NORDIC SEMINAR ON
Biomass Gasification and Combustion

Sponsored by
NTH
Division of Thermal Energy
and
THE NORDIC COUNCIL OF MINISTERS

Trondheim, August 30th, 1993
We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.
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15.40-16-00 EMISSIONS FROM SMALL SCALE BIOFUEL COMBUSTION - RESEARCH NEEDS. M. L. Karlsson, SP, Borås, Sweden.
OPENING

This seminar was arranged as a part of the Nordic Energy Research Program sponsored by the Nordic Council of Ministers. The aim of this program is to strengthen the basic competence in the energy field at universities and research organizations in the Nordic countries. The contact between research organizations and researchers is therefore of major importance. In the program 1991 - 1994 six areas are selected for cooperation:

- Energy & Society
- Solid fuels
- District heating
- Petroleum technology
- Bioenergy & Environment
- Fuel Cells

The annual budget is approximately 25 mill. NOK.

The topics today will deal both with biomass combustion and gasification and combustion of MSW/RDF. At previous seminars the topic has been concentrated to biomass combustion, but new processes such as gasification has been of increasing importance in Nordic research. Also the utilization of MSW/RDF for energy through combustion is a major activity. These new topics will also be addressed in the planning of the new Nordic cooperation 1995 - 1998.

This seminar will be followed with a workshop on the modelling aspects of combustion of biomass tomorrow. The presentations from the workshop are included in the proceedings as an appendix.

Johan E. Hustad
Nordic Professor
MODELLING OF MUNICIPAL SOLID WASTE DEVOLATILIZATION.
TGA RESULTS ON THE COMPONENTS OF MSW AND COMPARISON TO THE TGA
BEHAVIOR OF PINE.

Barbara Krieger-Brockett, University of Washington, USA
Modeling of Municipal Solid Waste Devolatilization:

TGA Results on the Components of MSW and
Comparison to the TGA Behavior of Pine

by

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Abstract

Mathematical modeling and experimental results regarding the devolatilization of lodgepole pine, municipal solid waste (MSW) and large particles of densified refuse-derived fuel (d-RDF) have been investigated previously. In this paper, we will present new thermogravimetric analysis (TGA) data on several MSW constituents. The TGA data will confirm that it is reasonable to use newsprint kinetic parameters to describe the volatiles release for MSW. Also, a comparison is made between the TGA data for d-RDF or MSW and pine, a species of interest in Scandinavia. This comparison is limited to the lowest heating rate in both studies, 5°C/min. Since both of these substances are considered renewable resources, a comparison of their thermal devolatilization behavior in small and large particles is of interest for developing well-designed gasifiers and combustors.

Introduction and Previous Work

Of the approximately 150 million tons per year of U.S. municipal solid waste (MSW) or an average of 3-4 lb waste per day per person, approximately 10% was recovered through recycling, 4% was processed for energy, and 86% was landfilled in 1985. Since then, increasing disposal costs as well as landfill closings have stimulated interest in the waste as a potentially large source of energy and chemicals. The raw MSW is highly variable but generally contains at least paper, yard and food waste, plastics, and non-combustibles such as metal and glass. The organic fraction of MSW has a heating value (dry) of about 5800 to 6600 Btu's per pound, approximately the BTU content of lignite coal. Each ton of MSW has the energy equivalent of a barrel of oil (Daugherty et al., 1986) and has an elemental composition between cellulose and wood owing to the large proportion of paper present. Thus, thermochemical treatment to either directly produce energy (by incineration) or fuel precursors to be upgraded (by pyrolysis, e.g., gasification or liquefaction) has become attractive. However, the heterogeneity of MSW remains an impediment to its use and to the study of its reaction behavior.

Pretreatment of MSW to provide somewhat uniform moisture content and composition appears to increase reaction stability and minimize combustion pollutants (Kilgrove, et al., 1990). This has been one rationale behind commercially available densified refuse-derived fuel (d-RDF). It is made by removing recyclables and non-combustibles, then drying and compressing the
remaining substances into pellets of relatively constant density and size. An inorganic binder is used to stabilize the pellets mechanically and biologically. Daugherty et al. (1986) have screened over one hundred of these binders to obtain an optimal one. This pretreatment process results in a uniform, transportable fuel with a higher volatile fraction and heating value than untreated MSW. Because of its improved fuel value, d-RDF potentially can be transported to central large scale sites having advanced reactors as well as extensive instrumentation to control conditions and minimize pollutants. Thus d-RDF is seen as an alternative to the proliferation of small, inefficient, polluting incinerators located in each community. However, little is known about the reaction rate behavior of this material under heating, the effect of particle size on reaction products, nor many other quantitative aspects. This information is required before converter design can optimally take advantage of this material for upgrading to fuels or before pollutants are minimized in the design of incinerators.

Our work has examined the large particle devolatilization of d-RDF in a single particle reactor and the engineering correlations of the experimental results are published in Lai and Krieger-Brockett (1992; 1993). A mathematical model of this system has been developed and is presented in Lai (1991) and Lai and Krieger-Brockett (1994). However, one of the important pieces of information regarding the kinetic model is the thermogravimetric behavior of the components of MSW. These have been measured in more or less adequate detail by some workers. The principal studies to date are: mass spectrometric studies of MSW pyrolysis (Evans et al., 1985); basic mechanisms of pyrolysis (Mallya and Helt, 1988); plastics thermal decomposition (Agrawal and Helt, 1986; Khalturinskhii, 1987; Hodgkin et al., 1982; fida et al., 1975; Ishii et al., 1987; Ishihara et al., 1990); and newspaper decomposition (McClusky, 1983; Agrawal et al., 1984). However, we were obliged to check others' results, and develop TGA data for the particular components used in our manufactured d-RDF pellets, especially polyvinyl chloride (PVC) and a particular binder Ca(OH)2. Our fabricated pellets were used to study the composition effects on d-RDF devolatilization under conditions of practical importance.

We also wish to compare the thermogravimetric behavior of d-RDF constituents to recent work by Grønli, et al, (1993) on pine and other woods. It is useful to have at least a qualitative sense of their relative thermogravimetric behavior since so much more is known about wood pyrolysis and combustion than about d-RDF pyrolysis and combustion. However, it must be cautioned that all TGA data is obtained on very small particles at slow heating rates, conditions which do not at all represent the actual situation in an incinerator or combustor. In the latter practical situations, large particles are used. The poor heat conductivity in the large particles prevents a uniform temperature profile and confines volatiles to the particle interior. There the volatiles can inter-react in secondary reactions and alter the thermogravimetric and pyrolysis behavior compared to that expected from small particles. This is likely to result in considerably different weight loss characteristics and particularly reaction products for large and small particles.

Experimental Details

The single particle reactor and experimental procedure is described in the previously mentioned articles by Lai and Krieger-Brockett. For the purposes of this paper, we will reiterate a brief description of the sample preparation. Since MSW contains so many classes of components, we reduced these to four principal classes for purposes of fabricating laboratory pellets of known composition. These classes were: (1) newsprint which simulates the behavior of all paper and cardboard; (2) equal parts low and high density polyethylene and poly vinyl chloride; (3) equal parts metal and glass; and (4) binder. The first three are combustible and devolatilize, the last two are non-combustible but the binder does provide some volatiles at higher temperatures as will be seen from the TGA data.
The four classes above were mixed and compressed into nominal 1 cm sized d-RDF pellets in proportions that were dictated by a special statistical experimental design (mixture design). This mixture design allowed us to unambiguously uncover the effects of each constituent on pyrolysis behavior. However, for determination of TGA behavior, we studied five of the same substances that were used to fabricate our d-RDF pellets. The ones that had the potential to form volatiles and exhibit weight loss were the three plastics, newsprint, and binder. Binder effects on RDF pellet integrity and biological stability were studied by Daugherity, et al. (1986) and we chose one of their best-performing and commonly used binders for our studies. The metal and glass always found in MSW or RDF were not studied by TGA.

**Results and Discussion**

Actual samples of the materials used to fabricate our d-RDF pellets were pulverized and examined in a thermogravimetric balance at several heating rates (5-30°C/min) using a small sample size (less than 9 g). Since these materials are poor heat conductors, the lowest heating rate data (5°C/min) are the most informative and least likely to have inaccurate measured temperatures that differ from the actual sample temperature. The results of the TGA at 5°C/min in helium are shown in Fig. 1 for newsprint and binder, and Fig. 2 for the three plastic materials. In Fig. 1 we can see that the binder does not begin to form volatiles until nearly 80% of the newsprint has devolatilized. Low and high density polyethylene exhibit reaction and weight loss at temperatures above 700 K in Fig. 2, a temperature where most of the newsprint and PVC already has been reacted to form volatiles. Thus for small particle samples and slow heating, most of the newsprint and PVC volatiles have left the reaction zone when polyethylene and binder devolatilize. The TGA data (all at 5°C/min) are placed in a somewhat busy composite graph in Fig. 3 along with the replotted TGA data on Pine from Grønli, et al (1992), used with permission.

The MSW and d-RDF are truly physical, not chemical mixtures. That is, the constituents are merely present in the same physical space and not chemically bound to each other. This is not true for wood. Wood is a chemical mixture of cellulose, lignin, and various materials that can be extracted by certain solvents (called "extractives"). The separated cellulose is retained as the original polymer. However, the polymeric lignin that one isolates from wood is chemically altered, many lignin bonds are broken in order to separate the lignin from the cellulose, and the resultant lignin is correctly called by the name of the process used to isolate it. Thus we have "Kraft lignin" or "Klason lignin" or "thermomechanical lignin", depending on what process was used to chemically isolate the lignin from the original wood. These lignins have different molecular weights, different chemical structures, and different trace inorganic species. As isolated chemicals, the lignins are unlikely to behave the same as the lignin bound in the wood matrix. This is true under TGA or under pyrolysis conditions. However, for MSW, no chemical bonds are broken when we separate the mixture into its constituent fractions. We could expect that the composite weight loss of pulverized MSW might be the same as the weighted sum of the individual MSW constituents' weight loss. However, this may be misleading because MSW is never pulverized but rather it is used as received or in large particles as d-RDF. The large pellet undergoing devolatilization confines the volatiles to its interior. There the volatiles can interact-react, form secondary reaction products, and pursue a totally different reaction trajectory, heat release, and resultant devolatilization weight loss than would be observed in a powdered small particle sample. For example, heated large pellets may form more char by condensation reactions of the reactive intermediates confined to the particle interior than small particles do since the reactive intermediates may readily escape. Because more char may be formed, the weight loss as a function of temperature is potentially different for large and small particles.
Fig. 1 TGA data for newsprint and a particular binder, Ca(OH)$_2$.

Fig. 2 TGA data for three plastics commonly found in MSW and d-RDF.
We may gain some insight by estimating which weight-loss curve would dominate the TGA behavior of a large d-RDF particle. The weight fractions that we studied using our 4 principal classes of constituents are:

\[
\begin{align*}
0.5 & \leq \text{newsprint} \leq 0.95; \\
0.00 & \leq \text{plastics} \leq 0.20; \\
0.05 & \leq \text{metal and glass} \leq 0.15; \quad \text{and} \\
0.00 & \leq \text{binder} \leq 0.08.
\end{align*}
\]

These ranges are typical for the variation in MSW and d-RDF as studied by the workers cited in Lai (1991). A typical "average" d-RDF could be about 75% newsprint/paper, about 10% each of plastics and metal/glass, and about 5% inorganics. From this we can expect that the newspaper might dominate the temperature versus weight loss curves for MSW or d-RDF.

We then compare the temperature versus weight loss for newsprint and pine in Fig. 3, where the curve for pine is the only one with symbols. From this comparison we see that d-RDF would be expected to begin its weight loss at a lower temperature than biomass or pine owing to the presence of both PVC and newsprint. Newsprint has various inorganic additives that increase brightness, change the paper texture, etc. These additives have been shown to catalyze the decomposition of cellulose in newsprint and lower the temperature at which it forms volatiles. Because of the relatively small fraction of polyethylene in MSW and d-RDF, we do not expect it to raise the temperature at which d-RDF appears to lose most of its weight. However, in spite of the reasonable assumption of using newsprint to model the weight loss of d-RDF, its kinetics are insufficient to predict the product distribution and reaction product slate from d-RDF devolatilization. For that we need detailed kinetics of product formation for each of the constituents of d-RDF or MSW. A similar comment may be made for mathematically simulating the products formed during biomass devolatilization - that is, detailed product formation kinetics are also needed to do an adequate simulation.
Fig. 3 TGA data for combustibles and binder commonly found in MSW and d-RDF and pine (diamond symbol).

Acknowledgments

The authors would like to gratefully acknowledge the Nordic Council of Ministers for their gracious invitation for one of us (BK-B) to participate in this Seminar on Biomass Combustion.

References


OVERVIEW OF IEA BIOMASS GASIFICATION ACTIVITY.

