, the same principles were used which are the basis for the concept of chemical similarity. This concept was extended to focus on fluid dynamics and forces. Care was taken to have similar conditions in the laboratory-scale unit from the fluid dynamical point of view. The formation and destruction of agglomerates was studied and used for the development of the model describing the fluid dynamics of the desulfurization process. With this newly developed model the effect of reactor design, water injection and operating conditions on fluid dynamics were evaluated. Laboratory-scale and pilot-scale results were used for comparison, and the model applied for industrial-scale. However, to generalize the concept of similarity to design and optimize processes utilizing cohesive particles further work will be needed.

The concept of chemical similarity has proven to be a powerful tool which can be used for the optimization and design of gas - solid processes. In practice it is often not possible to fulfill all the very stringent similarity rules. However, useful information can be obtained, if the researcher is aware of the problems in designing laboratory-scale tests. He or she will know the limitations and will use the obtained results in a proper way depending on the aim of the work.

7. APPENDIX

PAPERS I - X

LIST OF PUBLICATIONS

CURRICULUM VITAE