

**ON THE CHEMISTRY OF COMBUSTION AND  
GASIFICATION OF BIOMASS FUELS, PEAT AND WASTE;  
ENVIRONMENTAL ASPECTS**

**by**

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**Title: On the Chemistry of Combustion and Gasification of Biomass Fuels, Peat and Waste; Environmental Aspects**

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**Abstract:**

This thesis is a summary and discussion of seven papers, dealing with the chemistry of combustion and gasification of biomass fuels, including peat and municipal solid waste. All environmental aspects, as well as potential problems, associated with these fuels have to be studied closely before the desired increased utilization can be realized in a safe way. In the present work several approaches have been used to study the reduction of the emissions of SO<sub>2</sub>, NO<sub>x</sub>, N<sub>2</sub>O, Hg and uncombusted hydrocarbons. In addition, the processes of bed sintering, ash and deposit formation were addressed.

Equilibrium calculations were used as a first tool to determine feasible and unfeasible reactions in the processes studied. Initial surveys of elemental chemical composition and speciation of the elements in the biomass fuels were performed to obtain accurate and representative input amounts for the calculations. Much effort was then devoted to comparing the equilibrium results with corresponding experimental data from lab-, pilot-, and full-scale reactors. To extract maximum information from the experiments, they were performed according to statistical experimental designs. Two of the papers have concerned the direct minimization of emissions from practical combustion processes, where it was shown that the NO<sub>x</sub> emissions may be reduced by about 60%. By using intelligent fuel combinations the SO<sub>2</sub> emissions can be reduced by 40-90% and deposit formations and bed sintering may possibly be prevented. The work has shown that the proposed approach of equilibrium calculations combined with well designed experiments is a suitable procedure for increasing our general knowledge of these complex processes as well as for direct minimization of emissions from existing industrial plants. Several suggestions for future work are presented.

**Keywords:** Combustion chemistry, biomass fuels, peat, municipal solid waste, environmental aspects, sulfur dioxide, nitrogen oxides, mercury, modelling, ash and deposit formation, bed sintering

*"Everything that happens is due to the  
flow and transformation of energy ...  
Control the fire and you control  
everything. The discovery of fire ...  
lifted man from the level of the beast  
and gave him domination over the  
earth"*

*Morton Mott-Smith in his  
Introduction to Heat and  
its Workings 1933*



*Any fool can light a fire  
Only a few can shed light on the fires  
needed to avoid future darkness*

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# ON THE CHEMISTRY OF COMBUSTION AND GASIFICATION OF BIOMASS FUELS, PEAT AND WASTE; ENVIRONMENTAL ASPECTS

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This thesis is based on the following papers, in the text referred to by their Roman numerals I-VII:

- I            Chemical elemental characteristics of biomass fuels.  
              Nordin, A., Submitted to *Biomass & Bioenergy*
  
- II           Forms of ash forming elements in biomass fuels  
              Nordin, A., Schirazi, A. R., Eklund, L. Samuelsson, R., Langer, W.,  
              Lindqvist, O., Manuscript.
  
- III          Application of extensive equilibrium calculations to the study of ash  
              formation and sulphur capture during combustion and gasification of  
              peat and biomass fuels.  
              Nordin, A., Forsberg, S., Rosén, E., Manuscript.
  
- IV          Results from extensive measurements on a 25-MW circulating fluidized  
              bed combustor fired with biomass. Equilibrium model explaining the  
              NO emissions?  
              Nordin, A., *Proc. of the First Int. Conf. on Combustion Technol. for a  
              Cleaner Environment*, Villamoura, Portugal, Sept. 1991.

- V NO reduction in a fluidized bed combustor with primary measures and selective non-catalytic reduction; a screening study using statistical experimental designs.  
Nordin, A., Eriksson, L., Öhman, M., Submitted to *FUEL*.
- VI Optimization of sulphur retention in ash when co-combusting high sulphur fuels and biomass fuels in a small pilot scaled fluidized bed.  
Nordin, A., Accepted for presentation at the *Second Int. Conf. On Combust. Technol. for a Clean Environment*, also submitted to *FUEL*.
- VII Mercury speciation in flue gases - a comparison of results from equilibrium calculations with results from experiments.  
Nordin, A., Schager, P., Hall, B., Manuscript.

Additional publications of relevance in the present work, but not included in the thesis, are:

- 1            Chemical reactions in combustion of peat and biomass in two fluid-bed boilers, CFB (25 MW) and SFB (25 MW) in Östersund. The effect on  $\text{SO}_2$  and  $\text{NO}_x$  emissions by operating conditions and type of fuel.  
Nordin, A. Thermal Engineering Research Foundation, Report no. 389, 1991. In Swedish, abstract and figure texts in English.
2.           Investigation of chemical characteristics and particle size distribution in peat ashes from commercial combustion district heating plants. Burvall, J., Nordin, A., Levén, P., Wigge, B. Thermal Engineering Research Foundation, Report no. 439, 1992. In Swedish, abstract and figure texts in English.
- 3            Sulfur capture by co-firing sulfur containing fuels with biomass fuels - optimization.  
Nordin, A. Thermal Engineering Research Foundation, Report no. 455, 1992. In Swedish, abstract and figure texts in English.
- 4             $\text{NO}_x$  reduction of gases from gas turbines and diesel engines by combination with a boiler for solid fuel.  
Nordin, A. Eriksson, L. Thermal Engineering Research Foundation, Report no. 466, 1993. In Swedish, abstract and figure texts in English.





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# 1 INTRODUCTION

Combustion is a phenomenon familiar to virtually every man, woman and child and has been so ever since the Titan Prometheus stole fire from the Gods and gave it to man. The year of this act of great (ir)responsibility is not known but it is believed that the antropoid-ape used fire under controlled conditions as early as 2-12 million years ago. During all these years, biomass fuels were the natural choice for the purposes of heating, cooking and bringing light into the darkest corner of the cave.

## 1.1 Combustion and the environment

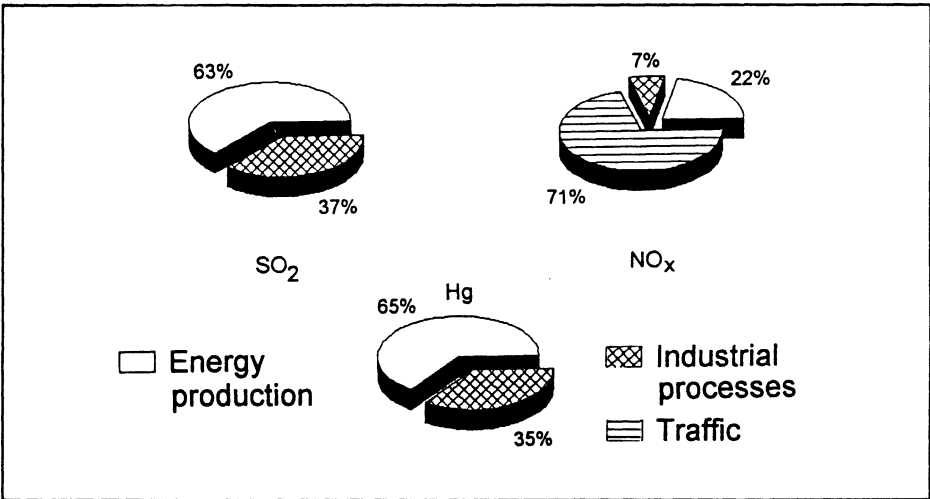
By the introduction of fossil fuels in the Middle Ages, terms such as "unendurable smoke" and "air pollution" were reported for the first time, and in the year 1276 King Edward II of England prohibited the burning of coal during the period that parliament was in session, with the following proclamation:

"Be it known to all within the sound of my voice, whosoever shall be found guilty of burning coal shall suffer the loss of his head"

Nevertheless, very little action followed, and it was not until 1952, when the "Killer Smoke" occurred in London, that public opinion and concern forced some initial attempts to clean up urban air. The most serious atmospheric pollution problems of today are, however, more of an intercontinental and global nature, and include the long range transport of acidic gases and mercury, as well as the depletion of the stratospheric ozone layer and the increasing greenhouse effect.

Even if there are some natural contributions to environmental pollution, most of the emissions are related to anthropogenic sources and, of these, combustion processes may give rise to literally hundreds, if not thousands, of different emitted trace species. Our knowledge of this subject is limited by our ability to detect and quantify the concentrations of such emissions, as well as an awareness of "new" toxic substances. Each year, improved analytical techniques and further research reveals "new" potential

pollutants. Some of the pollutants we are concerned with today, include NO, CO, NO<sub>2</sub>, N<sub>2</sub>O, SO<sub>2</sub>, HCl, "dioxines", "furanes", PCBs and additional chlorinated organics, Hg, Cd and other "heavy metals". Combustion processes account for the vast majority of these atmospheric pollutants<sup>1,2</sup>, and the relative importance of the major sources of three of them are shown in *Figure 1*.



**Figure 1.** Major sources of SO<sub>2</sub>, NO<sub>x</sub> and Hg emissions

In addition to the common processes for energy production (heating, electricity generation) and transportation purposes, many of the industrial processes are also more or less combustion related. With these facts as a background, it is clear that the research field of environmental aspects of combustion processes is quite challenging and the work has to be intensified to cope with the emission limits determined by nature itself.

**1.2 Biomass fuels - general perspectives**

King Edward II probably did not know anything about the greenhouse effect, yet his proclamation from 1276 is probably more pertinent than ever today. The present energy use, largely dependent on fossil fuels, is incompatible with a sustainable world. Bound carbon in these fuels is a product of formation and accumulation during many millions of years, and the present rapid rate of release of fossil fuel combustion products drastically changes the composition and behavior of our atmosphere. This will effect

not only the temperature of the planet, but also the atmospheric motion, moisture, clouds, sea level, winds and so on. Therefore, in addition to energy conservation and increasing the efficiencies of processes, the shift to renewable energy sources seems to be inevitable, if we want to take these environmental problems seriously.

As a result, much attention has been focused on the use of biomass fuels such as forestry waste materials, by-products, cultivated energy crops and even cattle manure as sources of energy (and chemical feedstock), as these fuels do not contribute to any increase of the atmospheric CO<sub>2</sub>. The use of renewable energy sources in the year 1980 as well as their future potential<sup>3</sup> for both Sweden and worldwide is shown in *Table I*.

**Table I.** Current use of renewable energy and estimated figures for the next two decades and long-term potential<sup>3</sup> (1TWh = 3.6·10<sup>15</sup> J)

Energy	In the world (10 <sup>18</sup> J)			In Sweden (TWh)	
	1980	2020	Potential	1991	2010
Biomass	44	70-130	135-395	70	127-169
Hydropower	19	30-50	70-90	64	>64
Solar	<0.1	8-22	35-175	<0.1	
Geothermal	0.3	2-3	10-100	<0.1	
Wind	<0.1	4-8	30-70	<0.1	
Tide, wave	<0.1	1-3	3-4	<0.1	
Renewable	63.3	115-216	280-840	134	>191-233
Total use	400	290-440	290-440?	370	370?

Even with the most careful estimates, the possibilities for the use of renewable energy sources seem to be enormous. In the short term (the next two decades), however, a supply based completely on renewable energy will not be sufficient. Therefore, it is a necessity to strive for higher production of biomass fuels and increased development of these energy sources. In Sweden, biomass fuels represent about 19 % of the total energy use and recent estimations indicate that an increase to about 170 TWh is plausible in the near future (~20 years). In the Northern and urban regions, the combustion of these fuels already dominates heat production.

What then is a biomass fuel ? Can peat and municipal waste be regarded as biomass? In the present work, both peat and municipal solid waste (MSW) are considered as renewable resources. It has been argued whether peat is a biomass fuel or a fossil fuel. No CO<sub>2</sub>-tax is currently exacted on peat combustion in Sweden, even if no official classification has been made. The present growth of peat, corresponding to about 15 TWh/year, exceeds the consumption (3.5 TWh/year) and furthermore, the exploited area can be back in the carbon cycle within some years. In addition, peat lands may naturally produce significant amounts of CH<sub>4</sub> and this gas is expected to contribute to about 18 % to the total future global warming<sup>4</sup>. As wetlands have been estimated to contribute to about 20 % of the total atmospheric CH<sub>4</sub>, an increased energy production from peat may therefore benefit the environment even more. However, these aspects are presently under debate and the figures presented are subject to large variations. The compositions of residues and wastes are also dominated by materials originating from biomass, and this fraction will increase as the recycling and replacement of other materials are increased. The majority of the waste is therefore part of the natural carbon cycle and its carbon content will return to the atmosphere either by being broken down by bacteria or by being combusted. Hence, waste used to displace any fossil fuel for energy production will also help to limit the greenhouse effect. When deposited, the MSW will probably produce more harmful products by the slow degradation process as well as by the many uncontrolled accidental fires.