Johan E. Hustad, NTH, Noray.
OVERVIEW OF IEA BIOMASS GASIFICATION ACTIVITY

By J.E. Hustad, Norwegian Institute of Technology, Norway

Abstract

The IEA Bioenergy Agreement 1992 - 1994 contains four different tasks. Fifteen countries have now signed the agreement. Task X Conversion consists of nine different activities each run by an activity leader. An overview of the biomass gasification activity is presented. In the agreement 1992 - 1994 there are nine countries participating in this particular activity. The means are information exchange, workshops, site visits, and continued focus on gasifier operation and improvements, and scale up. The overheads presented are given in appendix I. The summary report from the three year period 1989 - 1991 is given in appendix II.

Introduction

The IEA bioenergy agreement 1992 - 1994 contains four different tasks:

Task VIII
- Efficient and Environmentally Sound Biomass Production Systems.

Task IX
- Harvesting and Supply of Wood Biomass for Energy.

Task X
- Biomass Utilization

Task XI
- The Conversion of Municipal Solid Waste Feedstocks to Energy.

Fifteen countries are participating in the agreement: Austria, Belgium, Canada, Denmark, Finland, Italy, Japan, Netherlands, New Zealand, Norway, Sweden, Switzerland, United Kingdom, United States, CEC. Task X - Biomass utilization contains nine different activities: Biomass combustion, Liquefaction/Pyrolysis, Gasification/Gas Turbines, Biotechnology for fermentation, Anaerobic digestion, Straw utilization, Environmental systems and Interface activity.
Gasification activity

The objective of the gasification activity is to "Improve technologies for gasification of biomass and to promote their commercialization of the production of power, fuel gases, and synthesis gases by promotion information exchange and evaluation, identifying RD & D needs, and identifying and eliminating barriers to implementing the technologies." The means are "Information exchange, workshops, site visits, ad continued focus on gasifier operation and improvement, and scale up."

The activity leader is Suresh Babu, United States, and the participating countries are Canada, Denmark, Finland, Netherlands, Norway, Sweden, Switzerland, United Kingdom, United States. Two meetings are held in 1992 (UK and Canada) and two meetings in 1993 (Italy and USA). The meetings are often combined with one day host presentation of ongoing research and one day excursion. Ten different projects are identified and run with a project lead from different countries. These are:

- High pressure biomass feeders (Finland)
- Hot gas cleanup (Canada)
- Resource evaluation in IEA countries (UK)
- ALtholz gasification (Switzerland)
- Survey of gas turbines, IC engines and gas burners (Canada)
- MSW/RDF gasification (Sweden)
- Feed preparation for biomass gasification (Denmark)
- Low versus high pressure gasification (Canada)
- Analytical protocols (Finland)
- Cofiring fuel gases with natural gas (Norway)

The presented overheads are given in appendix I and the summary report from the activity during the previous agreement 1989 - 1991 are given in appendix II.
APPENDIX I

PRESENTED OVERHEADS.
Natural gas 17.4%
Oil 34.1%
Coal 24.1%
Biomass 14.7%
Nuclear 4.1%
Hydro 5.5%

World
Total = 373 exajoules
Population = 4.87 billion
Energy use per capita = 77 gigajoules

Natural gas 22.7%
Oil 38.3%
Coal 24.5%
Biomass 2.8%
Nuclear 5.9%
Hydro 5.7%

Industrialized countries
Total = 247 exajoules; 66 percent of world total
Population = 1.22 billion; 25 percent of world total
Energy use per capita = 202 gigajoules

Oil 25.8%
Coal 23.4%
Biomass 38.1%
Natural gas 7.1%
Nuclear 0.6%
Hydro 5.1%

Developing countries
Total = 126 exajoules; 34 percent of world total
Population = 3.65 billion; 75 percent of world total
Energy use per capita = 35 gigajoules

FIGURE 1: Primary energy use for the world (top), industrialized countries (middle), and developing countries (bottom) in 1985.
<table>
<thead>
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<th>Source</th>
<th>Technical Potential</th>
<th>Realizable Potential</th>
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<td>Wind</td>
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<td>Land use</td>
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<td></td>
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<td>Geothermal(wet)</td>
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<td>Resource uncertainty</td>
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<tr>
<td>Use of ocean heat</td>
<td>1</td>
<td>0.5</td>
<td>Economics, market penetration</td>
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<tr>
<td>Tides</td>
<td>0.04</td>
<td>~0</td>
<td>Insignificant compared with uncertainties of other estimates</td>
</tr>
<tr>
<td>Ocean current, waves</td>
<td>0.005</td>
<td>~0</td>
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<tr>
<td><strong>Total</strong>*</td>
<td><strong>15</strong></td>
<td><strong>8.7</strong></td>
<td>*In addition, direct solar heat constitutes an enormous potential</td>
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STATOIL
## BIOENERGY'S CHANCES IN THE EUROPEAN COUNTRIES

<table>
<thead>
<tr>
<th></th>
<th>AREA PER. INHAB.</th>
<th>URBANISATION % OF TOT. POPUL.</th>
<th>ENERG. IMPORTS % OF CONSUMPT.</th>
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BIOENERGY'S CHANCES IN THE EUROPEAN COUNTRIES

GROUPE 1: CHANCES FOR BIOENERGY LIMITED - (AREA AVAILABLE < 0.5 HA/INHAB.)

EC EFTA EASTERN EUROPE
BELGIUM
GERMANY
NETHERLANDS
UNITED KINGDOM

GROUPE 2: SOME CHANCES FOR BIOENERGY - (AREA AVAILABLE 0.5 - 1 HA/INHAB.)

EC EFTA EASTERN EUROPE
DENMARK SWITZERLAND CSFR
FRANCE HUNGARY POLAND
ITALY PORTUGAL

GROUP 3: GOOD CHANCES FOR BIOENERGY - (AREA AVAILABLE > 1 HA/INHAB.)

EC EFTA EASTERN EUROPE
GREECE AUSTRIA BULGARIA
IRELAND FINLAND ROMANIA
SPAIN NORWAY YUGOSLAVIA
SWEDEN
Present: Activity Participants

1. Paul Jollei (PJ), Universite of Sherbrooke, Canada
2. Ulrik Henriksen (UH), Technical University of Denmark, Denmark
3. Erik Winther (EW), Elkraft, Denmark
4. Hubert Stassen (HS), BTG Biomass Technology Group, The Netherlands
5. Johan Hustad (JH), Norwegian Institute of Technology, Norway
6. Erik Rensfelt (ER), Termiska Processer (TPS), Sweden
7. Rudi Buehler (RB), Ingenieurburo Umwelt & Energie, Switzerland
8. Philipp Hasler (PH), Ing. Buro, Verenum, Switzerland
9. Nick Barker (NB), ETSU, United Kingdom
10. Richard Bain (RLB), National Renewable Energy Laboratory, U.S.A.
11. Suresh Babu (SB), Institute of Gas Technology, U.S.A.

Apologies were received from E. Chornet (EC), Canada, H. Christiansen (HC) Denmark, Kai Sipila (KS), Finland, Esa Kurkela (EK), Finland, G. Huisman (GH), The Netherlands, and G. Smakman (GS), The Netherlands, for their inability to attend the meeting.
IEA GASIFICATION - TASKS

Task 1. Evaluation of High Pressure Biomass Feeders, Finland: VTT has completed this task and distributed reports on August 1992.

Task 2. Hot-Gas Cleanup, Canada: Mr. R. Graham has completed the task report.

Task 3. Resource Evaluation in IEA Countries, U.K.:

Task 4. Altholz Gasification, Switzerland: The major problem in writing a general task report that is of interest to many countries is the wide variation in Altholz composition. Separation and segregation of the contaminants may lead to further changes in composition. Some general comparisons and contrasts should be drawn between gasification and combustion of Altholz.

Task 5. Survey of Gas Turbines, IC Engines, and Gas Burners, Canada: RLB reported that NREL has completed an in-house study on gas turbines. He will determine whether the same report could be released for general use.

HS is requested to send any available information and publications on the review and evaluation of engines to EC. UH is now starting to look at the available engines and may be able to assist. NB will check with UK-Caterpillar and European Gas Turbines to obtain additional information.

Task 6. Report on MSW/RDF Gasification, Sweden: ER will compile a report including a review of previously published Andco Torrax, Purox, etc. gasification data, the Swedish reviews (including Mrs. Lindmans report), and an update of the most current activities, including the TPS process information.

Task 7. Report on Feed Preparation for Biomass Gasification, Denmark: UH will prepare the report with the extensive straw and chunk-wood handling and preparation data available in Denmark.

Task 8. Evaluation of Low Versus High-Pressure Gasification, Canada: SB distributed to the participants the low and high-pressure gasification process schemes prepared by the Liquefaction and Pyrolysis Activity.

Task 9. Analytical Protocols, Finland: VTT will shortly complete the report.

Task 10. Cofiring Fuel Gases With Natural Gas, Norway: This new task was well received. There is widespread interest in the review and evaluation of the benefits of cofiring biomass derived fuel gases with natural gas. Natural gas could be used to enhance the heating value of LCV fuel gases so that existing energy conversion equipment could be used. Natural gas will also assist load following in biomass gasification power generation systems.
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   2.2 Tars ..............................................................  
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3.0 CONTAMINANT LEVELS (Existing Gasifiers) .......................  

4.0 CONTAMINANT CONSTRAINTS ........................................  
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   6.3 Synthesis Gas ..................................................
Demoplants - Projects:

Bioneer, wood and peat up to 6 MW, 6 plants in SF and 3 plants in Sweden.

Omnifuel FB, Canada 20 MW.

Southern Electric Int. Inc., USA, 2 AFBG each 36 MW.

Catalyst Inc., USA, AFBG, steam cycle 5.5 MWe.

Ahlstrøm & Gøtaverken, Sweden, Finland, Portugal, fuel gas for lime kilns, 15 - 35 MWth.

Studsvik, ACFB, Florenze, Italy, 2x15 MWth, RDF gasification, fuel gas for lime kiln.

Sydkraft, Varnamo, demoproject.

IGT, Renugas process at Hawaii.

Brazilian projects.

Comprehensive review given by Babu & Whaley (Biomass & Bioenergy Vol. 2 Nos. 1 - 6, 1992)

Research projects:

Review on pressurized systems by Lund Univ.
Hawaii Biomass Gasification Facility
Details of Phases

Phase I: Design, construct, and operate gasifier
- Feed: bagasse
- Pressure: 1 MPa
- Feed-Rate: 45 Mg/day

Phase II: Install hot-gas cleanup unit and gas turbine gen-set at 3–5 MW scale
- Feed: bagasse
- Pressure: 2 MPa
- Feed-Rate: 90 Mg/day

Phase III: Install oxygen plant and slip-stream methanol synthesis unit
- Feed: bagasse
- Pressure: 2 MPa
- Electricity: 3–5 MW
- Methanol: 3800 liters/day
<table>
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<tr>
<th>LOCATION</th>
<th>GASIFIER TECHNOLOGY</th>
<th>SIZE</th>
<th>POWER GENERATION</th>
<th>STATUS</th>
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<tr>
<td>COTTISH BORDERS</td>
<td>UPDRAFT</td>
<td>5 MWe</td>
<td>SPARK IGNITION</td>
<td>DESIGN</td>
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<td>NNISKILLEN</td>
<td>DOWNDRAFT</td>
<td>100 kWe</td>
<td>DUAL FUEL ENGINE</td>
<td>OPERATING</td>
</tr>
</tbody>
</table>
UK DTI PROGRAMME

• WOOD GASIFICATION IS READY FOR DEMONSTRATION

• WASTE GASIFICATION NEEDS R&D

• TWO MARKETS FOR WOOD GASIFICATION
  < 200kWe
  >5MWe

• < 200kWe IS REPRESENTED BY ENNISKILLEN PROJECT. A SEMI AUTOMATIC GEN SET IS NECESSARY BEFORE IT CAN BE REPLICATED IN LARGE NUMBERS. OPERATED BY RURAL ORGANISATIONS.

• >5MWe WILL BE OPERATED BY POWER COs. UPDRAFT OR FLUID BED.

• R & D ON WASTE CONVERSION WILL CONCENTRATE ON ACID GAS RETENTION.

• CO-FIRING WITH FOSSIL FUEL WILL BE ASSESSED

• PYROLYSIS WILL BE ASSESSED
INTEGRATED GASIFICATION COMBINED CYCLE FOR SOLID FUELS. SCHEMATIC DIAGRAM.
### Biomass Gasifier Data

<table>
<thead>
<tr>
<th>Company/Process</th>
<th>Ahlström Updraft</th>
<th>Biosyn FB</th>
<th>RenuGas FB</th>
<th>LURGI FB</th>
<th>Clamecy FB</th>
<th>Rheinbraun HTW</th>
<th>Ahlström CFB</th>
<th>LURGI CFB</th>
<th>Battelle MSCF8</th>
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<tr>
<td>Gasifier Type</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Input Power</td>
<td>1 MW</td>
<td>100 kW</td>
<td>0.89 MW</td>
<td>120 kW</td>
<td>11.0 MW</td>
<td>10 bar</td>
<td>1 bar</td>
<td>1 bar</td>
<td>3.8 MW</td>
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<td>Pressure</td>
<td>1 bar</td>
<td>1 bar</td>
<td>22.0 bar</td>
<td>1 bar</td>
<td>7.2 bar</td>
<td>10 bar</td>
<td>1 bar</td>
<td>1 bar</td>
<td>870</td>
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<tr>
<td>Temperature</td>
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<td>837</td>
<td>815</td>
<td>720/1240</td>
<td>710/915</td>
<td>900</td>
<td>750</td>
<td>870</td>
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<td>Gasification Medium</td>
<td>air/steam</td>
<td>air/steam</td>
<td>air/steam</td>
<td>O2/steam</td>
<td>O2/N2/steam</td>
<td>air/steam</td>
<td>O2/steam</td>
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<td>peat</td>
<td>sawd./bark</td>
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<td>Moisture</td>
<td>52</td>
<td>12.8</td>
<td>10.8</td>
<td>5</td>
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<td>15</td>
<td>17</td>
<td>11.3</td>
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<td>1.4</td>
<td>0.4</td>
<td>1.0</td>
<td>0.3</td>
<td>0.2</td>
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<td>Steam Input</td>
<td>kg/kg wf</td>
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<td>Oxygen Input</td>
<td>kg/kg air</td>
<td>0.15-0.19</td>
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<td>0.14</td>
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<td>0.42</td>
<td>0.24</td>
<td>0.30</td>
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<td>1.49</td>
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<td>1.34</td>
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<td>Water and N2 Content of Product Gas</td>
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<tr>
<td>N2</td>
<td>vol%</td>
<td>45.4</td>
<td>18.6</td>
<td>11.0</td>
<td>16.3</td>
<td>2.6</td>
<td>0.2</td>
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<td>H2O</td>
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<td>25.3</td>
<td>25.0</td>
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<td>Composition of Dry Product Gas (N2 free)</td>
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<td></td>
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<td></td>
<td></td>
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<tr>
<td>H2</td>
<td>vol%</td>
<td>ca.28</td>
<td>18.8</td>
<td>32.5</td>
<td>21.1</td>
<td>24.1</td>
<td>36.1</td>
<td>31 to 36</td>
<td>33.4</td>
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<td>CO</td>
<td>vol%</td>
<td>ca. 40</td>
<td>30.9</td>
<td>10.7</td>
<td>36.6</td>
<td>37.0</td>
<td>28.1</td>
<td>29 to 44</td>
<td>33.5</td>
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<td>CO2</td>
<td>vol%</td>
<td>ca. 20</td>
<td>37.9</td>
<td>41.4</td>
<td>31.2</td>
<td>38.7</td>
<td>33.0</td>
<td>20 to 26</td>
<td>25.5</td>
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<td>CH4</td>
<td>vol%</td>
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<td>8.1</td>
<td>14.3</td>
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<td>8 to 14</td>
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<td>C2H4</td>
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<td></td>
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<td></td>
<td>0.7</td>
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<tr>
<td>C2H6</td>
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<td>0.3</td>
<td>0.5</td>
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<tr>
<td>C3H6</td>
<td>vol%</td>
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<td>0.3</td>
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<td></td>
<td>0.6</td>
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<tr>
<td>CmHn</td>
<td>vol%</td>
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<td>HHV Dry Gas</td>
<td>MJ/Nm3</td>
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<td>6.5</td>
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<td></td>
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<td>17.5</td>
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<tr>
<td>LHV Dry Gas</td>
<td>MJ/Nm3</td>
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<tr>
<td>Cold Gas Efficiency</td>
<td>%</td>
<td>77.0</td>
<td>93.0</td>
<td>96.1</td>
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<td>C-conversion, condensate excl.</td>
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<td>96.1</td>
<td>98.0</td>
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<tr>
<td>C-conversion, condensate incl.</td>
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<tr>
<td>Tar</td>
<td>g/kg wf</td>
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<td>2.8</td>
<td>13.1</td>
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<td>0.4</td>
<td>5.7</td>
<td>170.0</td>
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<tr>
<td>Char</td>
<td>g/Nm3</td>
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<td>1.26</td>
<td>1.60</td>
<td>0.87</td>
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</table>
EVOLUTION OF BIOMASS TECHNOLOGY AND PROJECTED ENERGY COSTS IN THE USA.
RURAL JOBS FOR AMERICA

Economic activity created by the biomass power industry already supports about 65,000 jobs in the U.S., with a great many of these in rural regions. By 2010 biomass power could support more than 233,000 U.S. jobs.

Jobs Supported by Biomass Power Annually
Electricity generation costs for alternative coal and biomass technologies

<table>
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<tr>
<th></th>
<th>Coal conventional</th>
<th>Coal gasification</th>
<th>Biomass gasification</th>
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<tr>
<td></td>
<td>Steam-electric b</td>
<td>1st gen. c</td>
<td>2nd gen. d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1st gen. e</td>
<td>2nd gen. f</td>
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<td>Capital a</td>
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<td>Fuel</td>
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## Generation costs

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<th>Plant type</th>
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<th>Variable costs&lt;sup&gt;b&lt;/sup&gt;</th>
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<tr>
<td></td>
<td>$/kW-year</td>
<td>$/kWh</td>
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<td><strong>Natural gas</strong></td>
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<tr>
<td>Conventional simple cycle&lt;sup&gt;c&lt;/sup&gt;</td>
<td>31</td>
<td>0.064</td>
</tr>
<tr>
<td>Best new simple cycle&lt;sup&gt;d&lt;/sup&gt;</td>
<td>28</td>
<td>0.060</td>
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<tr>
<td>Advanced simple cycle&lt;sup&gt;e&lt;/sup&gt;</td>
<td>59</td>
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<tr>
<td>Conventional combined cycle&lt;sup&gt;f&lt;/sup&gt;</td>
<td>44</td>
<td>0.041</td>
</tr>
<tr>
<td>Best new combined cycle&lt;sup&gt;g&lt;/sup&gt;</td>
<td>42</td>
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<tr>
<td>Advanced combined cycle&lt;sup&gt;h&lt;/sup&gt;</td>
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<td><strong>Coal</strong></td>
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<td>Conventional steam turbine&lt;sup&gt;i&lt;/sup&gt;</td>
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<td>Best new coal&lt;sup&gt;l&lt;/sup&gt;</td>
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<td>Hydroelectric&lt;sup&gt;k&lt;/sup&gt;</td>
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<td>Solar thermal&lt;sup&gt;m&lt;/sup&gt;</td>
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<td>Photovoltaic&lt;sup&gt;n&lt;/sup&gt;</td>
<td>70–140</td>
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</table>
APPENDIX II

IEA BIOMASS THERMAL GASIFICATION PROJECT

SURESH P. BABU and THOMAS P. WHALEY
Institute of Gas Technology, 3424 South State Street, Chicago, IL 60616, U.S.A.

ABSTRACT

The Biomass Thermal Gasification Project was started in late 1989 as Activity 4 of the IEA Bioenergy Agreement Task VII, Biomass Conversion. This paper reviews the project activities since its beginning, addressing biomass resources, state-of-the-art gasification technology, research needs, and the future project activities that are especially relevant to the nine (9) participating countries: Canada, Denmark, Finland, Italy, The Netherlands, Sweden, Switzerland, the United Kingdom, and the United States of America.

KEYWORDS
Agricultural residues; biomass; bioenergy; gasification; gasifier; IEA; thermal gasification; wood.

BACKGROUND

Biomass, a major component of renewable energy resources, is gaining worldwide recognition as an environmentally compatible fuel. It is estimated that the annual yield of biomass is approximately eight times the world's annual energy use. Hence, there is a significant potential to improve upon its current contribution of 14% to the world's energy consumption (Hall, 1991), with many environmental benefits. Although biomass can be used as an energy source in many ways, gasification is an attractive process because it produces a clean-burning fuel that can be used with new or retrofit gas burners and for many power generation applications. It can even be transported in pipelines for short distances to support small- to medium-size industrial complexes, and on selected sites the gas can be converted to liquid fuels, chemicals, or fertilizers.

The heat load for conventional power production using boilers and steam turbines is estimated to be 14.8 to 16.9 MJ/kWh (14,000 to 16,000 Btu/kWh), which could be reduced by 25% to 35% by resorting to integrated gasification combined-cycle power production schemes (Overend, 1991). At present, biomass gasification is commercially practiced primarily to produce a fuel gas. The largest operating gasification plants in Sweden and Finland are the circulating fluidized-bed gasifiers, rated at 20 to 35 MWth capacity. They are used exclusively to produce a fuel gas for firing lime kilns. On the lower end of the capacity scale, there are several 5-MWth updraft gasifiers operating in Sweden and Finland for district heating and for drying wood. The overall efficiency of the systems for power production is low, around 20%, and the exploitation to fully realize the benefits of biomass gasification — namely, biomass-to-power conversion efficiency of 50% — is yet to be demonstrated. The barriers to achieve this goal include the necessity to improve the system reliability, efficiency, environmental benefits, cost of biomass feedstocks, and a multitude of institutional policies to promote biomass-based energy conversion systems.
To advance the development and commercialization of biomass gasification in the participating countries, under the auspices of the International Energy Agency, Bioenergy Agreement, Task VII, Biomass Utilization, the project on Thermal Gasification of Biomass was started in September 1989. The objectives of the project are to improve the effectiveness and the environmental benefits of biomass gasification and to promote its commercialization for the production of power, fuel gases, and synthesis gas by —

- Promoting information exchange and evaluation
- Initiating and coordinating relevant research and development programs
- Providing special consideration to environmental factors
- Identifying and eliminating barriers to implementing gasification technologies.

The project accomplishments since the beginning of the project are presented in the following sections, along with the project plans for the next triennium (1992-1994).


The major accomplishments during the activity period (1989-1991) included exchange of significant publications and presentations on the current state of the art of biomass gasification by industrial experts. Information exchange is further promoted by the country reports prepared by the project participants (IEA, 1991a) and by visiting selected research and commercial gasification plant sites. Based on the state of the art of the gasification technology and keeping in perspective the potential for achieving the high process efficiencies, the RD&D needs that would assist in accomplishing this goal were identified. The information exchange will serve as the basis for developing and conducting a series of project activities that should assist all the participating countries in focusing on the technical and institutional barriers and in developing coordinated national energy plans to promote the commercialization of biomass gasification.

Using the bibliography, country reports, and the RD&D needs, several project activities were developed and prioritized. These project activities will continue for the next triennium (1992-1994), keeping in perspective the biomass resources and focusing on the evolving needs for biomass gasification in participating countries. Besides being beneficial to the participating countries in planning their national biomass energy programs, the project activities should contribute to a well-coordinated complementary RD&D effort among the participating countries. The team effort involved in all the project activities should also be beneficial for developing standardized interpretation and evaluation procedures for the many facets of biomass gasification systems.

Four project meetings were held during 1989 to 1991 (Orlando, U.S.A., Jan. 1990; Vezelay, France, June 1990; Neuchatel, Switzerland, Dec. 1990; Espoo, Finland, Sept. 1991). The last three project meetings also included plant visits to the Stein Industries/ASCAB high-pressure fluidized-bed gasifier at Clamecy, France; the Bioalternative moving-bed downdraft pyrolyzer at ENGOLLON, Switzerland; the Winkler peat gasifier at Oulu, Finland; the Ahlstrom Pyroflow circulating fluidized-bed gasifier at Pietersaari, Finland; and the Bioneer updraft moving-bed gasifier, also near Pietersaari, Finland. During the last meeting in Espoo, Finland, a 1-day symposium was held on the large-scale gasification systems. For this symposium, biomass gasification experts from Lurgi, Göteborg, Ahlstrom, Thomas R. Miles Consulting Engineers, and Bioneer were invited to present their experience with the development and operation of biomass gasification systems and to speak on the technology development needs.

Discussion of Project Accomplishments (1989-1991)

The project meetings provided the forum to present and discuss the biomass resources, state-of-the-art
indigenous gasification technology, the biomass gasification RD&D programs, and the future plans for biomass gasification in participating countries.

It is apparent from a review of the biomass resources that Canada, Finland, Sweden, and the U.S.A. have large resources that justify the construction of centralized biomass gasification plants with capacities ranging from 500 to 1000 dry tonnes of biomass per day. On the other hand, Denmark, The Netherlands, Switzerland, and the U.K., with comparatively smaller biomass resources, may only be able to justify the construction of gasification plants that are in the range of 50 to 100-tonnes/day capacity. Woody biomass is abundantly available in Canada, Finland, Sweden, and the U.S.A., whereas the herbaceous biomass is an important resource in Canada, Denmark, Italy, The Netherlands, Switzerland, the U.K., and the U.S.A. The biomass-handling and gasification systems are well-developed for woody biomass, as demonstrated by large-scale wood gasifiers in Scandinavia and the U.S.A. with capacities up to 35 MWth, whereas the gasification of herbaceous biomass is limited to small-scale systems.