No matter how the definitions are made, all these renewable fuels are favorable relative to the fossil fuels and an increased production and use will definitely benefit the environment in the long term, if fossil fuels are replaced. In conclusion, the study of the chemistry of combustion of biomass fuels is highly warranted for several reasons:

- i) Biomass fuels have the qualifications to be environmentally superior fuels for energy production, compared to fossil fuels.
- ii) Combustion scientists have primarily been concerned with those fuels most often burned as energy sources in the world: viz. coal, petroleum products and natural gas. Studies on the potential use of the "new" fuels have

mostly been focused on technical economic problems, i.e. how much biomass is available and at what cost. Only little attention has been given to the environmental and chemical effects of the energy conversion processes of these fuels.

- iii) Sweden has no significant sources of fossil fuels which is why an increased use of domestic fuels is advantageous for both economical and political reasons. Further, the world-wide estimated<sup>5</sup> supplies of oil, natural gas and coal will only last for about 40, 60 and 240 years respectively, whereas biomass fuels are infinite.

However, there are still some specific environmental problems associated with our domestic fuels. These include several undesired emissions; SO<sub>2</sub> from peat; Hg, Cd, HCl and chlorinated organics mostly from waste and NO<sub>x</sub>, N<sub>2</sub>O, CO and unburned products from all fuels. Other potential problems with these fuels include deposit formations, slagging and bed sintering, due to the different compositions of the ashes, compared to the "more traditional" fossil fuels. Furthermore, much of the present use of biomass fuels could be made considerably more efficient using improved conversion systems. All these aspects have to be studied more closely.

### **1.3 Aim and outlines of the present work**

The aim of the present work has been to contribute to our knowledge and understanding of the chemical processes of combustion and gasification of biomass fuels. Special stress has been laid on the formation and emission of SO<sub>2</sub>, NO<sub>x</sub>, Hg and HCl. In addition, some of the potential ash related problems of biomass fuels, i.e. slagging, fouling and sintering, are also addressed. The strategy during the work has been to utilize advanced chemical equilibrium calculations as a first tool to find the driving forces and possible directions of important reactions, as well as to determine the general behavior of the studied processes (*papers* III and VII). To allow for an extensive coverage of existing and potential biomass fuels, a comprehensive review and compilation of elemental chemical characteristics of these fuels was initially carried out (*paper* I). In *paper* II, the corresponding speciation characteristics of vital elements for some important

biomass fuels are presented. The calculated equilibrium values have been compared and verified with corresponding experimental results obtained in full scale reactors (*papers* IV, V), in pilot scale reactors (*papers* VI, VII) and in a lab scale reactor (*paper* VII). The pilot scale fluidized bed reactor, used in *paper* VI, was constructed in the present work. The purpose was to facilitate well controlled experiments, both for relevant comparisons with equilibrium results and for direct optimization studies. To allow for maximum extraction of information from the experiments, two of these studies were performed according to statistical experimental designs (*papers* V and VI).

## **2 COMBUSTION CHEMISTRY**

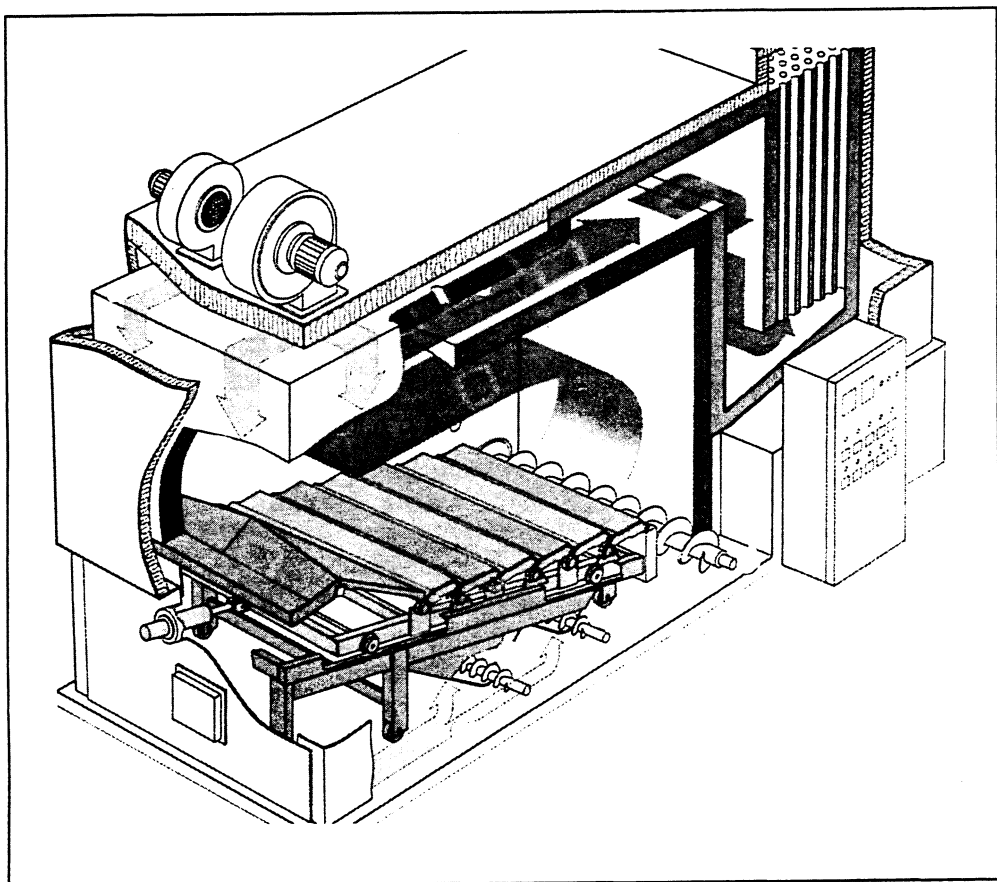
Historically, the development and construction of combustion systems have been more within the domain of mechanical engineers than of chemists or chemical engineers. Because of the increased concern about environmental pollutants from combustion sources, much chemical research work has been initiated and chemists are now consulted in both the design of new plants as well as in optimization of old ones.

### **2.1 Principles of some combustion techniques**

A short orientation of the principles of the most important firing techniques for biomass fuels will be given here. This will also permit the definition of some basic physical conditions needed for the forthcoming chemical analysis. The existing techniques include grate-, spread- and retort stokers, fluidized bed (FB) systems and pulverized fuel systems. In the techniques based on grates (*Figure 2*), such as the traveling, chain and vibrating grate stokers, the fuel is introduced by a hopper, onto the grate, by gravity. The feeding rates are either regulated by a grate opening that controls the thickness of the bed or by the frequency of the alternately pushing grate plates. As the fuel bed moves, the moisture is driven off initially, followed by ignition, burning and finally cooling when the ash is transported out. The stokers (grates) consist of different sections, where the flow rates and pressure of the combustion air (primary air) can be independently controlled. Measurements of the temperature within the bed and furnace<sup>6,7,8</sup> have shown relatively inhomogeneous profiles with maximum temperatures

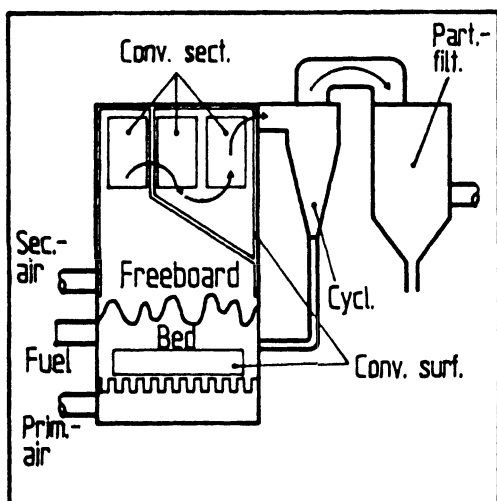


of 900-1100°C in the burning area of the bed, but as low as 200-500°C in the drying and ashing zones. The controlling possibilities for the different primary air inlets are therefore of vital importance for obtaining homogeneous temperature profiles, not only in the bed area but also up through the furnace. The temperature above the bed and in the freeboard normally ranges between 800°C and 1000°C. Spread stokers, which feed the fuel by distributing it on the top of the bed throughout the furnace, and retort (underfeed) stokers are less common for biomass fuels in Sweden.

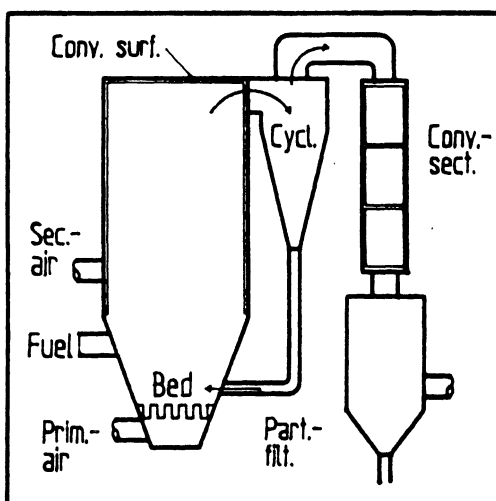


**Figure 2.** Illustration of the grate combustor used in reference 6

On the other hand, fairly many fluidized beds are used for biomass conversion in Sweden. At present, about 15 stationary fluidized beds (SFB) and about 15 circulating fluidized beds (CFB) are in operation with various contents of biomass fuels. Schematic drawings of these two types of FB systems are shown in *Figures 3 and 4*, respectively.



**Figure 3.** Schematic illustration of a stationary fluidized bed combustor



**Figure 4.** Schematic illustration of a circulating fluidized bed combustor

The primary air, introduced through a distributor, keeps a bed of sand (usually most  $\text{SiO}_2$ ) fluidizing. Secondary, and in some cases tertiary, air may be introduced higher up in the furnace to facilitate staged combustion. The freeboard in the SFB allows sufficient space above the bed for the larger particles to fall back to the bed, whereas in the CFB, cyclones are utilized for recirculation of particles. Therefore, the amount of primary air used, and thereby also fluidization velocity and retention times, depends on the type of FB as well as the particle size of the bed material. Normally, fluidizing velocities of  $1\text{--}3\text{ ms}^{-1}$  (for SFB) and  $4\text{--}10\text{ ms}^{-1}$  (for CFB) are required. The available retention time in the warm zone, below the convection section, is at least five seconds. For SFB's, deep beds (0.7–1.1 m) are the most commonly used, which give retention times in the bed of about 0.5 s. In the bed, oxygen rich bubbles are produced during the fluidization, whereas the "particle phase" possesses a reducing atmosphere. In-bed measurements of oxygen partial pressure, when combusting coal, indicate that the particle phase of the bed is under reducing conditions ( $p(\text{O}_2) < 10^{-11}\text{ bar}$ ) 80–90% of the time<sup>9,10</sup>. No comparative measurements have been found in the literature for combustion of biomass fuels, but probably about the same results would be obtained. The bed is normally operated at  $750\text{--}950^\circ\text{C}$ , which is considerably lower than both grate and pulverized fired combustors. However, the temperatures of the burning particles may exceed the bed temperature by  $20\text{--}200^\circ\text{C}$ , the largest difference being found for the

smallest particles and highest particulate phase oxygen concentrations<sup>c.f.11,12,13</sup>. The increase in particle temperatures has been recognized for all burning particles<sup>c.f.14</sup> and the major advantage of FBs is the possibility to use the lower combustion temperatures without decreasing the combustion efficiency. This inhibits the formation of thermal NO<sub>x</sub> and admits the removal of SO<sub>2</sub> by addition of sulfur absorbents. Such conventional absorbents may be CaCO<sub>3</sub> (limestone) or (Ca,Mg)CO<sub>3</sub> (dolomite) and the sulfur is retained in the ash as CaSO<sub>4</sub> (calcium sulfate).

In pulverized fuel combustion, the fuel has to be ground in mills to increase the surface area exposed to the combustion air. This permits a high combustion rate and high efficiency with relatively little excess air. However, the process is more difficult to control and may suffer from too high combustion temperatures (1200-1500°C), which can result in high emissions of NO<sub>x</sub> and formation of fireside deposits. Much work has been performed to minimize these problems in pulverized coal combustion but very little has been reported concerning biomass fuels.