During the project meetings it became clear that in addition to these feedstocks, Althölz or urban wood waste is becoming an important resource for gasification, as many of the participating countries, in particular, Switzerland and The Netherlands, impose severe limitations on its combustion or disposal by landfill. Hence, gasification is an environmentally preferable means of recovering energy from Althölz while accomplishing volume reduction at the same time. Because the chemical composition of urban wood wastes varies widely, the problems related to the ultimate disposal of the gasification inert residues can only be addressed after detailed characterization of the residual solids.

A common concern for all the participating countries is the mounting problem related to municipal solid wastes (MSW). To date, only a limited amount of fluidized-bed gasification tests were conducted with refuse-derived fuel (RDF) derived from MSW, in Sweden and the U.S.A. Hence, further development and demonstration of RDF gasification is a necessity.

Of the participating countries, Canada, U.S.A., Finland, and Sweden are among the five countries with the most abundant peat resources in the world. Peat gasification has been fairly well developed and demonstrated in Finland and the U.S.A.

Municipal sludge is another type of biomass that could be gasified to accomplish volume reduction while recovering energy with complete control over emissions. Recently, NOVEM of The Netherlands has sponsored a worldwide review of municipal sludge incineration and gasification technologies. The study concluded that most of the available technologies are expensive; sludge disposal costs range from $400 to $600/tonne. Schelde Environmental Technology is now developing a downdraft sludge gasification process, which should reduce the cost of sludge disposal to about $350/tonne (NOVEM, 1991).

State-of-the-Art Biomass Thermal Gasification Technology

A review of the state-of-the-art biomass thermal gasification technology shows that the moving-bed gasifiers have been studied and tested extensively. Of the several variations of the moving-bed systems, the updraft gasifier has been the most successful. The BIONEER gasifier commercialized in the early 1980's in Finland has been successfully operated with wood and peat at capacities ranging up to 6 MWth. In Finland, six plants are in operation for close-coupled district heating purposes while three BIONEER gasifiers were built in Sweden for district heating and drying wood chips (Kurkela, 1989; Rensfelt, 1984). In general, the moving-bed systems require a close control of feedstock size and moisture content and appropriate means to handle the high tar contents in the raw gases.

The Winkler fluidized-bed coal gasifier was successfully scaled up to gasify 25 dry tonnes of peat per hour in 1988 by Kemira Oy at Oulu, Finland. The major mechanical and process modifications included improvements to the peat lock hopper feeding system and the control of naphthalene by using higher gasifier operating temperatures and the addition of a benzene scrubber for naphthalene removal.
The application of fluidized-bed gasifiers to wood and other types of biomass requires the use of inert solids in the gasifier as determined by the development studies in Canada and the U.S.A. The Omnifuel fluidized-bed gasification demonstration unit in Canada operated successfully during 1982. The 20 MWth, 1.8-m-diameter air-blown demonstration gasifier operated at about 760°C (1400°F) and a pressure of 35 kPa (gauge) to produce a fuel gas for a plywood plant. From 1985 to 1989 Southern Electric International, Inc. (SEI) successfully operated two atmospheric pressure fluidized-bed gasifiers, each with 36-MWth capacity. The fuel gas product was used in a close-coupled clay-drying facility in Quincy, Florida. Catalyst, Inc., has built and operated the Energy Products of Idaho (EPI) atmospheric-pressure fluidized-bed gasifier at North Powder, Oregon. The gasifier operated in 1990 at 90% availability in close-coupled operation with steam-driven electric power plants to produce 5.5 MWe. Both of the SEI gasifiers had to solve problems related to fuel-gas leakage, high-temperature valve operation, expansion joints, and solids (wood and ash) handling systems. The improvements to the Catalyst, Inc., gasifier included double screening the feed, submerged wood feeding, and a modified distributor design for providing stable fluidization and the desired fluidized-bed pressure drop.

The biggest and most successful biomass gasification operations to date have been attributed to the Ahlström and Götaaviken circulating fluidized gasifiers employed in close-coupled operation with lime kilns in Sweden, Finland, and Portugal. These gasifiers have thermal capacities ranging from 15 to 35 MWth and the largest reactor is 2-m-diameter X 15 to 22-m-height. They are capable of handling a mixture of sawdust, screening residues, and bark (Siro, 1989). The gasifiers are operated at close to atmospheric pressure and 700°C with 1000 kg of circulating calcined limestone. One of the largest Ahlström gasifiers was built in 1983 at the Kymmene Corporation papermill at Pietarsaari, Finland. It was reported during a visit to this plant that at the existing oil prices in the mid-1980's, the plant was paid off in about 2 years time by replacing the oil with biomass-derived fuel gas for firing lime kilns.

A 35-MWth Götaaviken circulating fluidized-bed gasifier at the Värö pulp mill in Sweden has been in operation since 1988 (Olausson, 1991). A 15-MWth Studsvik circulating fluidized-bed gasifier was recently built for gasifying RDF in Florence, Italy. The plant is now in shakedown operations and full operation should be starting soon. All the circulating fluidized-bed gasifiers had to solve the normal start-up related problems. In some cases, fuel gas leakage leading to explosions in the feed hopper had to be solved before attaining reliable continuous operation (Rensfelt, 1984).

These biomass gasifiers represent an impressive array of low-pressure technologies, which, when combined with the current state-of-the-art raw gas cleanup, render themselves suitable for close-coupled operation with lime kilns, furnaces, and boilers. It is well known that the conventional Rankine steam-cycle system requires a heat input of 14.8 to 16.9 MJ/kWh (14,000 to 16,000 Btu/kWh). Recent studies and evaluations have shown clearly that by integrating high-pressure gasifiers with advanced gas-turbine systems, the heat load could be reduced by as much as 25% to 35% (Overend, 1991).

The potential for higher efficiency and the concomitant benefit of reducing CO₂ emissions (Roscillo-Calle and Hall, 1992) has been the main driving force behind the well-justified current revival of interest in biomass gasification. The recent biomass gasification initiatives in Sweden, the U.S.A., and Brazil are primarily motivated by the desire to fully exploit the benefits of the efficient use of biomass. The Sydkraft and Vattenfall projects in Sweden, the RENUGAS process scale-up and demonstration project in Hawaii, and the Brazilian gasification projects are primarily directed toward the development and demonstration of the next generation of gasification technologies that will be economical and that can lead to significant environmental benefits. In addition to these power projects, other advanced gasification schemes, such as the Battelle Columbus Laboratories Multi-Solid Fluidized-Bed gasification process and the MTCI gasification process, have been reactivated to explore other uses for biomass.

Biomass Thermal Gasification Bibliography

The thermal gasification project has prepared a bibliography report with a foreword introduction to the fundamentals of biomass gasification, including selected key publications, covering the literature.
Biomass Thermal Gasification Project

published during the last decade (IEA, 1991b). The bibliography is divided into the following subject categories:

1. Economic/Systems Analysis
   - Small Scale — Close-Coupled
     - Cold-Gas
   - Large Scale — Close-Coupled
     - Combined-Cycle
     - Synthesis Gas/Methanol

2. Feedstock Preparation/Handling
   - Comminution/Grinding
   - Drying/Dewatering
   - Transport/Flow/Feeding
   - Safety

3. Gas Cleaning
   - Internal Combustion (IC) Engines
   - Turbines
   - Synthesis Gas

4. Municipal Solid Waste (MSW), Refuse-Derived Fuel (RDF), and Sludge Gasification

5. Sampling/Analyses/Characterization

6. Environmental Assessment
   - Wastewater/Liquid
   - Airborne (Gas, Vapor, Particulate)
   - Ash/char (Solid).

The extensive coal gasification research and development programs conducted during the same time have investigated several innovative concepts for high-temperature gas cleanup, including particulates and alkali removal, and gas upgrading, many of which should also be applicable to the development of advanced biomass gasification systems. For this purpose, a summary of the U.S. DOE-sponsored research programs on coal gasification and gas stream cleanup systems was prepared based on the August 28-30, 1990, Tenth Annual Gasification Contractors' Review Meeting conducted at the Morgantown Energy Technology Center, Morgantown, West Virginia, U.S.A. (IEA, 1991c).

Project Activities

A wide range of project activities was discussed, selected, and prioritized as follows:

High Priority

1. Evaluation of process, economic, and environmental aspects of small-scale (up to 1 tonne/h), medium-scale (1 to 10 tonnes/h), and large-scale (>10 tonnes/h) biomass gasification systems (that is, feed preparation to energy conversion, including effluent disposal)

2. Process and economic evaluation of gas cleanup systems for specific end uses, including IC engines and gas turbines
Research Needs for Thermal Gasification of Biomass

During the project meetings, the research and technology development needs for the various subdivisions of the overall biomass gasification system were identified (IEA, 1992). The high-priority research needs for the various process subdivisions are listed below.

Medium Priority

1. Evaluation of (hot and cooled) gas conversion and utilization equipment for —
   -- low-energy gas burners
   -- IC engines
   -- fuel cells
   -- gas turbines
   -- synthesis of hydrocarbons, liquid fuels, chemicals and fertilizers

2. Reviewing and updating MSW/RDF gasification

3. Reviewing and updating sludge gasification

Low Priority

1. Review of state-of-the-art biomass feed preparation and handling for gasification

2. Systems analysis of integrating biomass gasification with other energy conversion or chemical conversion processes to replace fossil fuels

In the future, other project activities will be added to complement the resurgence of interest in biomass gasification in many parts of the world. The project participants are divided into expert working groups based on the expertise and current interests of the participants and assigned the responsibility to work cooperatively and report on the project activities.

Research Needs for Thermal Gasification of Biomass

During the project meetings, the research and technology development needs for the various subdivisions of the overall biomass gasification system were identified (IEA, 1992). The high-priority research needs for the various process subdivisions are listed below.
Feed Preparation and Handling
1. Impact of biomass feedstock quality requirements for dedicated biomass feedstock management
2. Development of versatile feed-handling systems for the wide variety of biomass feedstocks

Drying and Feeding
1. Measurement, characterization, and control of emissions from dryers (for example, volatile compounds)
2. Development and scale-up of biomass feeding systems with low inert gas demand and low power consumption for application to high-pressure gasifiers (up to 3 MPa) for handling a wide variety of biomass feedstocks

Gasification
1. Research on soot formation from tar and soot reactions leading to soot control and destruction
2. Kinetic studies on the fate of contaminants in biomass feedstocks (for example, fuel, N, Cl, S, P, and heavy metals) during gasification
3. Determination of the effect of gasifier additives, including catalysts, for minimizing tar production, capturing contaminants, and lowering the operating temperature

Gas Cleanup and Gas Upgrading
1. Gasification or reforming of condensable hydrocarbons (secondary processing of the whole raw-gas stream or condensate)
2. High-temperature removal of particulates, alkaline compounds, and other contaminants from fuel gases derived from biomass and Althölz gasification

Final Processing and Gas Utilization
1. Characterization of emissions from gas-fired internal combustion engines

Effluent Handling and Processing
1. Determination of solids (ash, catalyst) leachability and proper disposal methods

Wastewater Treatment
1. Treatment of wastewater from biomass gasification wet scrubbers

Miscellaneous Topics
1. Identification of specific environmental advantages for gasification compared with other biomass energy conversion schemes
Interaction With Other Activities

The thermal gasification project will continue to monitor the other biomass utilization activities. To advance the development and commercialization of thermal gasification of biomass, the project will conduct selected joint activities with other projects including straw utilization, biomass pyrolysis, environmental systems, and production/utilization interface.

REFERENCES


$^{13}$C-NMR CHARACTERIZATION OF TAR LIQUIDS AND CHARS

Mats Lindblom, Lund University, Sweden
$^{13}$C-NMR Characterization Of Tar Liquids And Chars.

1 Introduction

$^{13}$C-NMR analysis of tar liquids most commonly results in a fairly complex spectrogram, since the tar constituents are quite numerous. Up to 250 different compounds has been mentioned. No information about the specific compounds, one by one, can be extracted from such a spectrogram. However, the spectrogram can provide useful information about the major structure and the functionality of the different carbon atoms. The alkyl-, aromatic-, polyaromatic-, carbonyl- and phenyl bound carbons all result in a specific chemical shift related to the solvent peak. The content of the different functionalities can also be determined by area calculations. The whole tar sample is analysed without any further pretreatment, except from introducing a small amount of solvent to the sample. This report will only present the results from $^{13}$C-NMR and solid state NMR. A complete characterization of the high temperature pyrolysis tars and chars would include a comparison of these results with results from elemental analysis and other methods.