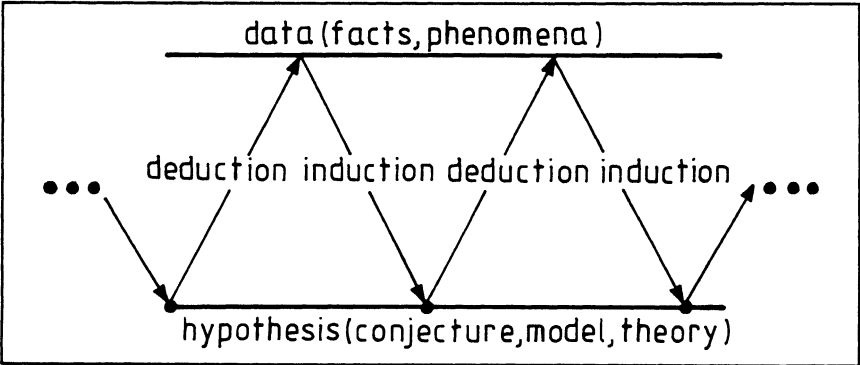
The described combustion systems are the simplest techniques to produce energy from biomass fuels. In addition to these, the FBs can be pressurized to somewhat increase the efficiency. Pyrolysis of biomass is an attractive process if all three products; gas, tars and charcoal can be used. Further, gasification with air is used to produce new fuels such as "higher-energy gas". For biomass gasifier systems up to 10 MW, the preferred type has been the fixed bed, either in updraft or downdraft mode. This type is re-known as the mobile producer gas units used for direct fueling of vehicles during World War II. For the last two decades, development has concentrated on high efficiency and high throughput systems, primarily SFB and CFB reactors<sup>15</sup>. The pilot plant unit in Studsvik, which is referred to in the present study, operates at an air to fuel ratio of about 0.3, to yield gasification temperatures in the range of 800-900°C. The retention time in the hottest zone is about five seconds.

## **2.2 Use of various models**

Combustion and gasification are extremely complex processes, which may involve thousands of chemical species and a much larger number of possible reactions. Even

for oxidation of such a simple fuel as methane, the reaction mechanism is quite complicated and not yet fully understood<sup>16</sup>. The complexity drastically increases for the more multifarious solid fuels, and in spite of all the research performed, the combustion processes of solid fuels will probably never be completely described by physical and/or chemical models. Biomass fuels are, due to the limited research work and different chemical compositions, even harder to treat with advanced chemical kinetic models. In fact, Gardiner<sup>17</sup> stated that "some fuels like wood are too complex to deal with in detail at a molecular level". In addition to the chemical complexity, intricate interactions between the chemical and physical processes such as fluid mechanisms, heat transfer, radiation and physical mixing are of vital importance.

All learning in science advances by an iterative process<sup>18</sup>, where an initial hypothesis (simple model) leads to certain consequences, that may be compared with experimental data (Figure 5). When the model and experimental results disagree, this leads to either a modification of the old model or the formulation of a new model and a second validation cycle may be initiated. By the nature of this scientific process, "old" models are therefore frequently rejected to the benefit of other more sophisticated ones. The most important step in the understanding of combustion chemistry is an example of such a rejection, namely when Lavoisier in 1774 recognized that the apparent disappearance of matter (phlogistone) in flames was an illusion. In this case the rejection of the old theory was highly justified (even if he suffered the loss of his head) but in most cases, science benefits from the simultaneous use of several competing or complementary models.



**Figure 5.** Illustration of the iterative process of learning in science

Combustion processes include everything from fluidized bed combustion to detonation of explosives. Even if an ultimate model would have to work well for the whole range of processes, it is obvious that different models are suited for different processes, at least until "the ultimate and final" model is developed. Several (complementary) approaches are presently utilized for increasing our understanding of combustion processes. These include the following models (with increasing complexity):

- global equilibrium
- local and staged (reactor) equilibrium
- kinetically restricted equilibrium
- global kinetics
- quasi-global kinetics
- detailed kinetics

Combustion processes are also, as indicated above, intricate interactions between many "separate" physical and chemical processes and much work is in progress to unite all these separate sciences to a more complete model. The chemical aspects may here be implemented in sophisticated computational fluid dynamic techniques for simulation also of fluid flow and heat transfer. Such a combined model has, for example, been used to study a flue gas desulfurization technique in a packed bed<sup>19</sup>, including both three-dimensional transit flows as well as detailed kinetics. This advanced approach can also accurately be used for gas phase reactions, if the detailed kinetic model is first reduced to a somewhat simpler and more "condensed" form.

All these models discussed are different kinds of *hard models*, i.e. based on chemical and physical "theories" or "laws of nature". Frequently the mechanisms underlying a combustion process are not fully understood, or they are too complicated to allow an exact hard model to be postulated. This is true, for example, for the complex mixture of both homogeneous and heterogeneous formation and reduction reactions of NO in a fluidized bed environment. The lack of both kinetic data of heterogeneous reactions and measurements of density profiles on the active catalyst surface limits the use of kinetic models for a full description. In the case of the complex chemistry of ash and

deposit formation, hard models including all chemical and physical aspects are also far from being fully applicable. In such circumstances, a *soft model* (empirical) may be useful, particularly if it is desired to approximate the response over limited ranges of the variables.

In fact, to be able to describe, visualize and evaluate the complex combustion processes, sophisticated models are needed. As a complete and fully correct model will probably never be available, several types of less sophisticated but appropriate models have been used, and evaluated, in the present work. In chapter 3, hard models will be discussed, whereas in chapter 4, the development and use of soft models will be described.

### **2.3 Review of some previous work**

An increased utilization of biomass related fuels and the introduction of "new exotic" fuels, such as energy crops and biomass waste, have many environmental benefits, but also require careful studies of potential new chemical problems associated with these fuels. Only little information can be found in the literature and most of the previous work has concerned combustion of pulverized coal. In the following, a brief review of the findings from these studies is presented, as well as some of the few studies of biomass fuels.

During the last two decades, much work has been focused on the reduction of SO<sub>2</sub> emissions and many flue gas cleaning systems are now commercially available. Secondary devices, such as wet scrubbers are efficient and can also be applied to all different types of processes. However, they are more expensive than primary techniques. A commonly used primary technique, for direct in-furnace desulfurization, utilizes CaCO<sub>3</sub> or (Ca,Mg)CO<sub>3</sub> as solid absorbents. This technique is especially favorable in the FBC, with the low combustion temperature and good mixing conditions in such reactors. Also without additives, a varying amount of sulfur may be captured by the alkali and alkaline earth metals originating from the fuel<sup>20,21,22</sup>.

In addition to the possibilities for sulfur retention, the fate of inorganic elements during

combustion or gasification is extremely important for the efficiency and availability of combustion and gasification plants. The inorganic constituents in the fuels, transformed into "ash" during combustion, may deposit onto heat transfer surfaces or other surfaces of the convection equipment. These processes are referred to as slagging, if the deposits are in a molten or highly viscous state, or fouling, if the deposits are built up largely by species that have vaporized and then condensed. *Slagging* is often found in the "radiant" (from the flames) section of the furnace, while *fouling* occurs in the cooler furnace regions, where the heat exchanger equipment is located. In addition, *acidic deposits* caused by  $\text{SO}_3$  or  $\text{H}_2\text{SO}_4$  may occur at lower temperatures.

The negative effects of slagging and fouling are:

- decreased heat transfer efficiency of the boiler
- increased pressure drop
- increased corrosion

Here, research publications dealing with fireside deposits and sintering behaviour for combustion of coal and other fossil fuels are numerous<sup>23-33</sup>. Sulfur capture in ash and formation of deposits in pulverized combustion of British coals have been the subject of at least two extensive reviews. The one by Raask<sup>34</sup> from 1982 was based mainly on his own extensive work. He reported that retention of sulfates in the ash and boiler deposits accounted for between 12 and 18 % of the total sulfur in the coals. A later review from 1992 by Osborn<sup>35</sup>, covering 101 references, also includes retention and deposit formation of chlorine. The presentations from several international conferences dealing with fireside behavior of mineral impurities in fuels, have been summarized by Bryers<sup>36</sup>. Fireside corrosion in pulverized coal combustion was reviewed by Harb and Smith<sup>37</sup> in 1990 and a review of fireside corrosion in recovery boilers was given in 1988 by Tran et. al.<sup>38</sup>.

In spite of the large amount of work, a precise and quantitative knowledge of ash formation and deposition processes during combustion of coal has not yet been

obtained, due to the complexity of the processes involved. In general, the main mechanisms can be separated into three broad areas<sup>35</sup>:

*Particulate deposition* such as inertial impaction, interception, gravitational settling, diffusion (Brownian/Eddy) and thermophoresis. All of these are of a more physical than chemical nature.

*Vapor diffusion* is the condensation of volatilized inorganic ash components, either directly on the colder surfaces or as liquid droplets forming an aerosol mist in the flue gas.

*Chemical reaction* implies a broad area of transformation processes, which leads to formation of products with lower melting points and reduced viscosity.

High sulfur coals have shown a higher tendency for slagging, but this is probably due to the fluxing action of pyritic Fe and to the sticking properties of unoxidized pyrrhotite particles<sup>35</sup>. However, vapor diffusion with alkali and alkaline earth sulfates has also been recognized as important for fouling deposit formation.

For biomass fuels, the chemical elemental compositions, as well as the speciation, differ considerably from the fossil fuel compositions. The higher amounts of alkali and alkaline earth metals in these fuels could possibly be expected to involve more slagging, fouling and sintering problems, especially if co-combusted with a sulfur or chlorine containing fuel. An extensive research work has been performed by Hupa et al.<sup>c.f.39,40</sup>. Some of the results obtained showed that combustion of wood and bark alone, or co-combustion of the wood fuels with coal or peat, did not result in formation of any disturbing deposits. However, if oil and the wood fuels are co-combusted, thick deposits, consisting of alkali and alkaline earth sulfates, were formed.

Sintering of the bed material, in fluidized beds, has been reported in a number of publications on combustion<sup>c.f.41,42</sup>, and in at least one for gasification<sup>43</sup>.



## $NO_x$ and $N_2O$

Numerous studies have been performed concerning different aspects of  $NO_x$  formation, reduction and control in combustion processes. Chemical reactions of nitrogen compounds have been the subject of intensive studies for more than 50 years. A review of the mechanisms and modelling of nitrogen chemistry in combustion was given by Miller and Bowman<sup>44</sup> in 1989 and recently extensive modelling of both  $NO_x$  and  $N_2O$  was presented by Kilpinen<sup>45</sup>.

In combustion, nitrogen oxide (NO) usually contributes at least 90 percent of the total emissions of the nitrogen oxides collectively termed  $NO_x$ . Due to the slow rates of the reactions between the nitrogen and oxygen in air at lower temperatures (below about 1300°C), different mechanisms have been distinguished during combustion at different temperatures:

- > 1200-1400°C
  - *thermal* NO, formed according to the Zeldovich<sup>46</sup> mechanism from oxidation of atmospheric nitrogen
  - *prompt* NO, formed according to Fenimore<sup>47</sup> by oxidation of intermediates in an early phase of the flame front. Produced rapidly in large burners and fuel rich flames, but in general a negligible contribution to the total NO
- < 1200-1400°C
  - *fuel* NO, formed by oxidation of nitrogen contained in the fuel.

The formation of  $NO_x$  in both fluidized bed and grate fired boilers therefore originates predominantly from the nitrogen contained in the fuel. In pulverized fuel combustion at higher temperatures, formation of thermal NO can be significant. Reviews of  $NO_x$  emissions emanating from FBCs were made by Cooper<sup>48</sup> and Lee and Hiltunen<sup>49</sup> in 1989.

Recent work has shown that nitrous oxide ( $N_2O$ ) is also a pollutant with significant

emissions under certain conditions<sup>50,51</sup>. The measured increased atmospheric concentration of  $N_2O$  has proven to be a contributing factor to both the greenhouse effect and the depletion of the ozone layer. In the beginning of the 80's the emissions from combustion sources were overestimated, due to an inadequate sampling method. This was reported at a workshop in Paris<sup>52</sup> in 1988 and studies presented after this have shown low emissions of  $N_2O$  from pulverized coal and grate fired plants. However, several investigations<sup>c.f.53</sup> have shown typical  $N_2O$  emissions of 20-150 mg/MJ (40-250 ppm) from fluidized bed combustion. The higher emissions from FBCs are due to the lower combustion temperatures in these processes. At higher temperatures (above 950°C) the  $N_2O$  is rapidly decomposed.