2 Experimental

Recording the $^{13}$C-NMR spectra of the H.F. (TAE) and the L.F. (KYL) tar liquids were carried out in a Bruker AC250 spectrometer. The spectrometer is equipped with a superconducting electromagnet made of copper sheathed niobium-titanium wire in the coils which is immersed in liquid helium at 4.2 Kelvin. The magnet has a field strength of 5.8 T and the $^{13}$C-resonance is acquired at 62.9 MHz. The spectra were recorded with inverse gated decoupling and all the spectra were taken as a mean value of between 5000 to 30000 scans. The samples were dissolved in deuterated methanol or chloroform and the chemical shifts were referenced to the actual solvent peak. The d$_6$-MeOH and d-chloroform have shifts of 48.0 and 53.8 ppm referenced to d$_3$-trimethylsilane. The classification of the functional groups is made according to their chemical shifts, described by [1] and [4].

3 Results

3.1 TAE tars

Most of the TAE-tar spectra have very broad resonance signals because of the great number of constituents in the tar samples. The complexity of the resonance signals tend to diminish moving from lower towards higher pyrolysis temperature and the resonance peak signals become more separated from each other at higher temperatures.
A study of the carbon functionality distributions in the TAE-tars shows:

- A CH$_3$/CH$_2$-ratio near 1:1 throughout the whole temperature range as well as for different residence times for a specific temperature. This indicates an average length of two carbons in the aliphatic chains.

- The total amount of aliphatic [0-25 ppm] and [25-40 ppm] drops from 39%, at 800°C and 1.7s gas residence time, to 11% at 1200°C 1.2s.

- The amount of aromatic carbons [90-130 ppm], is only 20-35% when the pyrolysis conditions are at their lower limits.

- The aromaticity increases at more severe pyrolysis conditions. The amount of bridgehead aromatic carbons tends to stabilize at 20-24%. The decrease of the aliphatic functionality is in relation to the increase in aromatic carbon functionality.

- The total amount of oxygenates is near 30-35% at 800°C and decreases to 17% at 1000°C and 3.3s but increases to 25% at 1200°C and 1.2s, but the residence time is shorter in the last case. Furthermore, the produced amounts of the TAE tars at 1200°C with a longer gas residence time than 1.2s were too small for being collected.[6]
Except for the aliphatic OH-functionality [55-90 ppm], which seems to be fairly sensible to an alteration in pyrolysis temperature, the amount of oxygenates is only slightly reduced by higher temperature.

While comparing these results to each other must be remembered that the solubilities of the different TAE tars in deuterated methanol are different. The samples from 800°C were completely soluble. Tar samples from 1000°C and higher were only partly soluble in d₆-methanol. TAE34 (1000°C) dissolved well only in d-chloroform, this is probably due to the more aromatic structure in the high temperature tars. An attempt was also made to use d₆-dimethyl-sulphoxide as a solvent using Chromium(III)-tris-acetyl-acetonate as relaxation agent but the resulting spectra were weak because of a too small amount of the actual sample.

Figure 2. TAE-tars at 800°C.

3.2 The Light Fraction Tars

Unfortunately, most of the samples from the lighter tar fraction, the KYL tars were contaminated with acetone in an attempt to dehydrate the samples for other analytical purposes. Acetone has its characteristic signals at 30 ppm for the methyl carbons and at 210 ppm for the carbonyl carbon, related to TMS. However, one of the samples,
KYL16, could be used then it had not been contaminated with acetone. KYL16 was produced at the same conditions as KYL17 and serves as a duplicate for a comparison of the remaining functionalities.

- Drying with activated silica has caused a considerable loss of tar constituents in some tar samples but not in all.

-A comparison of the different tar fractions; KYL16 to TAE17 shows that the KYL16 has a much higher content of carboxylates. The KYL17 contains 16% of carboxylates, TAE17 only 4%. The TAE17 contains more aliphatics, nearly 40% and twice as much of aromatic bridgehead carbon functionality as KYL16.

4 Experimental of solid state NMR

Solid state NMR of the wood chars were recorded on a Bruker AC250 spectrometer equipped with a CP-MAS unit which consists of:

- Pneumatic magic angle spinning probe (MAS-probe).

- High Power Amplifier for 62.9 MHz/ 300W Pulse.

- High Power Amplifier for 250 MHz / 120 W continuous wave.

All the spectra were recorded at a spinning frequency of 5600Hz in a sample basket made of zirkonia. A duplicate spectrum of C31 was also recorded at 4000Hz to identify the sideband resonance signals.

5 Results of the solid state NMR

5.1 The Chars

It was not possible to record any spectrum from the chars that were produced at more severe conditions than 1200°C, 1.2s gas residence time. This is probably due to the lower hydrogen content in the high temperature chars which disables the cross polarisation between the $^1$H and the $^{13}$C resonance signals.

- The amount of branched aliphatics drops from 3% at 800° to none at 1000°-1200°C.
Figure 3. The influence of temperature on the char functionality.

At 800°C, some of the resonance signals within the range of [55-90ppm] probably arise from hydroxylic functionality in the cellulose components, such as pyranose and furanose. This would indicate that some of the original wood structure still is left in the charred particles at 800°C. But there is a significant increase of hydroxylic functionality at longer residence time. This could be an effect of char gasification with steam from the product gas. At 1000°C the hydroxylic functionality content has become low; near 2-3%. However, even at 1000°C the content of hydroxylic functionality increases with a longer residence time with a concomitant decrease in the aromatic- and bridgehead carbon functionality. The increment could be caused by secondary reactions between the char and the pyrolysis gases.

The phenolic and the carboxylic contents are 7% and 2-3% in the 800°C chars. The contents diminish to 3% and 1% respectively in the most severely treated char that could be analysed by the NMR-technique.

5.2 Solid state NMR of the wood feedstock

A sample of the salix wood used in our pyrolysis experiments was also analysed by solid state NMR. It shows a dominating resonance signal at [55-90ppm] arising from furanose and pyranose rings in the wood structure. There is also a fairly large quantity of
aromatic carbon functionality, which is expected to be found in the lignine. The functionality distribution is shown in figure 4.

![CP-MAS NMR of Wood Salix Salix](image)

**Figure 4.** *Salix salix*. Functional group distribution from solid state NMR.

### 6 Discussion

These $^{13}$NMR data has been considered as accurate within approximately 5% relative error. Nevertheless, the reliability of these $^{13}$NMR data would need to be studied further. One uncertainty is due to assignment of the resonance bands of the different functionalities. Some bands are overlapping each other, in a way that cause uncertainty about the functional group concentration, when they occur at adjacent bands. Some authors have noticed a lower response from carbonyl functionality in $^{13}$NMR data than it was found from other techniques[5].
7 References and literature
<table>
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FORMATION AND REDUCTION OF NITRIC OXIDES FROM FIXED BED COMBUSTION OF WOOD

R. Keller, ETH, Switzerland
ABSTRACT
Nitric oxides (NO) from wood combustions originate mainly from the nitrogen contained in the wood. The goal of this work is to minimize the NO formation during the staged combustion of wood. For this study a special 25 kW test reactor which consists of the fixed bed gasification chamber, the reduction chamber and the combustion chamber was built. Concentrations of carbon, hydrogen and nitrogen in particle along the axis of the fixed bed and the distribution of the fuel nitrogen on gasification gases were determined. Under optimized staged combustion conditions with a heated reduction chamber and a residence time of 0.5 s NO2 emissions from wood combustion were reduced from 200 mg/m³ (at 11% O2) to 93 mg/m³. With multiple staged combustion of wood NO2 emissions of 74 mg/m³ can be achieved.

INTRODUCTION
The pollutant nitric oxide (NO) is formed during wood combustion from the nitrogen contained in the wood; thermal nitric oxide are only of secondary importance since the typical combustion temperatures in wood firings are between 800°C and 1200°C [Nussbaumer Th., 1989]. Among the nitrogen oxides, nitric oxide is the main product from wood combustion. The NO emissions are calculated at a oxygen content of 11 vol.% in the dry flue gas. The NO emission are given as NO2 emission. The NO2 emissions from wood chips combustion are between 200 and 300 mg/m³ (at 11%
O₂). If chip boards are burnt, the nitrogen in glue and bonding lead to typical NO₂ emissions between 500 and 1000 mg/m³.

The concept of air staged combustion consists of injecting secondary air into the furnace downstream of the primary zone, which is characterized by substoichiometric levels of combustion air (Figure 1).

Figure 1  Principle of air staging

The emissions of NO from staged combustion of wood depend on the total excess air ratio, primary air ratio and the temperatures in reduction and combustion zone, the residence time in the reduction zone and the quantity of nitrogen in the wood. CO emission, combustion temperature and moisture content have practically no effect on NO emissions from wood combustion [Keller R., 1993].

Formation and Reduction of NO

Figure 2 shows the most important reactions of the formation and reduction of NO from fuel nitrogen during wood combustion. The overall conversion of wood nitrogen to NO is given by a volatile and char contribution. During pyrolysis of wood more than 20 wt% of nitrogen remain over temperature range of 600-1000°C in the char [Keller R. and Nussbaumer Th., 1992]. The nitrogen from the volatile fraction consists of HCN, NH₃, NO and N₂. HCN is converted homogeneously to NH₃ which reacts with NO to form molecular nitrogen or further NO. Only small reductions of NO can be achieved with carbon monoxide, hydrogen or methane over the temperature range of 700-1200°C. The components react preferentially with oxygen in the combustion products [Muzio L.J. et al., 1977]. After gasification NO can be reduced by homogeneous reaction with ammonia or by heterogeneous char or wood ash catalysed reaction with carbon monoxide to form molecular nitrogen. Ammonia can act as a source of NO and as a means for the reduction of NO. In the reduction zone of staged combustion the main reaction is between amino species and nitric oxide.

\[
\text{NH}_3 + \text{H} + \text{OH} + \text{O} \rightarrow \text{NH}_2 + \text{NO} \rightarrow \text{N}_2
\]
At a primary air ratio of 0.7, a temperature of 1150°C and a residence time of 0.5 s a decomposition of NH$_3$ and NO of 60% and 70% was measured [Keller R., 1993]. HCN is under this conditions stable. The decomposition of HCN in the reduction zone was studied by injecting a mixture of HCN/N$_2$ in the reduction zone. Only 15% of HCN is decomposed at a reduction temperature of 1050°C and a residence time of 0.5 s.

Nitrous oxide is formed mainly from the reaction of NO with NH or NCO, but is inhibited by CO and H. For wood combustion the nitrous oxide emission are below 2 ppm in this under stoker firing [Keller R., 1993]. Ash is formed from mineral matter during gasification and combustion. The conversion from fuel nitrogen to nitrogen in wood ash is only 0.5%.

**Figure 2** Schematic of fuel-nitrogen conversion during wood combustion [Keller R., 1993]
EXPERIMENTAL

For this study a special 25 kW test reactor was built. The aim is to separate the gasification of wood, the reduction of NO and the combustion of the gas. For combustion research the modular test rig can be operated with a wide range of excess air ratio (1.2-2.5), temperature in the reduction zone (850-1250°C) and residence time in the reduction zone (0.1-2 s). The main components of the test rig are the gasification chamber (fixed-bed, co-current, updraft), the reduction chamber and the combustion chamber (Figure 3). The reduction chamber can be heated electrically. The feed rate is in the range of 1.5 - 6.5 kg/h, usually 5 kg/h. In the combustion chamber the hot gases are burnt with secondary air.

The mass flow rates of primary and secondary air are measured continuously. Gas temperatures in the gasification, reduction and combustion chamber are recorded with aid of thermocouples. The composition of the exhaust gas is analysed by different on-line analyser. The NO in exhaust gas is measured by chemiluminescence method. HCN, NH₃, NO in the pyrolysis gas are determined by Fourier transform infrared spectroscopy (FT-IR) with a long-path gas cell. The detector is mercury-cadmium-telluride (MCT). The spectra are recorded at 0.25 cm⁻¹ resolution. The contents of major elements in the samples are analysed by Carlo Erba elemental analyser.

Figure 3  Schematic diagram of the low-NOₓ test rig for two-stage and multiple staged combustion
RESULTS AND DISCUSSION

Profiles in the fixed bed

To investigate the reactions in the fixed bed, the bed was suddenly cooled during combustion with liquid nitrogen. 70 samples of the fixed bed were examined by C, H and N elemental analysis [Joho D., 1993]. The average particle size of wood chips was between 20 and 40 mm.

The temperature along the reactor is presented in Figure 4. The temperature rises from 200°C to 800°C. The most important temperatures are the initial temperature for pyrolysis at 235°C, the temperature for maximum activity at 280°C and the temperature needed for complete ashing at 365°C [Aho M., 1987]. The temperature profile is qualitatively in agreement with calculation of the gas temperature along the fixed bed from the coupled equations describing the transient heating, drying and pyrolysis of particles and the equations for the heat and mass transfer [Saastamoinen J., 1989].

Figure 4 Temperature profile with height of the fixed bed

Figure 5 shows the measured vertical concentration profiles of hydrogen content of particles in the centre and near the wall of the fixed bed. There is a decrease of the hydrogen content from 5.5 wt.% to 0.5 wt.%. The decrease near the wall begins much earlier than in the centre.
Variation of the hydrogen content in the particle with height of the fixed bed

Figure 6 illustrates the vertical concentration profiles of carbon content of particles in the centre and near the wall of the fixed bed. The first peak in the profile is due to partial combustion of wood chips, the carbon content decreases from 55 wt.% to 40 wt.% The second peak with a maximum carbon content of 90 wt.% is due to the gasification reactions. No ash with very low carbon content was found.

Variation of the carbon content in the particle with height of the fixed bed

The molar C/N ratio as a function of the height of the fixed bed is shown in Figure 7. The ratio is generally greater than 200. The C/N ratio decreases from 500 to 200 at the injection of primary air. The nitrogen enrichment reaches a minimum at the injection of primary air. This indicates that the carbon components are released faster than the nitrogen components.
Figure 7  
Variation of the molar C/N ratio with height of the fixed bed

Figure 8 presents the distribution of nitrogen content on the surface area of the fixed bed. It can be seen that not all nitrogen in char is released during gasification, due to the low temperature (500°C-700°C). The nitrogen content on the surface area varied from 0.05 wt.% to 0.25 wt.%. This problem can be eliminated by operating the fixed bed at high temperatures with multiple air staging to complete the devolatilization of fuel bound nitrogen.

Figure 8  
Distribution of nitrogen content of particle on the surface area of the fixed bed (diameter of gasification chamber = 0.14m)
Figure 9 shows the correlation between nitrogen and carbon content of all samples of the fixed bed. The increase of carbon and nitrogen content is due to devolatilization of major products as carbon monoxide, carbon dioxide, hydrogen, methane and water vapour. The maximum nitrogen content is 0.55 wt.%. The decrease of the carbon and nitrogen content is due to combustion of char and devolatilization of nitrogen.

![Correlation between nitrogen and carbon content of all samples of the fixed bed](image)

**Model of the fixed bed**

There are five different regions in the fixed bed (Figure 10):

The first zone is below the injection of the primary air. The concentration of carbon is the same as of wood. Due to the temperature below 200°C, there is a drying zone of wood chips in the first zone. The mean residence time of particle is about 10 minutes.

The second zone is near the injection of primary air. Locally about 20% of wood chips are burnt. Near the injection of primary air temperature increase up to 1000°C.

The third zone is the reaction zone. The carbon content increases rapidly from 40 wt.% to 90 wt.%. Wood chips are gasified at a temperatures between 250-350°C. The mean residence time of the pyrolyzing particle in this zone is 1 minute.
The forth zone consists mainly of char with a carbon content between 75-95 wt.%. In this region the temperatures are between 500-700°C. The NO formed in the partial combustion zone is reduced by direct heterogeneous reaction with char (2 NO + 2 C = N₂ + 2 CO) or by the char catalysed reaction with carbon monoxide (2 NO + 2 CO = N₂ + 2 CO₂).

The fifth zone is the combustion of char. About 30-40% of char nitrogen is converted to NO, due to heterogeneous reaction of NO on bound carbon atoms. This region contains a mixture of char and ash. The mean residence time of char particle is 1 minute.

![Model of fixed bed](image)

Figure 10  Model of fixed bed

**Distribution of the fuel nitrogen on gasification gases**

The conversion of fuel nitrogen to NO was defined as follows, under the condition that the concentrations of hydrocarbons except methane are negligible:

\[
U(t) = \frac{c_B \, M_N \left[ NO(t) \right]}{n_B \, M_C \left[ CO(t) + CO_2(t) + CH_4(t) \right]} \tag{1}
\]

where \( U = \) conversion from fuel nitrogen to NO [-]; \( c_B = \) carbon content of fuel [wt%]; \( n_B = \) nitrogen content of fuel [wt%]; \( M_C = \) molecular weight of carbon [kg/kmol]; \( M_N = \) molecular weight of nitrogen [kg/kmol]; \( CO(t), CO_2(t), CH_4(t), NO(t) = \) concentration of CO, CO₂, CH₄, NO [vol.%].
As shown in Figure 11, the main nitrogenous components are nitrogen oxide, ammonia and hydrogen cyanide. Detailed gas FTIR analysis were performed on the gasification gas; however, no other significant nitrogenous intermediate were found. These data were obtained at a distance of 10 cm above the bed.

As the primary air ratio was decreased, the concentrations of the intermediate nitrogenous species ammonia and hydrogen cyanide increased. With increasing primary air ratio, more NO is formed in partial combustion zone, which is reduced to molecular nitrogen. The maximum conversion from fuel nitrogen to the total fixed nitrogen is 80%. As consequence of this, more than 20% of the fuel nitrogen is reduced to molecular nitrogen in the fixed bed. The amount of fuel nitrogen converted to HCN under gasification conditions decreases from 20% at primary air ratio of 0.4 to 0% at a primary air ratio of 0.9. This high conversion to HCN from wood gasification suggest that CN species may be the intermediates in the formation of fuel NO in the combustion. The ratios of NH3/HCN are between 1.6 and 3 depending on the primary air ratio. The conversion of total nitrogen reaches a minimum at a primary air ratio of 0.8.
**Influence of primary air ratio on NO emission**

There are two possibilities for the determination of the primary air ratio $\lambda_{\text{prim}}$:

1. **calculation from the excess air ratio $\lambda$, air flow of the primary air $V_{\text{prim}}$ and air flow of the secondary air $V_{\text{sec}}$:**

   \[
   \lambda_{\text{prim}} = \lambda \frac{V_{\text{prim}}}{V_{\text{prim}} + V_{\text{sec}}}
   \]  

2. **calculation from the concentrations of components (CO, CH$_4$, CO$_2$, H$_2$) of gasification gas:**

   The equivalence ratio $\text{ER}$ is defined as the oxidant to fuel weight ratio divided by the stoichiometric ratio. The equivalence ratio can be determined by following assumption:

   - primary air ratio $< 1$
   - no hydrocarbons except methane
   - the moisture has no effect on the product gas
   - the char is completely oxidized to CO and CO$_2$

   The reaction of gasification is:

   \[
   \alpha \text{CH}_m\text{O}_n + \beta \text{O}_2 = a \text{CO}_2 + b \text{H}_2\text{O} + c \text{CO} + d \text{CH}_4 + e \text{H}_2
   \]  

   The expression for carbon, oxygen and hydrogen balance are:

   \[
   a + c + d = \alpha \tag{4}
   \]

   \[
   2a + b + c = n\alpha + 2\beta \tag{5}
   \]

   \[
   2b + 4d + 2e = m\alpha \tag{6}
   \]

   From these equations, the equivalence ratio can be expressed as:

   \[
   \text{ER} = \frac{(1 + \frac{m}{4} - \frac{n}{2})(\text{CO}_2 + \frac{\text{CO}}{2} - \frac{\text{CH}_4}{2} - \frac{\text{H}_2}{2}) - (2n - m)(\text{CO}_2 + \text{CO} + \text{CH}_4)}{2(\text{CO}_2 + \text{CO} + \text{CH}_4)} \tag{7}
   \]

   For wood gasification ($m = 1.4$, $n = 0.7$) equation (7) reduces to:

   \[
   \text{ER} = \frac{(\text{CO}_2 + \frac{\text{CO}}{2} - \frac{\text{CH}_4}{2} - \frac{\text{H}_2}{2})}{2(\text{CO}_2 + \text{CO} + \text{CH}_4)} \tag{8}
   \]

   From the composition of the hot gas, the equivalence ratio can be calculated at different places in the gasification zone. Figure 12 demonstrates the radial profile of the equivalence ratio in the reduction zone. The equivalence ratio is higher than the primary air ratio calculated by the air flows. The
agreement is good for higher equivalence ratio and primary air ratio. The equivalence ratio near the wall region is smaller than in the centre of the tube.

![Radial profile of equivalence ratio in the reduction zone (primary air ratio = 0.49, reduction temperature = 1050°C, Reynolds number = 1850)](image)

A main objective is to optimize the primary air ratio for NO reduction. The total air flow (primary and secondary air) has been kept constant, the amounts of primary and secondary air were varied simultaneously. First stage air was varied between 30 and 110 percent of the stochiometric amount.

The results for burning wood chips with a heated reduction chamber are shown in Figure 13. The excess air ratio was maintained at 1.7 in this experiment. The CO concentrations were under 200 ppm for this experiment. The NO emissions for two-stage and multiple staged combustion of wood show a minimum at a primary ratio of 0.7. Multiple staging leads to 20% lower NO emissions than the classical staging with the same optimum condition in the reduction zone. The lowest NO2 emissions achieved by multiple staged combustion with a heated reduction chamber are 74 mg/m³ (at 11% O2), corresponding to a conversion from fuel nitrogen to NO of 12%. The comparison of the two-stage and multiple staged combustion shows that the multiple staged combustion is more effective at a higher primary air ratio.

Without a reduction chamber the NO emissions decrease from 217 to 171 mg/m³ (at 11% O2) by multiple staged combustion. The gasification temperature increase from 950°C to 1050°C. The lower NO emissions of multiple staged combustion are due the higher temperature in the fixed bed and the decomposition of formed ammonia with oxygen injection.

In multiple stage combustion oxygen is added to hot gasification gas in order to increase H, OH and O radical concentration in the gas, which lead to NH₃ decomposition to amino species and which again react rapidly with NO to form N₂ [Klipinen P. and Leppälähti J., 1992]. Kinetic calculation
shows that the presence of 2 vol.% methane stop the decomposition of NH₃. For this reason multiple staged combustion is not effective at low primary air ratio [Kilpinen P., 1992].

![Figure 13](image-url)

**Figure 13** Effect of primary air ratio on NO emissions for two-stage and multiple staged combustion of wood (excess air ratio = 1.7, reduction temperature = 1150°C, residence time in the reduction zone = 0.5s)

The excess air ratio can be decreased from 1.6 by multiple staged air to 1.4 without increasing CO emissions (<200 ppm). As consequence of this, the efficiency increase from 89% to 91% at exhaust gas temperature of 160°C.

**Influence of temperature in the reduction zone on NO emission**

The temperature and residence time in the reduction chamber can also influence the NO reduction. For staged combustion the temperature in the reduction zone was varied from 950-1250°C. The lowest NO₂ emissions achieved are 93 mg/m³ (at 11% O₂) with a primary air ratio of 0.7, a residence time of 0.5 seconds and a reduction temperature of 1150°C. This corresponds to a reduction of 50% compared to a under stoker system without reduction chamber at a optimal primary air ratio of 0.7. The increase of NO emission at high temperatures is due to the formation of HCN from the reaction between NO and hydrocarbon radicals (CH₃ + NO = HCN + H₂O). *Figure 14* shows the NO emissions of the test reactor compared to the Pyros firing system with a thermal heated reduction chamber, which is described earlier [Graf S., 1991]. Temperature in the reduction zone higher than 1000°C could not be reached in the reduction chamber of the Pyros firing system. The NO emissions from Pyros and the test reactor agree very well at the optimum primary air ratio of 0.7. For practical use the preheat of the primary air is a possibility to increase the reduction temperature.
CONCLUSIONS

A 25 kW reactor which consists of gasification chamber (fixed-bed, co-current, updraft), reduction chamber and combustion chamber has been tested. Experiments have shown that:

1. There are five different regions of the fixed bed: drying zone of wood chips, partial combustion of wood chips, gasification zone, char zone and combustion of char. Radial temperature and concentration measurement confirm that the fixed bed is three-dimensional in concentration and temperature.

2. The nitrogenous species during gasification of wood are NO and mainly NH₃ and HCN. The main reaction in the reduction zone is between amino species and NO. Only small amounts of HCN are decomposed.

3. Low NO emissions (100 mg/m³ at 11% O₂) corresponding to a reduction of 50% can be achieved during wood combustion in a test reactor with a heated reduction chamber when the reactor is operated at a primary air ratio of 0.7, a temperature in the reduction zone of 1050-1250°C and a residence time of at least 0.5 seconds.

4. Multiple air staging is another effective technique for control of NO emission and leads to 20% lower NO emission than the two-stage combustion at the same conditions.
REFERENCES


GREENHOUSE GAS EMISSIONS FROM WOOD STOVES

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ABSTRACT

The use of biomass for energy accounts for 127 TWh (457 PJ) in the Nordic countries Denmark, Finland, Norway and Sweden which is 9% of the total energy consumption. Combustion of biomass is CO₂-neutral in the greenhouse effect balance. However, emissions of NOₓ, N₂O, CO and CH₄ contribute either direct or indirect to the greenhouse effect. Experiments have been performed in three different wood stove units, a traditional stove and two new stoves. The two new stoves consist of a staged combustion unit and a catalytic stove. The emissions of NOₓ, N₂O, CO and UHC in addition to O₂ and CO₂ are measured with continuous analyzers. The emissions of NOₓ tend to decrease (in ppm) during the combustion cycle, while the emissions during the combustion cycle in g/kg wood increase in the charcoal phase compared to the pyrolysis phase. The average NOₓ emissions are higher for the catalytic stove unit and for the staged stove, but the average CO and UHC emissions are lower. The emissions of N₂O are in general low, below 10 ppm. The total emissions of greenhouse gases for different wood stoves are calculated and compared to oil combustion.