### *Mercury*

Mercury contained in any form in a fuel will evaporate as  $Hg(g)$  from the high temperature combustion zone. During the cooling of the flue gases,  $Hg$  may react with different gas components to form other  $Hg$  compounds. The resulting speciation of  $Hg$  is most crucial for both the possibilities of abatement and for the fate of  $Hg$  in the atmosphere. There is no simple clean-up process for elemental mercury and most flue gas cleaning systems mainly remove the oxidized forms, e.g. divalent mercury bound to particles. So far, several studies can be found concerned measurements in full scale plants, but very little information is available from laboratory experiments performed under controlled conditions (Hall<sup>54</sup>, Schager<sup>55</sup> and Vogg et al.<sup>56</sup>).

## **3 APPLICATION OF EQUILIBRIUM CALCULATIONS**

### **3.1 History and previous applications**

To emphasize the tradition of equilibrium model calculations at our department, which includes the appreciated development of the SOLGASMIX program, a review of equilibrium calculation methods and applications within the field of combustion is justified.

### *Equilibrium calculations*

Before 1950, all chemical equilibrium calculations were performed by hand and a review of these procedures is given by Kobe and Leland<sup>57</sup>. The nature of the equilibrium computations is complex, mostly because of the linear and non-linear relations which have to be solved. Even a simple case of a mixture of ideal gases would result in difficulties. During World War II, new methods of hand calculation had to be developed to facilitate "some studies of combustion chemistry" and a reduction method of the numerous equations to be solved was presented by Damköhler and Edse<sup>58</sup>. In 1947, Brinkley<sup>59</sup> formulated an algorithm permitting calculations for systems with a large number of species. Both the interest in explosions in rockets and the explosive development of computers with "rocket speed" led to new interest in equilibrium computations from about 1950, and numerous programs are now available for computing chemical equilibria. The most effective ones are based on the approach suggested by White et al. in 1958<sup>60</sup>. This method involves the computation of the composition that minimizes the Gibbs free energy of the system. For a review of the method see Smith and Miessen<sup>61</sup> and Mather<sup>62</sup>. A major step was taken by Eriksson in his development of the programs SOLGAS<sup>63</sup> and SOLGASMIX<sup>64</sup>. The Fortran codes of these programs were widely spread and a large number of other programs now available are based on these codes. An updated version of SOLGASMIX is called CHEMSAGE<sup>65</sup> (SOLGASMIX based advanced Gibbs free energy minimizer) and the modifications include addition of an extensive library of routines for nonideal models for solid and liquid mixture phases, routines for reactor modelling and calculation of thermodynamic functions. The latest version (CHEMSAGE 3.0) also permits mapping of systems, locations of phase boundaries and includes a graphical post processor.

In parallel to the development of computer codes for equilibrium calculations, data bases of thermodynamic data have been compiled. These are managed by comprehensive data administration software packages and a list of publicly available systems, called integrated thermochemical data banks (ITD), was presented by Bale and Eriksson in 1990<sup>66</sup>. In the present study, the ITD called SGTE from the Scientific Group Thermodata Europe, with an additional local data base, was used.

### *Combustion applications*

Equilibrium calculations have frequently been used to study high temperature chemical processes for energy production. Previous studies concerning the fate of the inorganic constituents in these processes are presented in *Table II* (recovery boilers not included).<sup>67-84</sup>

In addition, chemical equilibrium modelling of mercury in combustion processes has been performed by Mojtahedi et al.<sup>85,86</sup> and Mathews<sup>87</sup>.

The conclusions from this review are that the separate and ideal systems of gas reactions of alkali and alkaline earth metals seem to be well studied for the combustion of coal but no biomass fuel seems to have been studied. Also the stability of sulfates and sulfides are relatively well studied but only by the use of ideal solution models. Very few studies have concerned the competing reactions between silicates, sulfates, chlorides, carbonates, oxides, and phosphates and non-ideal solution models have only been used occasionally.

It should be noted that the condensed products formed by the inorganic elements will appear in the ash material as solid phases and/or as constituents in the liquid phase(s). In the calculational treatment of a solution (liquid or solid), its thermodynamic properties must be considered. As a first approximation, ideal solution models can be used, which facilitate the equilibrium calculations but which will not give fully correct results. To obtain reliable values, non-ideal solution models should be used in the calculations (see *paper III*)

**Table II. Previous applications of equilibrium calculations on ash and deposit formation**

1) IMCC (IMCP) = Ideal Mixing of Complex Components

Publ. year	Authors	Reference	Elements (inorg.)	Cond. Si-species considered	Solution model	Exp. comparison	Comments
1961	Boll, Patel	67	Si, Fe, Na, S, P, Cl	2FeO-SiO <sub>2</sub>	-		
1973	Spencer et.al.	68, 69	Si, Al, Fe, Ca, K	Na <sub>2</sub> O-SiO <sub>2</sub> (1:1, 2:1) K <sub>2</sub> SiO <sub>3</sub> -Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	Ideal	Yes	MHD, slagging combust.
1974	Pebler	70	C, H, O, N, S	-	-		
1977	Alvin et.al.	71	K, Na, Cl, S	-	-	Full scale	Trace elements, FBC
1980	Bessman et.al.	72	Si, Al, Ca, Fe, S	Several		-	
1982	Hastie et.al.	73	Si, Al, K	Several	IMCC		
1982	Wibberly, Wall	74	Si, Na, Cl, S	Na <sub>2</sub> O-SiO <sub>2</sub> (1:1, 1:2, 2:1)	-		
1983	Carling et.al.	75	Si, Al, Na, Cl	Several	Ideal		
1983	Kohl et.al.	76	Ca, Mg, K, Cl, S	Several	-		
1984	Smith et.al.	77	Si, Al, Ca, Mg, K, Na, S	Na <sub>2</sub> O-SiO <sub>2</sub> , MgO-SiO <sub>2</sub> K <sub>2</sub> O-SiO <sub>2</sub> , CaO-SiO <sub>2</sub>	Ideal	Exp. combustion rig	
1985	Hastie, Bonell	78	Si, Al, Ca, Mg, K, Na	Several	IMCC		
1988	Blander et.al.	79	Si, Ca, Mg, Fe, Na	Several	Ideal		
1989	Mojahedi et.al.	80, 81	K, Na, Cl, S	-	Subregular (K, Na) <sub>2</sub> -(CO <sub>3</sub> , S)	PFBC, PFBC	
1989	Huffman et.al.	82	Fe, S	-	Ideal	Yes	Transf. of pyrite
1991	Lindner et.al.	83	Si, Na, Cl, ?	?	IMCC	Yes	
1991	Vuthaluru et.al.	84	Si, Al, Ca, Mg, Na	Ca-, Mg-, Na-silicates ?	Yes		

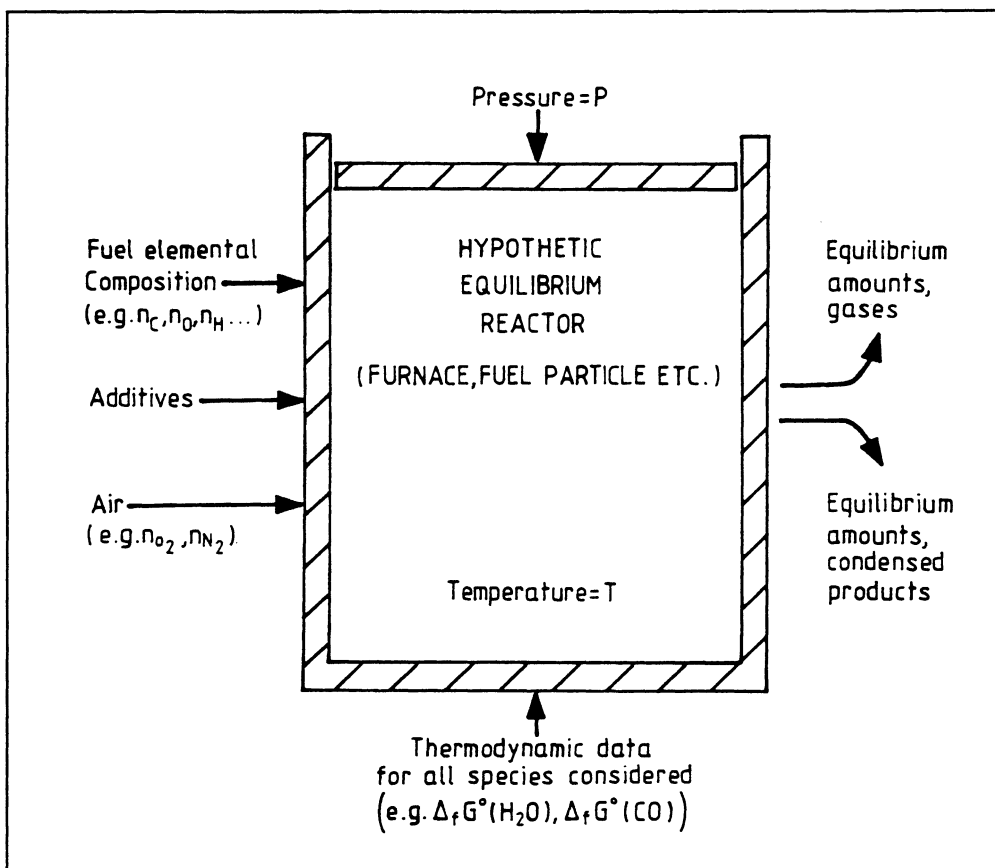
### 3.2 Basic principles of the equilibrium modelling

For a complete interpretation of a chemical process, i.e. determination of the fate and final products of the reactants, as well as the thermal behavior of the system, three important questions have to be answered. These are

- 1) What is the initial state of the system, i.e. amounts, and speciation of the reactants, as well as temperature and pressure?
- 2) What is the final equilibrium state of this system, and what are the changes in thermodynamic properties?
- 3) How quickly do the reactions approach the equilibrium state and by what mechanisms (reaction paths) do the molecules interact to cause the reactions to proceed?

A complete answer to question 3 would also include information about question 2 but, as discussed previously, such general kinetic models are not yet applicable for most combustion related processes. In addition, fluid dynamics would, ideally, also have to be taken into account. It is clear, however, that the processes are too complex to be treated in this way and a simpler approach has to be used. Here, the equilibrium model always provides the possible directions and driving forces for a complex system. Furthermore, at combustion temperatures the reaction rates are relatively fast, and many of the products can be expected to be rather close to their equilibrium levels.

The principles of the calculations may be visualized with a hypothetical reactor (*Figure 6*). This reactor could consist of either the whole studied combustion process (global equilibrium) or, as well, local interesting processes, such as the reduction phase in a fluidized bed or in a fuel particle. Input amounts of the reactants, the temperature and the pressure of the system are required as input data for every calculation point. Thermodynamic data for all species considered as well as activity data for solution models, are also needed.



**Figure 6.** Illustration of the hypothetical equilibrium reactor

#### 4 APPLICATION OF EXPERIMENTAL DESIGN AND MULTIVARIATE ANALYSIS

Global chemical equilibrium is seldom completely attained in practical processes or in the chemical systems studied. Even if a pre-experimental equilibrium study always facilitates the experimental research procedure, the importance of optimal experimental techniques and designs can not be underestimated. By the equilibrium calculations, possible and impossible directions of the process or separate reactions can be determined. If kinetic data are missing or if the process is too complicated to be treated with hard models, the use of soft models may help a lot. In this chapter the role of experimental design, for developing soft models, and multivariate analysis of large data matrices is discussed. In *papers IV and V* the same brief discussion with illustrating

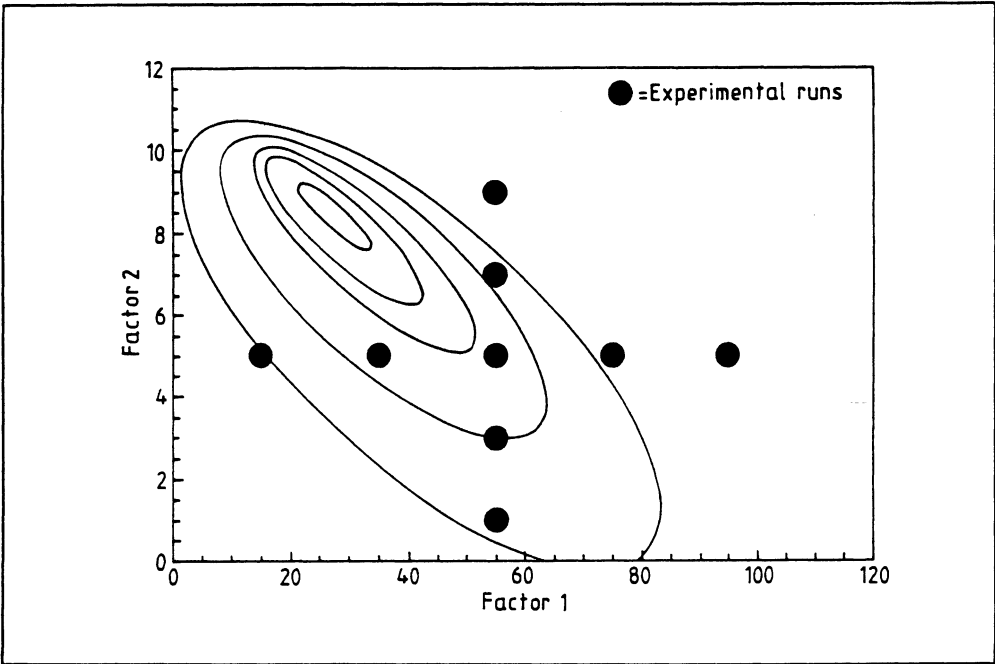
"case studies" can be found.

#### **4.1 General aspects of process optimization**

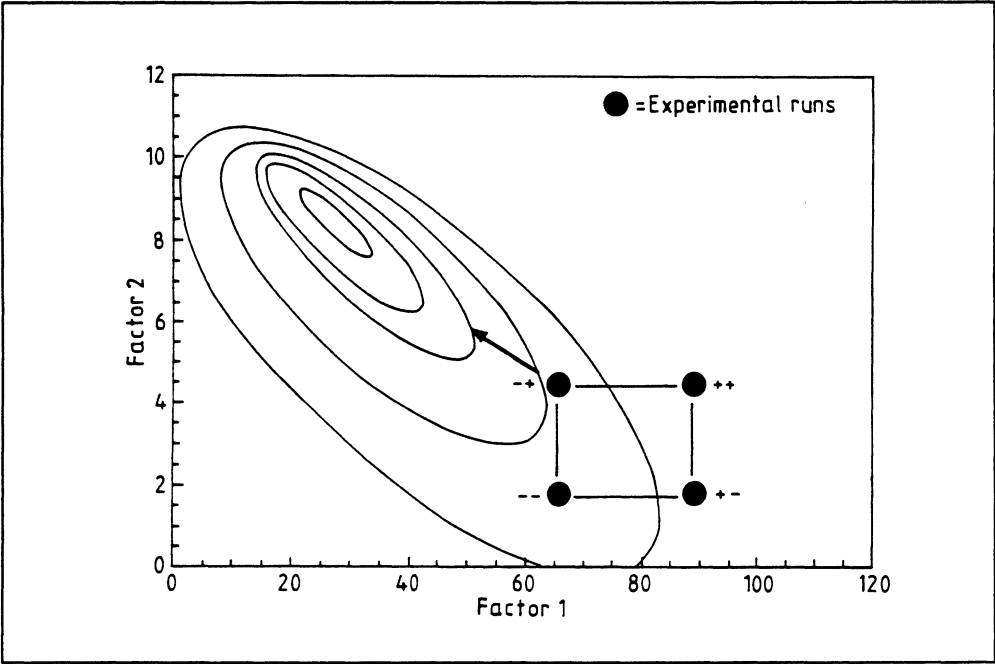
In recent years, extensive research work has resulted in successful modifications of the combustion processes, significantly decreasing the emissions. Such minimization of combustion related emissions is best accomplished at the construction stage of the process plant, by using intelligent engineering design based on the best available chemical and physical knowledge. However, many plants are still running far from their optimum capability, such that even after the completion of the plant, much can be undertaken to further reduce undesirable emissions and to improve combustion efficiency. This without installing expensive secondary reduction measures.

In process optimization (or evaluation) there has always been a strong belief that order to determine how one factor influences a response, all other factors must be held constant while only varying that particular factor. As a result, many investigations are still carried out using the inefficient "Changing One Separate factor at a Time" (COST) approach (see *Figure 7*). The COST approach might lead to incomplete mapping of the behavior of the system, often resulting in poor understanding as well as incorrect conclusions. It was shown by Fisher<sup>88</sup> in the 1930's that the COST approach is applicable only when there are no interactions among the studied factors. Interaction effects are measures of how the "slope" of the response (y) changes, with respect to a factor, as another factor changes. In combustion processes, the response is usually highly affected by interaction terms, and therefore the COST approach can not be recommended. Instead, both process evaluation and optimization benefits from the use of statistical designs<sup>89,90</sup>. These are informationally optimal mathematical schemes in which all important factors are changed "simultaneously", thereby facilitating finding process relations as well as the real process optimum. The designs are often coded using signs of plus and minus for the high and low levels, respectively, in *Figure 8* an example is given.





**Figure 7.** Illustration of the COST approach



**Figure 8.** Example of a factorial experimental design for two factors

To obtain information on the influence of one single factor on a response, at least two experiments have to be performed. Normally  $2^k$  experiments are required for evaluating a process with  $k$  factors. If non-linear relations are also to be estimated, more experiments are required. The number of experiments depends not only on the number of factors involved, but also on the degree of information desired (the complexity of the estimated model). A full second order polynomial empirical model is often sufficient for adequately describing a combustion related system, at least in a selected limited experimental domain. For a more complete investigation, main effects, as well as quadratic and interaction terms have to be determined. The model function can be written as:

$$\begin{aligned}
 y = & \beta_0 + \\
 & \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \dots + \\
 & \beta_{11} (x_1)^2 + \beta_{22} (x_2)^2 + \beta_{33} (x_3)^2 + \dots + \\
 & \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \dots + \beta_{123} x_1 x_2 x_3 + \dots \quad (1)
 \end{aligned}$$

where  $y$  is the response,  $\beta_0$  the constant term,  $\beta$ 's the regression coefficients and  $x_i$  the varied factors. Such a model can be estimated by using a full factorial design. In general,  $l^k$  experiments are required, where  $l$  is the number of levels and  $k$  the number of factors. However, when using a full factorial design to study a combustion process influenced by a multitude of factors, the number of experiments rapidly grows, making it impractical to carry out all experimental runs. It is therefore desirable to reduce the number of experiments while still retrieving the most information. This is accomplished by screening studies, utilizing for example a fractional factorial design<sup>7</sup> (FFD).

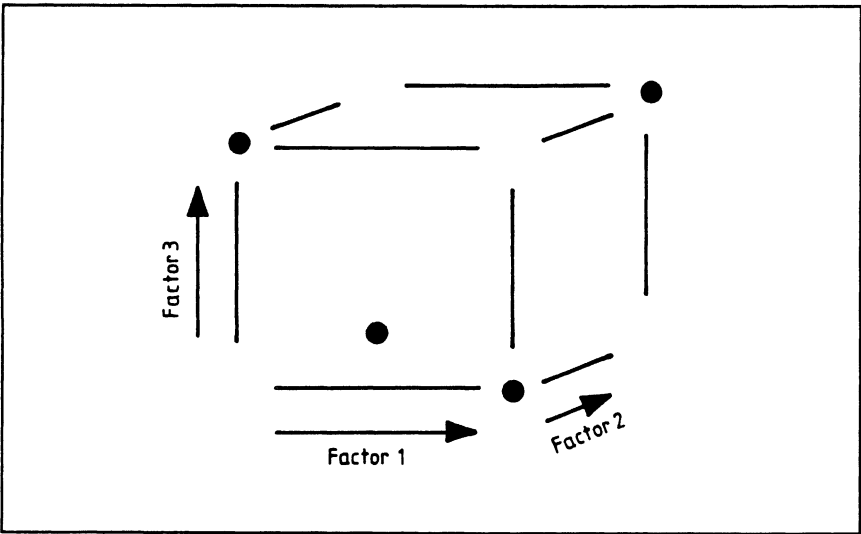
## 5.2 Screening

The main purpose of a screening study is to identify the most influential (of a number of potentially important) factors and those that may be regarded as inert. As experimental designs for screening studies, FFD's are most commonly used. Often a FFD is augmented with a few experimental runs in the center, to stabilize the design and allow for the evaluation of the experimental reproducibility. Non-linearities of the process relations will also be discovered by the addition of these experimental runs. A

fractional factorial design will always result in confounding among the estimated effects. For example, a  $2^{5-1}$  design will result in main factor effects confounded with four factor interactions and two factor interactions aliased with three factor interactions. Fortunately, three or four factor interactions usually have rather low importance compared to main effects and two factor interactions<sup>7</sup>. Hence, FFD's are useful designs for screening purposes. *Figure 9* is an example of a  $2^{3-1}$  FFD. A  $2^{5-1}$  design can be further reduced to a  $2^{5-2}$  design, which will result in main effects confounded with two factor effects.

In this context, it should be noted that there exist other types of screening designs, such as the Plackett-Burman designs<sup>91</sup>. These designs require few experiments but have the disadvantage that no interaction effects can be estimated.

*Paper IV* is an example of two screening studies using different fractional designs.



**Figure 9.** Example of a reduced factorial design for three factors

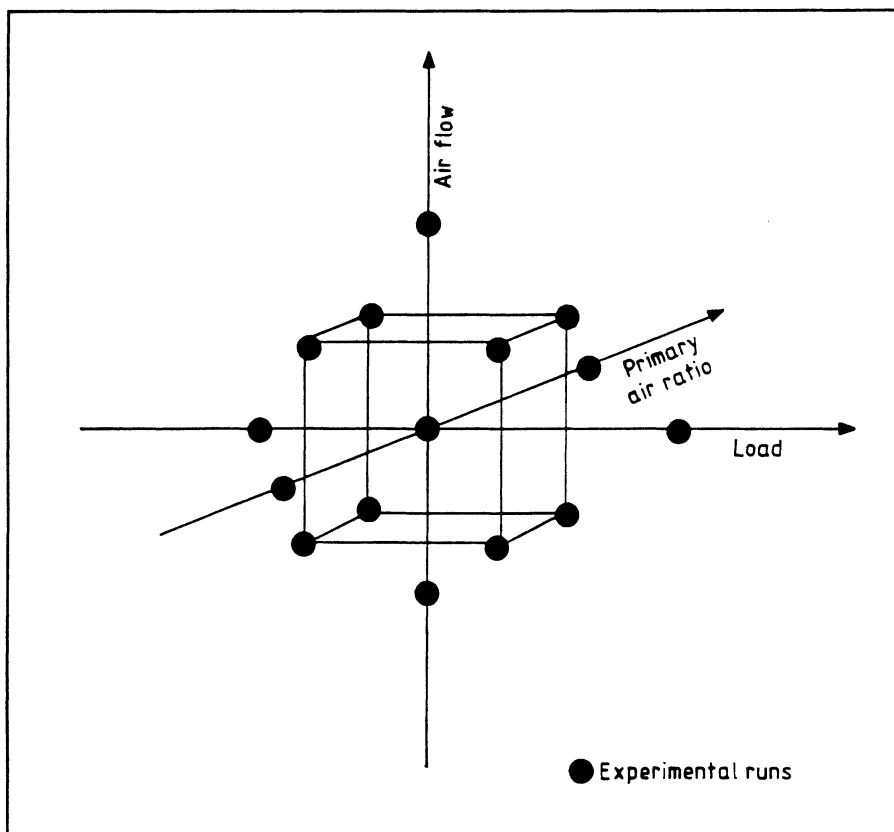
### 4.3 Optimization

Once the most influential factors have been identified, the next step is to optimize the process with respect to these factors. This can be accomplished by using either a full, or some kind of extended, factorial design. Other designs often used in optimization are

Simplex designs<sup>92</sup> and D-optimal designs.

In response surface methodology (RSM), most commonly factorial or extended factorial designs are used to obtain representations of the output or response of the process expressed as a function of the studied factors. The optimum can then be found either by the simplex method or the so-called steepest ascent method<sup>93</sup>. In two and three dimensions the response surface can also be visualized by graphs. The experimental objectives attributed to RSM may not only be optimization, but also modelling and prediction. The semi-empirical model used in RSM is usually a quadratic polynomial in all factors, including also the quadratic and interaction terms (see eq. 1, p.25). Separate response surfaces can be determined for different responses, using the same underlying design. If composite response functions are developed, several response parameters may also be optimized simultaneously.