Key words: Biomass, Emissions, NOₓ, N₂O, CO, UHC

INTRODUCTION

The use of biomass for energy accounts for 127 TWh (457 PJ) in the Nordic countries Denmark, Finland, Norway and Sweden which is 9% of the total energy consumption (Hustad and Sønju, 1992). In Finland and Sweden the major consumers of biomass energy are the pulp and paper industries using bark and black liquor. In Denmark, direct combustion of straw in small boilers for domestic heating is essential. In Norway, about 2 mill. wood stoves and fireplaces are in practical use in households. These small units (less than 20 kW) account for approximately 50% of the total biomass energy consumption in Norway.

Combustion of biomass is CO₂-neutral in the greenhouse effect balance. However, emissions of NOₓ, N₂O, CO and CH₄ contribute either direct or indirect to the greenhouse effect. It has previously been reported (Karlsvik et al., 1993) that traditional wood stoves and fireplaces have substantially higher emissions of particles, CO and UHC (unburnt hydrocarbons) than new stoves with a catalytic afterburner and new stoves with staged combustion.
Combustion of wood in a wood stove is a batch process, and wood consists of approximately 85% volatiles and 15% charcoal and ash. The combustion of volatiles is, however, a more rapid process than charcoal oxidation. On a time scale, volatile combustion accounts for approximately 50% of the total burnout time for a wood log. A reasonable approximation is to look at the wood log combustion as a two step sequential process. It has previously been shown (Nussbaumer, 1989 and Nussbaumer, 1993) that emissions of CO and UHC are strongly dependent on the standard of technology and the excess air ratio in small wood boilers. Emissions of NO\textsubscript{x} measured from wood combustion in an electrically heated furnace (Nussbaumer, 1993) show that NO\textsubscript{x} emissions increase with increasing nitrogen content in the fuel. Using argon instead of air did not decrease the NO\textsubscript{x} emissions, giving reasons to conclude that thermal NO\textsubscript{x} is not important in the temperature range from 800 °C to 1300 °C.

Experiments in a CFB boiler fired with wood chips (Leckner and Karlsson, 1992) also show that the NO\textsubscript{x} emissions can directly be related to the nitrogen content in the fuel, and measurements ranging from 50 ppm to 100 ppm at 6% O\textsubscript{2} were reported. Emissions of N\textsubscript{2}O were in the same experiments reported to be low, up to 10 ppm. NO\textsubscript{x} and N\textsubscript{2}O emission results from batch combustion systems are scarce, although some results are available from coal combustion in a batch fluidized bed reactor (Tullin et al., 1992). From these experiments, the evolution and subsequent combustion of the volatiles resulted in a peak in NO and N\textsubscript{2}O concentrations. In the char combustion phase, the NO and N\textsubscript{2}O concentrations were lower, but the longer time scale for char combustion compared with the combustion of volatiles, made the contribution to the NO and N\textsubscript{2}O emissions from char combustion significant relative to that from volatiles. According to Arai et al. (1986) the char nitrogen from high volatile coal fuels is released more in the form of NH\textsubscript{3} due to higher hydrogen content and this NH\textsubscript{3} will be oxidized to N\textsubscript{2} or NO. In coal combustion, the conversion of volatile nitrogen to N\textsubscript{2}O is generally accepted as proceeding through the production and subsequent oxidation of HCN by the volatile nitrogen compounds. Three pathways have been proposed on the mechanism of conversion of char nitrogen to N\textsubscript{2}O: (1) the release by the char of HCN with subsequent gas phase oxidation, (2) the direct oxidation of the char nitrogen to N\textsubscript{2}O, and (3) the reaction of char nitrogen with NO to form N\textsubscript{2}O. Pathway (3) was recently proposed by Tullin et al. (1992) to be dominant in the char oxidation phase based on experiments with coal in a fluidized bed reactor in the presence of oxygen.

**EXPERIMENTAL APPARATUS**

Experiments have been performed in three different wood stove units, a traditional stove, a staged combustion unit and a catalytic stove. The stoves are placed on a weight for continuous measurement of the weight and thus the burning rate as a function of time. The combustion gases enter a dilution tunnel after the chimney (Karlsvik et al., 1993). Emissions of NO\textsubscript{x}, N\textsubscript{2}O, CO, CO\textsubscript{2}, O\textsubscript{2} and UHC are measured in the chimney with continuous analyzers. The emissions of NO\textsubscript{x} are measured with chemiluminescent and the emissions of N\textsubscript{2}O are measured with an infrared analyzer at 3.5 μ where CH\textsubscript{4} do not interfere. However, the analyzer for N\textsubscript{2}O were limited to do measurements below a CO concentration of 500 ppm and thus excluding many results. Experiments are performed both with birch, spruce and pine. The nitrogen content in all the fuels was 0.2% by weight.

**RESULTS AND DISCUSSIONS**

Experiments have been performed in a traditional stove, a catalytic stove and in a stove unit with staged combustion. Emissions of NO\textsubscript{x}, N\textsubscript{2}O, CO and UHC have been measured during a combustion cycle at different average loads (combustion rates) ranging from 1.1 kg wood/h to 2.6 kg wood/h.
The burning rates as a function of time for the different experiments for the catalytic stove are shown in Fig. 1 and for the staged combustion unit in Fig. 2. The burning rate varies a lot during the combustion cycle and in the volatile combustion stage it is at an average much higher, up to a factor of 6 to 8, than in the charcoal burnout phase where there are no feedback mechanisms from the volatile flame to the wood log. The average burning rate for each experiment is calculated based on the total wood consumption and the total burnout time. For two of the experiments with the catalytic stove it is difficult to distinguish between the volatile combustion phase and the charcoal burnout phase since the burning rate decrease almost linear with time. This is not the case in any of the experiments for the stove with staged combustion.

In Fig. 3 the emissions of CO and UHC as a function of time are shown for a particular experiment (S12) in the catalytic stove. The results show typical trends, high values during the volatile combustion with CO values from 10 g/kg wood to 30 g/kg (0.3 - 0.4 vol %) and UHC values about 2 g/kg (200 ppm). Both the CO emissions and the UHC emissions decrease considerable entering the charcoal combustion phase and keep up a very low value during the whole charcoal burnout time. Fig. 4 shows the opposite trend for the CO emissions in the staged combustion unit (experiment D7), being lowest in the volatile combustion phase with values around 10 g/kg (0.2 vol %) increasing up to 300 g/kg (0.6 vol %) in the charcoal phase for this particular experiment. The UHC emissions in the staged combustion unit do not vary so much during the combustion cycle and values around 5 g/kg - 10 g/kg (100 ppm - 250 ppm) are measured. The
The emissions of CO and UHC is very dependent of the combustion temperature, shown for CO as a function of the tertiary air temperature for the staged combustion unit in Fig. 5. It has previously been shown (Karlsvik et al., 1993) that the emissions of both CO and UHC for traditional stoves are very dependent on the average burning rate in an experiment, being highest at low average burning rates, typically less than 1 kg wood/hour. At the same average burning rate, the emissions of both CO and UHC are considerable lower for these new stoves with catalytic afterburner and the staged combustion unit compared with traditional stoves and fireplaces (Karlsvik et al., 1993).

It is very interesting to see from Fig. 6 that the emissions of NO\textsubscript{x} (in ppm) is fairly constant during the volatile combustion phase, close to 50 ppm (12 % O\textsubscript{2}) which corresponds to 0.5 g/kg wood. Also seen is a decrease (in ppm) during the char oxidation phase. The emissions during the combustion cycle for N\textsubscript{2}O is, however, somewhat different since these emissions tend to increase slightly during the combustion cycle, from 3 ppm to 4 ppm (0.05 g/kg), and for this particular experiment (S2) a decrease is observed at the latest end of the cycle.

The emissions of NO\textsubscript{x} in g/kg wood as a function of the time for the catalytic stove at a burning rate of 1.11 kg/h (S12) is shown in Fig. 7. Since the emissions of NO\textsubscript{x} (in ppm) decrease only somewhat in the charcoal phase and the burning rate decrease considerable, the emissions in g/kg increase as can be seen from Fig. 7.

Fig. 8 shows the emissions of NO\textsubscript{x} in g/kg for the staged combustion unit at a burning rate of 1.72 kg/h (D7). The figure shows the same trend with increasing emissions of NO\textsubscript{x} in g/kg as a function of time as for the catalytic stove. The emission level for NO\textsubscript{x} is, however, higher by a factor of two, both in the pyrolysis phase and in the charcoal phase, for the catalytic stove compared with the staged unit.

Fig. 9 shows the emissions of NO\textsubscript{x} (ppm) in the
Fig. 8 Emissions of NO\textsubscript{x} (g/kg wood) in the staged combustion unit (D7)

Fig. 9 Emissions of NO\textsubscript{x} (ppm) in the traditional stove

Fig. 10 NO\textsubscript{x} conversion factor in the catalytic stove

traditional stove at two different burning rates. At the lowest burning rate of 1.33 kg/h the emissions are close to 45 ppm as an average in the pyrolysis phase, decreasing to an average value of 25 ppm in the charcoal phase. At the highest burning rate of 1.98 kg/h the emissions are 35 ppm as an average value, and decreasing only slightly down to approximately 30 ppm in the charcoal phase. Calculating these emissions in g/kg give approximately the same average value for both burning rates, 0.3 g/kg in the pyrolysis phase increasing up to 0.7 g/kg in the charcoal phase.

Fig. 10 shows the conversion factor from fuel nitrogen to NO\textsubscript{x} in the catalytic stove for all the four experimental runs as a function of the carbon conversion. The conversion factors are determined from the gas flow rate $V$ [Nm\textsuperscript{3}/h] and the concentrations of the relevant species $(\text{[NO], [N}_2\text{O], [CO], [CO}_2, [C}_2\text{H}_4})$ [kmol/Nm\textsuperscript{3}] as showed in the following equations (Tullin et al., 1992):

\[
\text{Fuel-N Conversion} \rightarrow \text{NO} = \frac{\int_0^t V[NO]dt}{m_e X_n/M_n}
\]

\[
\text{Fuel-N Conversion} \rightarrow N_2O = \frac{2\int_0^t V[NO]dt}{m_e X_n/M_n}
\]

\[
\text{Carbon Conversion} = \frac{\int_0^t V([CO]+[CO}_2+3[C}_2H_2]dt}{m_c X_c/M_c}
\]

where $m_e$ [kg] is the weight of the wood batch fed to the stove, $X_n$ and $X_c$ are the weight fractions of nitrogen and carbon in the wood, and $M_n$ and $M_c$ [kg/kmol] the atomic weights of nitrogen and carbon.

The total conversion factor varies from 10 % to 21 %. In three of the experiments the results are close, but in the experiment with the lowest average burning rate the conversion factor increases by a number of two. When burning rates in the catalytic stove are reduced below approximately 1.5 kg wood/h, no volatile flame is observed in the combustion chamber. Oxygen can then penetrate into the logs resulting in direct oxidation of char nitrogen on the log surface in addition to production of NO\textsubscript{x} through combustion of volatile NH\textsubscript{3}. The contribution
from both sources give a higher conversion factor in this particular experiment compared to the other experiment where the oxygen is consumed in the diffusion flame above the log.

Fig. 11 shows the NO\textsubscript{x} conversion factor for the staged combustion unit. The figure shows two sets of curves, one curve for burning rates between 1.23 kg/h and 1.72 kg/h where the conversion factor is approximately 7% to 8%. This result is comparable with the results in the catalytic stove in the same burning rate range (1.54 kg/h). The other two curves show conversion factors in the range of 14% to 16% at burning rates of approximately 2.6 kg/h. Tullin et al. (1992) found conversion factors ranging from 24% to 34% (particle diameter 1 - 2 mm) at 1023 K decreasing with increasing O\textsubscript{3} concentration. At a higher temperature of 1073 K, the conversion factor increased to be between 30% and 70%. Also here a decrease at increased O\textsubscript{3} concentration was observed. At even higher temperatures of 1123 K, the conversion factor decreased again to be between 30% and 40%. Åmand and Leckner (1991) found NO conversion factors less than 5% burning different coals in a CFB. They found the conversion factor to increase with increasing bed temperature and increasing excess air ratio. Nussbaumer (1993) found conversion factors to decrease with increasing nitrogen content in the fuel. At 0.2% nitrogen in beech a conversion factor of 36% was reported.

Fig. 12 shows the N\textsubscript{2}O conversion factor in the catalytic stove. In this particular experiment, the CO emissions were below 500 ppm during the whole combustion cycle which allowed calculating a conversion factor. From the figure it can be seen that this conversion factor is low, approximately 2% and it can further be seen that the conversion curve is linear. N\textsubscript{2}O measurements in all stoves showed low values, below 10 ppm in good agreement with results from CFB combustion (Leckner and Karlsson, 1992).