A three- level factorial design uses high, low and intermediate levels. The factorial design can also be superimposed on a star design according to *Figure 10* and this design is called a central composite design - circumscribed (CCC)<sup>94</sup>. Other variants are the inscribed (CCI) and the face-centered (CCF) composite designs. In these designs all factors are investigated at five levels and the experimental regions are spheres or hyperspheres. For two, three and four factors, the factorial part is a full factorial, whereas for five or more factors it is a fractional factorial which will allow the estimation of linear and interaction terms (as well as the quadratic terms). A fourth design for RSM is the Box Behnken design where the experiments are located at the middle of each edge of a hypercube. All these designs allow the estimation of intercepts, slopes and curvature. In the coded factor space, in which the factorial points are  $\pm 1$  from the center, star points are usually located at a distance  $\alpha = n^{1/4}$  from the center, where  $n$  is the total number of design points (experiments) on the cube.



**Figure 10.** Illustration of a CCC design for the study of three factors

In combustion processes there are often practical constraints on the experimental space. D-optimal designs can then be used as alternatives to factorial designs. The D-optimal designs are computer generated designs which will result in designs that span the largest possible volume in the practical experimental region. The D-optimal designs are also used for screening studies.

#### 4.4 Multivariate analysis

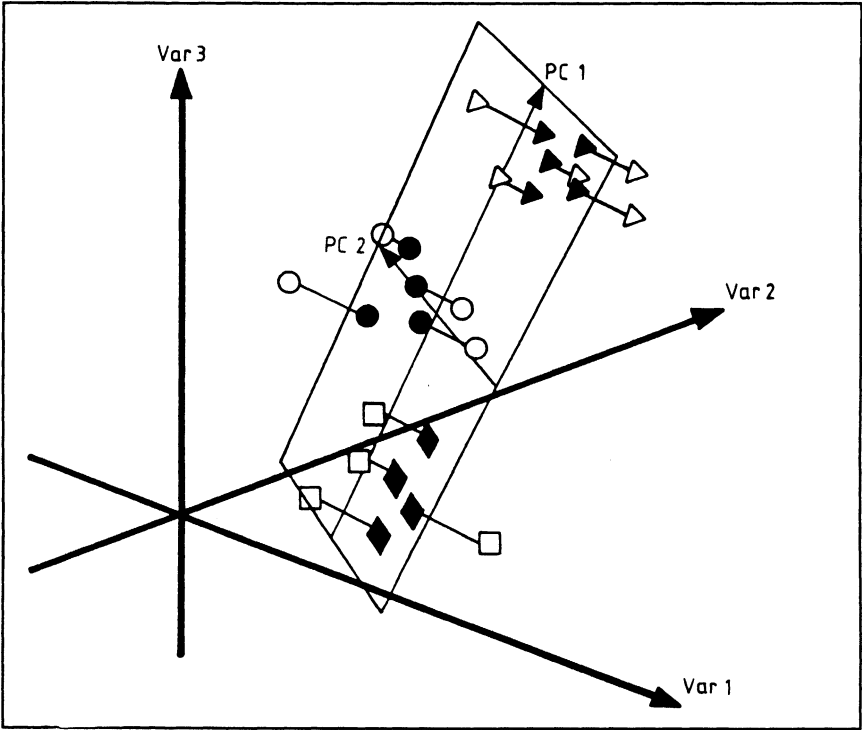
After the experiments have been performed the analysis is rather straightforward. The measured data are fitted to a polynomial by the matrix least squares method. To facilitate construction of the designs, modelling and analysis procedures in the present work, the computer program MODDE<sup>95</sup> was used.

In *paper V*, concerning the reduction of sulfur emissions, an example of a study

including both a screening and an optimization can be found.

*Principal Component Analysis (PCA)*

A brief description of PCA is given here, but further details can be found in the literature<sup>c,f,96</sup>. PCA is a projection method with excellent graphical display capabilities of the major variation/covariation patterns in multivariate data. Here all the determined variables (chemical elements, heating value) for all objects (fuel samples) can be simultaneously taken into account for the analysis. As a result, interpretable representations or plots of data will be obtained where each object is represented by a point, usually shown on two-dimensional score plots (*Figure 11*). Plots of this kind, which display the maximum variance within the data, are especially useful for sorting and classification. Furthermore, the method can handle data sets with missing data.



**Figure 11.** Geometric illustration of PCA based on three variables (here; chemical elements).

Each sample is a vector in the data matrix that is to be analyzed, where the vector in this case corresponds to measured elements, moisture or heating values. The PCA separates the original data matrix ( $X$ ) into a new structure ( $TP'$ ) and noise ( $E$ ). This can

be written as

$$X = Ix + TP' + E$$

where  $x$  is the mean vector included in the model in order to redistribute the data about the mean. The structure of this model is seen as the product of the score matrix ( $T$ ) and the loading matrix ( $P'$ ). The PCA can be viewed as a projection of  $X$  down on a  $A$ -dimensional subspace (dimensionality of  $TP'$ ) by means of the projection matrix  $P'$  and the object coordinate matrix  $T$ .

By examining the loadings on each principal component variable patterns can be obtained, indicating those properties of the fuels that are associated with the discrete directions. A positive loading correlation is a variable with high positive loading for a particular component. Objects with high score values for the same component then have high contents of this variable. The statistical significances of the PC components are determined by using a cross validation procedure<sup>97</sup>.

In *paper I*, a classification of 280 fuel samples with respect to properties relevant for combustion applications, was performed. By using principal component analysis, the huge matrix of fuel samples was reduced to 17 representative reference fuels.

## **5 CONSTRUCTION OF THE EXPERIMENTAL SET-UPS USED IN THE PRESENT WORK**

### **5.1 Mobile data acquisition system**

To facilitate easy access to data from existing and additional analytical instruments as well as operating parameters in large scale boilers, a mobile data acquisition system was constructed. It consists of a portable personal computer (286), equipped with a National Instruments interface card for the IEEE-488 general purpose interface bus (GPIB), and a portable combined multiplexer and digital multimeter (Keithely 740). An easy to use (and to modify) program, written in Turbo Pascal, handles the ten channels and enables statistical analysis and plotting of the measured results as well as transferral of the data

to post processing programs.

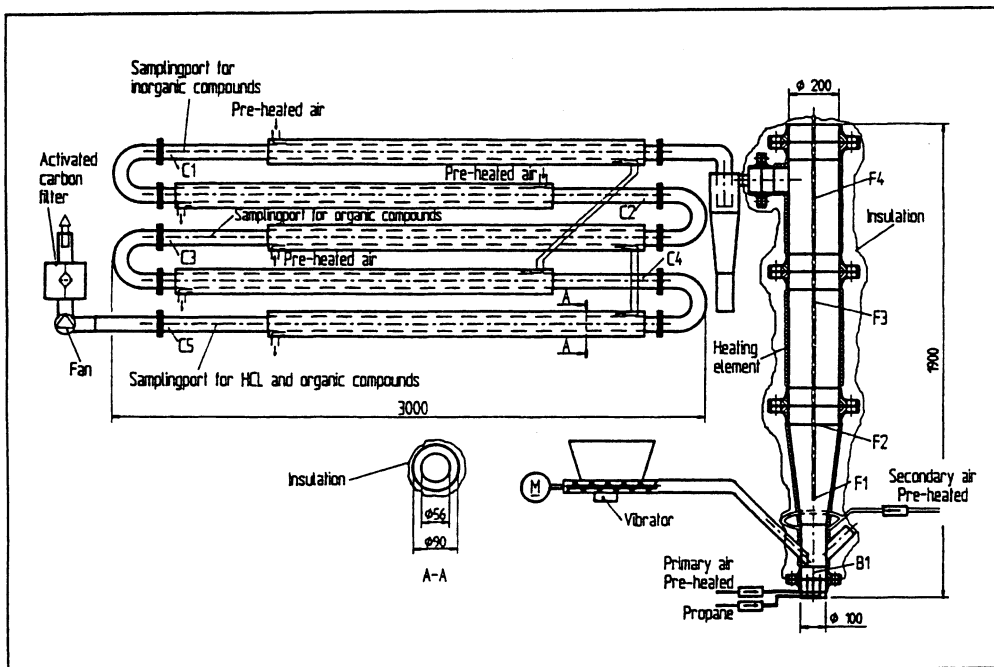
In addition to the handling of conventional gas analyzers, the system includes probes for in situ analysis of oxygen fugacity in a furnace (and bed) as well as three meter long probes for temperature measurements. The oxygen probes are 800 mm long and consist of galvanic cells, including a solid electrolyte of calcia stabilized zirconia, with a reference system (Cu/Cu<sub>2</sub>O) inside. This mobile system has been used in the studies of the large scale plants, for example the CFB and FB in Östersund (*paper IV*), and a grate fired boiler in Åsele<sup>98</sup>.

## **5.2 Pilot scale fluidized bed reactor (5 kW)**

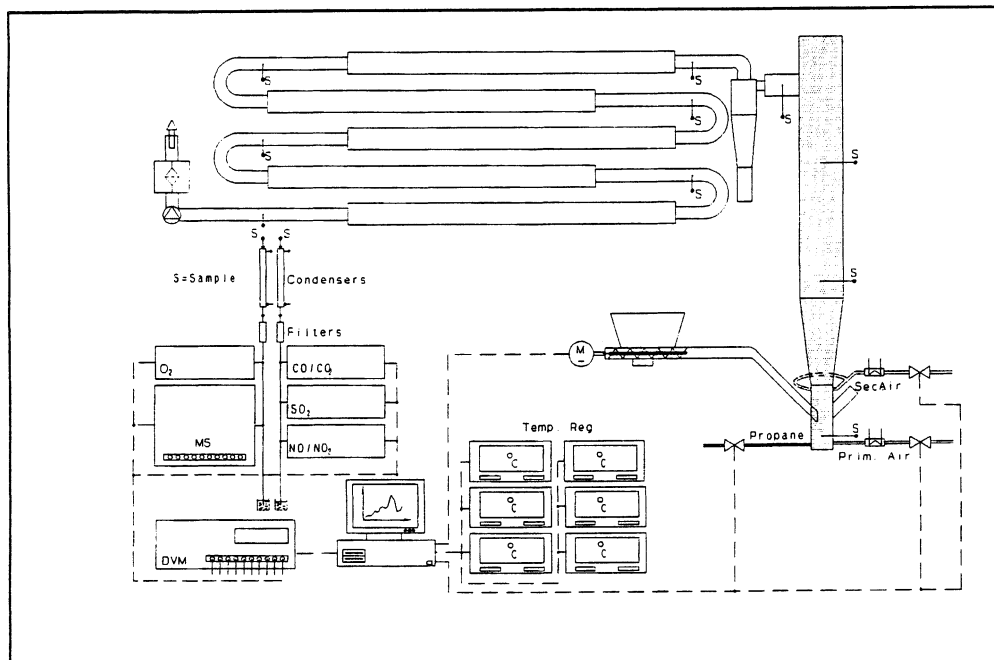
A small pilot scale fluidized bed reactor (5 kW) was constructed in order to facilitate the performance of well designed experiments under highly controlled conditions (*Figures 12, 13 and Table III*). The reactor was designed for environment related studies of combustion of domestic fuels, for instance formation and destruction of dioxines from incineration of municipal solid waste and reduction of nitrogen oxides in combustion of biomass fuels and peat. Unequivocal and accurate results with universal applicability from optimization studies require that all parameters are fully controllable, that they can be independently varied and that the reactor can also simulate real plant conditions. Because of the complex processes studied, much work was devoted to optimizing the controlling possibilities and flexibility of the reactor.

The gases O<sub>2</sub>, CO<sub>2</sub>, CO, SO<sub>2</sub> and NO can continuously be determined, using a paramagnetic cell (Servomex), IR (Siemens 22P for CO/CO<sub>2</sub>), IR (UNOR 6N) and chemiluminescence (Beckman 955) instruments. In addition, a quadropole mass spectrometer (V&F, CIMS 500) is used for the determination of all gases and vapors with atomic masses units up to 500.





**Figure 12.** Schematic view of the pilot scale fluidized bed reactor



**Figure 13.** Schematic view of the control and analysis details of the FBC reactor

**Table III.** Some data on the FBC reactor

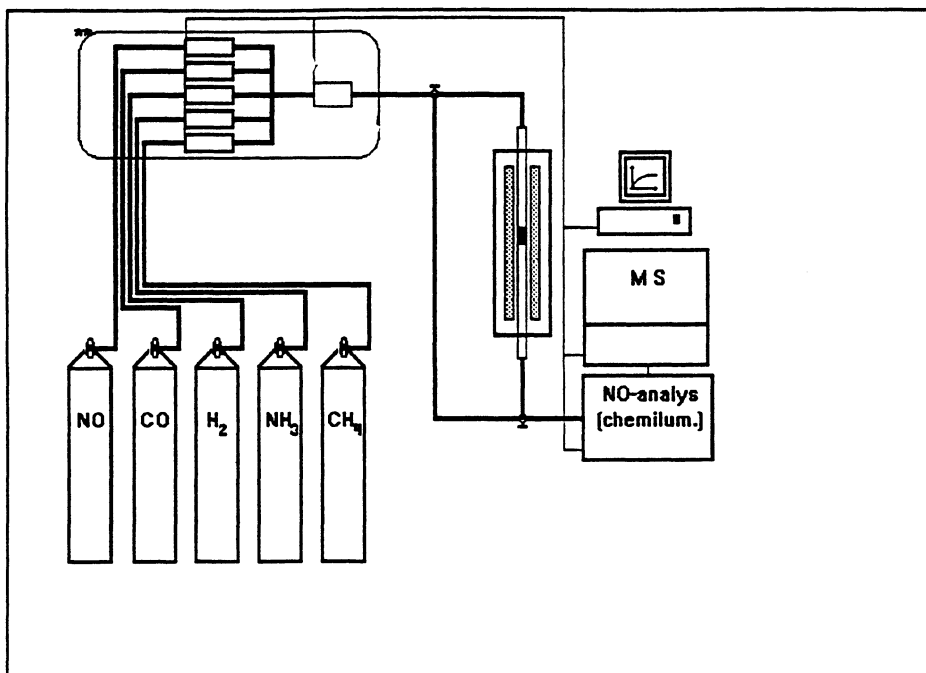
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Diameter, $d_{bed}$	10 cm
Area, bed surface	79 cm <sup>2</sup>
Bed height	6-13 cm
Bed material	450 cm <sup>3</sup> (670 g) quartz sand (99%), 125-250 $\mu$ m
Bed temperature	670-890°C
Min. fluid velocity, $u_{mf}$	5 cm/s (vid 750°C)
Bed height at $u_{mf}$	5.7 cm
Bed expansion (max)	100%
Retention time, bed	0.1-0.2 s
External heat, bed wall	0-100 W
Fuel feeding	Closed container with screw feeding, falling tube to above the expanded bed. Calibrated with each fuel ( $r > 0.999$ ).
Primary air	0-120 dm <sup>3</sup> /min, 0-650°C
Secondary air	0-100 dm <sup>3</sup> /min, 0-650°C
Area, free board	310 cm <sup>2</sup>
Average gas flow free board	~ 0.33 m/s
Temperatures in free board	900-500°C
Height of the reactor	1.8 m (2 modules, 1.2 m each)
External heat, free board	0-1400 W
Total retention time, reactor	1.5-3.0 s

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### 5.3 Fixed bed reactor for kinetic studies

To be able to study the catalytic effects of ashes and bed material from combustion of different biomass fuels on the reduction of NO, a fixed bed reactor for kinetic experiments was constructed (see *Figure 14*). The reactor consists of a 80 cm long quartz tube with an inner diameter of 2.4 cm. A quartz filter, on which to place a bed with the sample, is mounted in the middle of the tube. The bed consists of quartz sand to which different ashes or materials from the potentially catalytically active wall may be added. A furnace equipped with a Eurotherm 818 temperature controller keeps the temperature of the bed within 1 °C of the preset value. The temperature is measured with a Pt/Pt(10 %Rh) thermocouple in a quartz tube. Three mass flow controllers enable different gas mixtures to be studied. Determination of NO and NO<sub>2</sub> is facilitated by the same chemiluminescence instrument as mentioned in the previous chapter, and other gas products formed may be quantitated by the mass spectrometer.



**Figure 14.** Experimental set-up for kinetic experiments

## 6 SUMMARY OF RESULTS OBTAINED AND CONCLUSIONS

### *Chemical characterization of biomass fuels (Papers I and II)*

Many different solid fuels with varying compositions are (and more will be) used for energy production. Their chemical characteristics are important both from environmental perspectives and for the operational performance of the energy conversion processes. To achieve representative input amounts of appropriate biomass fuels for the equilibrium calculations in *paper III*, an initial literature review was performed. The evaluation of this survey of chemical elemental characteristics of 280 samples of biomass fuels, including waste and peat, is presented in *paper I*. The compiled fuel samples were further classified by principal component analysis with special respect to elements important for ash and deposit formation. From this analysis, a total of 17 biomass "reference fuels" with representative compositions were tabulated, as well as the variances within them.

During combustion, the inorganic components of the fuels are subject to complex chemical and physical transformations, which are highly dependent on the original forms of these elements in the fuels. During the last years, significant advances have been made in determining the forms of inorganic elements in coals, but for peat and biomass fuels, very little information can be found. In *paper II*, the results of a literature review is presented, as well as a comparison of three different experimental methods for separation of the organic and inorganic fractions of S, Ca, K and Na present in peat and a biomass fuel. Dry ashing, using low-temperature ashing (LTA), and very low-temperature ashing (VLTA) techniques were used, in addition to wet ashing by oxidation with hydrogen peroxide. The dry ashing techniques were followed by X-ray diffraction analysis (XRD) for identification of phases in which these elements occur in the fuels. From the literature review it was concluded that the elements of interest are mainly organic or ionic bound in the biomass fuels, whereas coal and peat are more influenced by the geological conditions at the site of formation.

Several minerals were experimentally identified in the coal sample and these agree with what has been reported in the literature. However, the results from the ashing and

analysis of both peat and the biomass fuel indicated several difficulties. Only quartz was identified in the raw and VLTA samples and the LTA treatment of the lucerne resulted in formation of several crystalline phases which obviously were not present in the raw sample. The results from the preliminary wet ashing experiments further indicated that more mineral matter was dissolved than organic matter oxidized.

The main conclusion from *papers I and II* is that there is a need for further research work to gain more knowledge of the forms of occurrence of the inorganic elements in biomass fuels, especially separation of inorganic and organic bound metals in peat.

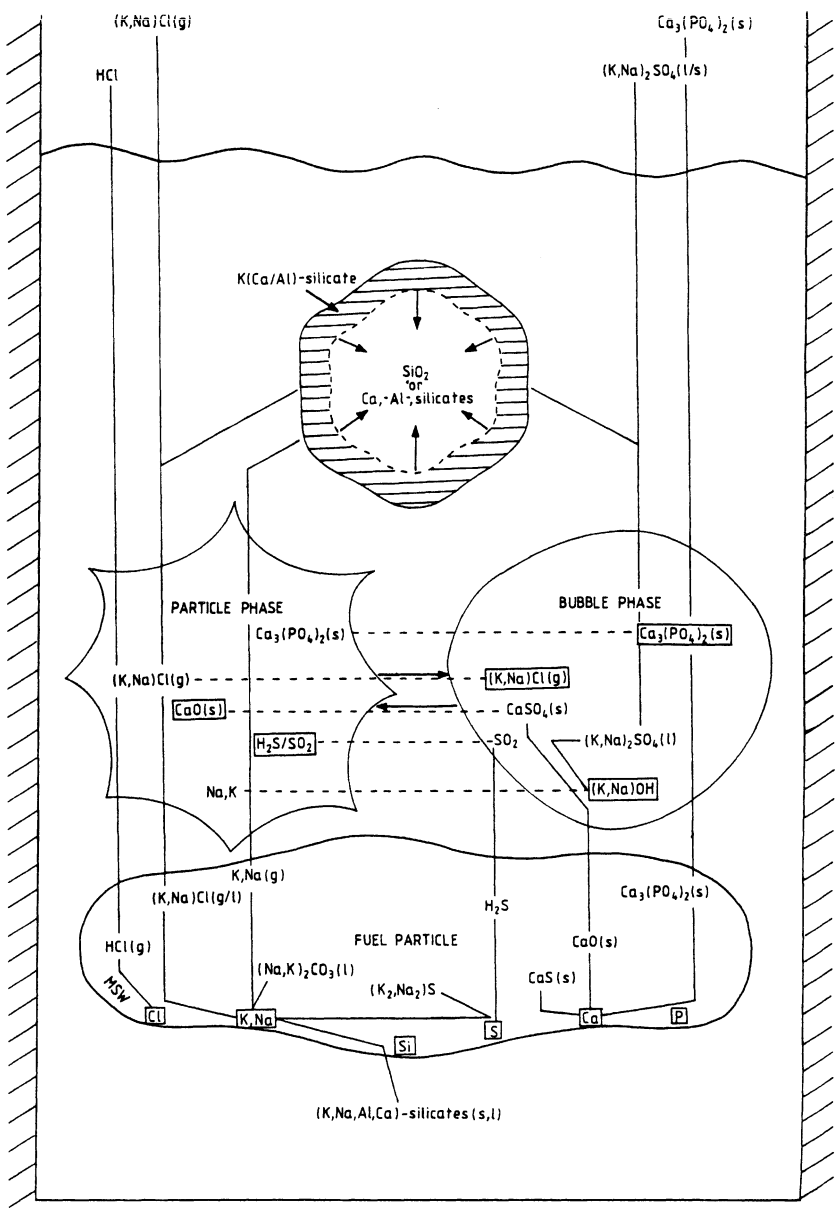
### *Equilibrium calculations for examining ash formation (Paper III)*

As discussed in a previous chapter, little work has been performed to study the processes of ash and deposit formation from biomass fuels. This is also true for the combined chemistry of alkali and alkaline earth silicates and salts, in general. Equilibrium calculations have been utilized to some extent, but in most cases in simplified ways, by considering relatively few species only and not adopting solution models.

The extensive equilibrium calculations performed in the present work (*paper III*) include the behavior of the elements C, H, O, N, S, Cl, P, Si, Al, Fe, Ca, Mg, K and Na during combustion and gasification. A total of 150 stoichiometric condensed species, ten non-ideal solid solutions and two non-ideal liquid solutions were considered in the calculations. Equilibrium relationships were evaluated over a wide range of operating conditions ( $600^{\circ}\text{C} < T < 1600^{\circ}\text{C}$ ,  $0.0 < \lambda < 1.5$ ). An initial evaluation (screening) of available binary and ternary phase diagrams for the components  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{P}_2\text{O}_5$  was performed.

The calculations resulted in enormous amounts of detailed information, which species and phases will be formed during various operating conditions. From the results it was concluded that the proposed product compositions were, in general, more dependent on the fuel compositions than the operating conditions. In spite of this fact, an attempt to illustrate the general trends valid for the fuels is presented in *Figure 15*. Here the

possible transformations and interactions of some of the most interesting elements in a hyphothetic FBC are given.



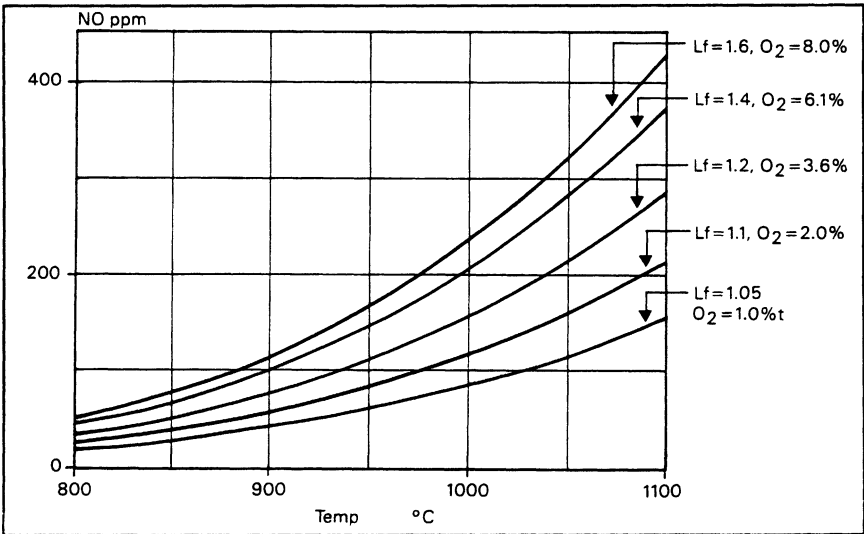
**Figure 15.** Illustration of the fate of some of the most important elements during combustion of biomass fuels

Some general comparisons with experimental results indicated that the equilibrium model is a well suited approach to gain more knowledge of the complex chemistry of biomass combustion and gasification processes.

The main conclusion from the work is that an appropriate and useful data base have been established. In combination with the extensive biomass characteristics from the previously discussed papers, this will allow for several valuable future investigations. After further validation and optimization of the solution models, this approach can be applied on several combustion and gasification related processes.

*Studies of NO emissions from FBC (Papers IV and V)*

The equilibrium calculations, based on the assumption of infinite reaction time and complete mixing, show that the NO concentrations are insensitive to (1) the type of fuel used and (2) fuel nitrogen content. The equilibrium NO concentration is a function of two factors only - excess air and reaction temperature - and thus it is possible to present the relation graphically. *Figure 16* depicts the NO concentration versus temperature and O<sub>2</sub> concentration for peat combustion and it was shown that the use of other fuels did not significantly alter this distribution.



**Figure 16.** Equilibrium concentrations of NO versus temperature and oxygen concentration ( $L_f = \lambda$ , air to fuel ratio)

In *paper IV*, the results from representative large scale measurements (CFB, 25 MW) were compared with data from corresponding equilibrium calculations. A relatively good agreement was obtained for all the studied fuels, at all temperatures (800-1000°C), O<sub>2</sub> concentrations (2-11%<sub>dry</sub>) and primary to total air ratios (35-70 %). However, the measured NO concentrations were somewhat higher than the equilibrium values for a specific cyclone gas temperature in the exit of the cyclone. This deviation increased with increasing cyclone temperature and oxygen concentration. As probably most of the important reactions occur on the surface of the particles and as these have been shown to have a higher temperature than the measured gas temperature<sup>11-14</sup>, this observed deviation seems explicable.

The initially formed and mostly relatively high NO concentrations would be expected to approach a final equilibrium level if given sufficient reaction time. The rate of this approach is controlled by the kinetics of different reduction routes and depends on temperature, fuel composition, bed material and type of combustion process used. The most important results of *paper IV* were (i) the observed close approach to chemical equilibrium conditions; (ii) the significant reduction in NO emissions measured across the cyclone; and (iii) the independence of fuel nitrogen content and air staging on NO emissions. All these facts support the conclusion that the reactions involved in both destruction and formation of NO under these conditions are sufficiently fast to reach equilibrium. Since NO formation and destruction during combustion are generally considered to be nonequilibrium processes, a discussion is given which includes some possible explanations of the observations of this work:

- *the high temperatures in the bed and throughout the cyclone*
- *the extended and intensive combustion zone*

as well as some possible general explanations

- *effect of high particle loading in the combustion zone of the FBC*
- *catalytic effect of biomass ashes*
- *effect of fuels with high volatiles contents*



The relevance and applicability of the results obtained in *paper IV* are open to discussion, but the agreement with equilibrium still remains and suggests that equilibrium NO levels can be reached under certain conditions in a CFB reactor. However, investigations have to be performed to make these conclusions fully clear. In the Appendix, outlines and experimental plan for a future study to elucidate these effects are presented. The results of some initial experiments are also given.

The reduction of NO emissions was also studied using another CFB boiler (20 MW), equipped with an installation for selective non-catalytic reduction (SNR). Here screening experiments were carried out as described in *paper V*. The influence of both primary measures and SNR was evaluated, using  $2^{5-1}$  and  $2^{5-2}$  fractional factorial designs for the two fuels, crushed peat and wood waste, respectively. Polynomial models were deduced from statistical analysis of the experiments, and a good agreement between modelled and measured data was obtained. By using a designed experimental procedure, CFB operating conditions yielding a NO reduction of 60-80 % could be obtained. It was found that primary measures and the SNR were of approximately equal importance. Most important factors for the NO reduction were air to fuel ratio, the amount of  $\text{NH}_3$  added, the load and the fraction of lower secondary air, but the reduction is also influenced by small interaction effects.

*In Paper IV*, it was further shown that high concentrations of  $\text{N}_2\text{O}$  can effectively be destroyed (according to equilibrium results) at higher temperatures.

#### *Optimization of sulfur retention (paper VI)*

According to the equilibrium calculations, co-combustion of a fuel, rich in one or several of the elements Ca, K or Na, with a sulfur rich fuel can result in a considerable reduction in  $\text{SO}_2$  emissions. A theoretical sulfur capture of 100 % seems to be attainable for most fuel combinations (50/50%<sub>w</sub>). The processes are, however, complex and to minimize  $\text{SO}_2$  emissions in practice, experiments were performed, according to statistical experimental designs, in a small pilot scale fluidized bed (5 kW). Hereby, a sulfur retention of 70-75 % for a peat/wood fuel mixture and 90-95 % for a mixture

of coal and an energy crop (lucerne) was obtained. Fuel feeding rate (load), primary air ratio and total air flow were identified as the most influential operating factors, while bed temperature and oxygen concentration seem to be the most crucial physical/chemical factors for the sulfur retention. The products  $\text{CaSO}_4$  and  $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$  were identified in the ashes and dust. The NO emissions were also decreased by the  $\text{SO}_2$  reducing measures, although the fraction of primary air was increased. This was probably due to a lower bed temperature at optimum sulfur capture conditions. The  $\text{SO}_2$  emissions could be reduced without any increase in CO emission. From some preliminary studies, it was shown that the slagging/fouling tendency was not influenced by an increasing sulfate formation. The deposition rates obtained in the present study ranged between  $0.5\text{--}50 \text{ mg/s}\cdot\text{m}^2$ , which can be compared with those reported by Raask<sup>34</sup> for pulverized coal combustion ( $0\text{--}1.5 \text{ mg/s}\cdot\text{m}^2$ ). The preliminary value from combustion of the grass/coal mixture is alarmingly high ( $50 \text{ mg/s}\cdot\text{m}^2$ ) and further experiments are desired.

By using the unique pilot plant reactor, several interesting and relevant experiments will be performed in the future. Some of the preferential issues to be studied are:

- fouling, slagging and sintering behavior of the "new" biomass fuels and combinations of fuels
- chlorine capture in the ash and simultaneous determination of emissions of chlorinated organic species, including "dioxines"; determination of correlations between combustion efficiency and emissions of organic pollutants, including PAHs, "dioxines", "furanes" and PCB. Is CO really a suitable indicator for all noncombusted products and can the formation of the most toxic products be prevented using a higher combustion efficiency in the reactor, as suggested by the equilibrium results ?
- determination of the lowest temperatures and retention times that will allow the NO concentrations to reach equilibrium levels; determination of actual gas and ash compositions in the freeboard (from combustion of

different biomass fuels) to serve as a base for future kinetic experiments and calculations on NO and N<sub>2</sub>O reduction processes

- accomplish conditions for separate (independent) variation of the chemical factors (T<sub>bed</sub>, O<sub>2</sub>, CO, fluid. vel., retention time,.....) to allow for experimental designs and multivariate evaluation of the chemical relations as well; establish an empirical model for particle (surface) temperatures in a fluidized bed

$$T_p = f(T_{bed}, d_{bed\ mtrl.}, C_{fuel}, H_{fuel}, H_2O_{fuel}, \rho_{fuel}, d_{fuel,ash_{fuel}}, O_2, fluid.vel.)$$

### *Mercury speciation in flue gases (Paper VII)*

An investigation concerning the fate of mercury in combustion and in the exit flue gases is presented in *paper VII*. Three complementary approaches was used in order to elucidate the parameters determining the speciation of mercury in these cases. Paper VII concerns the fate of Hg in combustion and in the exit flue gases. Here, chemical equilibrium calculations were used to determine the distributions of mercury compounds in different combustion atmospheres, corresponding to different fuels and operating conditions. The equilibrium results were then compared with corresponding results from experiments in a pilot plant flue gas generator as well as from a laboratory scale "continuous flow reactor".

The results show that at combustion temperatures exceeding 700°C, mercury will evaporate predominantly as Hg (g). However, by cooling the flue gas, both HgCl<sub>2</sub> and HgO may form, with HgCl<sub>2</sub> favored both from equilibrium and kinetic considerations. The general trends obtained from the experimental work agree with the calculated equilibrium results, and the approach proved to be useful for both increased understanding of the speciation in the whole combustion process as well as for planning and evaluation of laboratory scaled experiments. The work further indicates some discrepancies between the equilibrium and the experimental results which could be due to undesired reactions in the analytical equipment. It would therefore be a good idea to re-examine some of the experiments with the newly constructed "stop-flow reactor" which enables in-situ measurements of Hg.

During the work on *paper VII*, it was obvious that the available thermodynamic data for  $\text{HgO(g)}$  was very uncertain. Calculations using the upper and lower error limits showed totally different occurrences of  $\text{HgO(g)}$ , from dominating at all temperatures up to  $1600^\circ\text{C}$ , to not formed at all. However, the experimental results from the present work indicate that the tabulated values<sup>98</sup> probably are rather close to the true ones. To obtain more accurate results from the equilibrium calculations, as well as to be able to perform kinetic calculations in the future, improved thermodynamic data for  $\text{HgO(g)}$  have to be determined. An experimental set-up has recently been constructed and initial experiments will be performed in a near future.

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## APPENDIX

The most important result in *Paper IV* was the observed close approach to equilibrium NO concentrations. An explanation for this result must be found, and some initial studies have already been performed. These are illustrated in *Figure 17* and can be regarded as initial screening studies. So far, experiments 1-7 have been performed, where 1-6 were performed in the pilot reactor and 7 in the fixed bed reactor.

All the experiments in the pilot reactor were performed with the same wall and bed temperature (850°C), oxygen concentration (6 %<sub>dry</sub>), with only primary air and the same total air flow. This should have resulted in equivalent conditions for the separate experiments. NO was added to the primary air to give an initial concentration of 500 ppm. Sampling of the gas was performed preceding the first convection tube.

The results obtained so far can be summarized as follows:

- No reduction was observed with only NO as a reactant in the quartz reactor (7). The effect of some biomass ashes was studied in addition to quartz.
- No reduction of NO as the only reactant gas in the FB reactor (6)
- Considerable reduction (75 %) of NO with addition of propane (combustion atmosphere) in the FB reactor (5)
- No further reduction with addition of a significant amount of a biomass fly ash to the FB reactor with NO and propane (3,4)
- The coal and grass mixture and addition of 500 ppm NO in the FB reactor resulted in a exit NO concentration of 300 ppm (1)

From these experiments, no conclusions can be drawn considering a potential catalytic effect of the biomass fly ashes as significant reduction was already obtained with

propane. This may be due to catalytic active wall materials in the reactor used and comparable experiments in a quartz reactor have to be performed to study this effect more closely before further work can be continued in the pilot reactor.

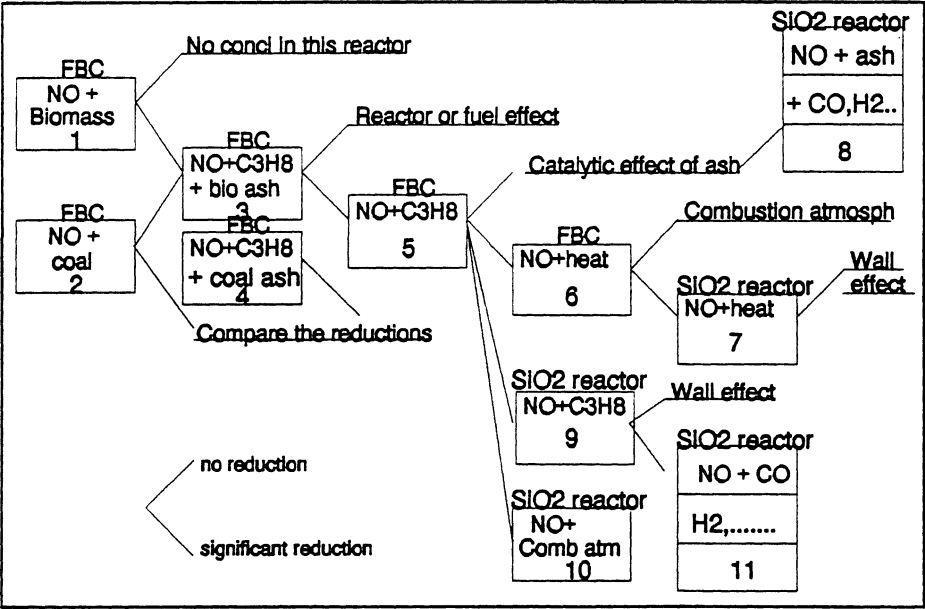


Figure 17. Illustration of the experimental plan for NO reduction experiments