Tab. 1 give the contributions to the emissions of different greenhouse gases calculated in CO\textsubscript{2} equivalents at an average burning rate of 1.2 kg/h from different wood.

<table>
<thead>
<tr>
<th>CO\textsubscript{2}</th>
<th>CO</th>
<th>CH\textsubscript{4}</th>
<th>NO\textsubscript{x}</th>
<th>N\textsubscript{2}O</th>
<th>CO\textsubscript{2} eq.</th>
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<td>0.028'</td>
<td>1.7'</td>
<td>4.5'</td>
</tr>
<tr>
<td>K</td>
<td>74'</td>
<td>0.6'</td>
<td>0.028'</td>
<td>1.02'</td>
<td>4.5'</td>
</tr>
</tbody>
</table>

Tab. 1

TS = Traditional Stove
CS = Catalytic Stove
SAC = Staged Air Combustion
K = Kerosene
* = SPT (1990)
combustion technologies compared with combustion in small oil furnaces (SFT, 1990). Small oil/kerosene furnaces give total greenhouse gas emissions of approximately 80 g/MJ calculated in CO$_2$ - equivalents. Traditional stoves give approximately 70% of that value and catalytic stove and the staged combustion stove give 8% and 20% of that value, respectively. For the oil/kerosene furnaces the major contributor to the total value is the CO$_2$ itself. For the traditional stoves, the major contributor is the emissions of CO and CH$_4$, and for the catalytic stove there are no major contributor and the contribution is distributed among all the emissions. For the staged combustion unit, the major contributor is the CO emissions. Combustion of wood waste can have a positive effect on the emissions of greenhouse gases also compared to the natural decomposition of the biomass in the nature itself.

CONCLUSIONS

Wood is the most used biomass fuel for energy purpose in Norway. Combustion of biomass is CO$_2$-neutral in the greenhouse effect balance. However, emissions of NO$_x$, N$_2$O, CO and CH$_4$ contribute either direct or indirect to the greenhouse effect. Experiments have been performed in a traditional stove, a catalytic stove and in a stove unit with staged combustion. Emissions of NO$_x$ and N$_2$O (to a limited extent) have been measured during a combustion cycle at different average loads (combustion rates) ranging from 1.1 kg wood/h to 2.6 kg wood/h. Emissions (in ppm) of NO$_x$ decrease and emissions of N$_2$O tend to increase only slightly during the combustion cycle. The average NO$_x$ emissions are higher for the catalytic stove by a factor of approximately 3 than for the staged stove. N$_2$O emissions are in general low in all stoves. Conversion factors of NO$_x$ are found to vary totally from approximately 7% to 21% for both new stoves and a clear dependence on load with higher conversion factors with increasing load are found in the staged combustion unit. For the catalytic stove the conversion factor for one experiment at low load was found to be high probably due to contributions also from direct oxidation on the log surface due to absence of a volatile flame. N$_2$O conversion factor was only possible to calculate in one particular experiment and found to be 2%. Combustion of biomass in traditional stoves reduce the emissions of greenhouse gases compared to combustion of oil/kerosene. However, there is still a considerable potential for further reduction of greenhouse gases in biomass combustion through development and implementing new technologies.

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EMISSIONS FROM RDF COMBUSTION

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EMISSIONS FROM RDF COMBUSTION

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INTRODUCTION

The disposal of refuse has during the last years been a matter of increasing concern for many municipalities. The environment options for waste disposal has no been focusing much. This means that first the waste generation must be reduced. Then recycling of a portion of the waste must be considered before a solution with combustion of waste is chosen.

Two methods are currently in use for the combustion of MSW. These methods are:

A) Mass burning of unprocessed MSW
B) Using a refuse-derived-fuel (RDF) product, which consist of the burnable, organic fraction of raw MSW.

In contrast to mass burning systems, the RDF-system is pre-processing the raw MSW to make a more homogeneous fuel product. By processing the MSW, it is possible to recover RDF and other materials. The RDF process is a low cost approach to resource recovery. RDF is a merchant fuel, and can be used in existing boilers alone or as a supplement to conventional fuels as oil and coal. It is important that the RDF processing technology and RDF quality matches the energy user requirements. The RDF-processing-systems is of great importance to the RDF quality, and different steps in the RDF process is shown in figure 1.

RDF-PROCESSING-SYSTEMS AND VARIOUS TYPES OF RDF

RDF facility typically consists of two separate systems which is a front end processing system, we call it "the waste treatment process", and a back end combustion system, containing the combustion units. This is marked out in figure 1.
The RDF processing facilities is a complex mixture of processing and material handling equipment. The processing line must be as simple as possible, and it is necessary to failure the RDF products to match the end use-system. The mechanical process has two basic functions. Those are:

- sizing and homogenization
- separation of the MSW components.

From figure 1 we see that different technologies or processing units, produces various types of RDF. Let us follow the lines from raw MSW and to the fuel product.

**c-RDF**
When MSW is processed to a particle size above 6 inches, we call it a coarse RDF, c-RDF. First the MSW is tipped on the floor, and a coarse separation is done. Than the material is fed into a shredder, the size of the processable waste is reduced to the desired particle size. The shredder begins the homogenization process. The shredded MSW is processed through magnets to recover ferrous metals. The material after the magnet separator is a coarse RDF.

**f-RDF**
When the MSW is processed to a particle size of 3/4 inch, it is classified as fluff RDF, f-RDF. The raw MSW is first shredded in a primary shredder. After the primary shredder, the mass flow is air classified to separate the light fraction material from heavy material. The light material is processed through magnets to recover ferrous metals, and then through a screen to remove inorganic. The light organic fraction is secondary shredded to nominal 3/4 inch particle size, which is classified as fluff RDF.

**P-RDF**
The basic processing is similar to f-RDF. The combustible fraction is pulverized by using a hot ball milling. There have been some technical problems with this process of the powder RDF.

**d-RDF**
When the combustible fraction of the secondary shredded material is densified by a pellitizer into pellets or briquettes, and we get a densified-RDF, d-RDF.
RDF 1
If the light fraction from the air classifier or the mechanical separator is not processed any more, this fraction is the first grade of RDF, RDF 1.

RDF 2
The heavy fraction from the mechanical or air classifier is processed through a magnet for recovery of ferrous metals. The non magnetic waste fraction is processed through trommels for separation of the inorganic fraction and sizing the organic fraction. The combustible fraction is a second grade RDF, RDF 2.

RDF 3
When the MSW flow is processed through a primary shredder, mechanical separator, magnetic separator, drying equipment and pelletizer we get the RDF product which are produced at Søndre Vestfold Avfallselskap in Larvik, NORWAY. This RDF we call RDF 3, and it has a density like d-RDF.

RDF 4
At Hålogaland Ressurselskap in Narvik, Norway they produce an extruded RDF.

THE QUALITY OF RDF
The principle of a RDF processing system in Norway is shown in figure 2. The raw MSW and commercial waste is either source separated or not source separated.

The not source separated MSW or raw MSW is mostly landfilled, incinerated or processed to a RDF through different unit operations. The source separated material is either collected by a fetching system or a bringing system. The material going into the fetching system is divided into two fractions. This is a dry fraction and a wet fraction. The dry fraction can be used as fuel and the wet fraction is used as compost.

In the bringing system only dry material is collected.

It is of great interest to estimate the fuel quality of the material in the processing system in figure 2. The quality data we want to look at is the heating value, the moisture, the ash content, the particle
size, the stability by storing, the composition and the density.

The data is graphical shown in figure 3 and figure 4, and they show the effect of the RDF-processing. The position number on the x-axis in figure 3 and figure 4 is corresponding to the position number in figure 2.

The calorific value is shown in figure 3, and it is higher for the source separated material than the raw MSW. The shredder and the magnet separator has little influence on the calorific value. First when the MSW is screened and dried the heating value increases. The pelletized RDF material from both the MSW and the collected material has nearly the equal heating value.

The moisture content is shown in figure 4, and it is growing higher when the MSW material is shredded and magnet separated. The moisture is reduced by screening the material. Screened MSW material has higher moisture content than material from the dry source separation system.

The ash content is shown in figure 5, and it is highest for the MSW material. The ash content is reduced by magnet separation and screening of the MSW material. The screened MSW material has nearly the same ash content as the source separated material.

The variation of the particle size is shown in figure 6, and it is high for the start position for all the materials. By shredding, the particle size is reduced, and much more homogeneous. When the material is pelletized, the particle size has only a little variation.

The storing stability of the material is shown in figure 7, and it is best for the dried and pelletized MSW material, and for the material from the source separated bringing model. The shredded MSW material has the lowest stability.

By magnet separation and screening of the MSW material, the content of inorganic and wet organic components is reduced as shown in figure 8. The content of paper and plastic is increasing by processing the MSW, and the content of paper and plastic is nearly equal to the source separated material.

The density of the MSW is shown in figure 9. The density is increasing when shredding and pelletizing, but it is reduced by screening and drying.
The RDF have several benefits compared with MSW. It is a more homogeneous fuel than MSW regarding both particle size, density, moisture, ash and calorific value. The RDF has higher calorific value, and lower moisture and ash content. The RDF can be transported to other locations for combustion, it can be stored, and has the opportunities for firing in almost all industries and segments of the economy as an alternative fuel. Because of the high energy density, they can build smaller combustion facilities with the same energy capacity.

**COMBUSTION OF RDF IN FB AND MOVING GRATE**

It has been necessary to obtain basic combustion characteristics for the various fuels of RDF. This is necessary for both the RDF producers, RDF users, the industry designing and producing combustion systems, the energy and air pollutant authority.

At NTH/SINTEF we have two combustion units where the combustion conditions and emissions are investigated for different fuel qualities of RDF.

The combustion test units are a fluidized bed reactor and a modified biomass moving grate reactor.

The fluid bed reactor is a bobbling FB with a capacity of 500 KW, and shown in figure 10. The fuel can be fed into the bed in three different positions, and the bed is fitted with a cooling system. The modified biomass moving grate reactor in figure 11, has a capacity of 400 KW, and has a primary and secondary combustion chamber, and a cooled grate.

The fuel quality and composition of the RDF used in the tests is shown in figure 12. The calorimetric heating value varies from 19600 KJ/kg to 25996 KJ/kg. The moisture content varies from 7.7 % to 28 %. The ash content varies from 2.3 % to 13.5 %.

Sampling the flue gas consists of measuring the concentrations of the components CO, CO₂, O₂, SO₂, HCl, NO₂, mercury, total particles and heavy metal in the dust.
EMISSIONS AND OPERATING CONDITIONS BY BURNING RDF

The operating and environmental results from the fluid bed reactor and moving grate is shown in figure 13 and figure 14. As operating results the O$_2$ level and the free board temperature in FB and primary and secondary temperature in moving grate is included.

The environmental results includes the emission level of CO, NO$_x$, SO$_2$ and HCl.

The main RDF in the test program is the RDF 3 from SVA. This RDF is briquettes of 30 mm. Both chips, plastic and additives is added into the RDF, and the RDF is then mentioned as example RDF/chips, RDF/plastic. Then we than can see the effect of mixing new material into the original RDF.

In figure 13, the O$_2$ level with stable combustion conditions for both FB and moving grate is at 4.5 % to 6 %. By adding chips into the RDF, the O$_2$ level is growing higher for FB. For moving grate, the O$_2$ level is reduced a little.

The low free board temperature in FB is compared with the primary temperature in moving grate, and the medium temperature in FB is compared with the secondary temperature in moving grate.

With RDF 3, the low free board temperature in FB is above 900 °C, while the primary temperature in moving grate is above 800 °C. By adding chips into the RDF, the temperature is reduced a little. When plastic is added into the RDF, the temperature in FB increases about 100 °C, up to 1020 °C.

When burning RDF 3, the medium free board temperature in FB is 1070 °C, and this is at the same level as the secondary temperature in moving grate. When chips is added into the RDF, the FB temperature is reduced till 1060 °C, while the secondary temperature in moving grate is relatively stable. The medium free board temperature increases about 50 °C by adding more plastic into the RDF 3.

By reducing the particle size of RDF (RDF 4) in FB, the low and medium free board temperature is more homogeneous.

In figure 14, the CO, NO$_x$, SO$_2$ and HCl level is shown. The results shows that it is possible to operate
both the FB and moving grate at a low CO level. Normally the combustion units were operated at a
CO level of 40 mg/Nm³ at 11 % O₂.

The normal emission of NOx was about 250 mg/Nm³ at 11 % O₂ for both FB and moving grate. By
changing the operating conditions in the moving grate and the RDF quality in FB, the NOx level was
reduced till about 70 mg/Nm³ at 11 % O₂.

The SO₂ emissions was at a level of 170 - 180 mg/Nm³ for both FB and moving grate. By adding
straw, chips and paper into the RDF, the SO₂ emissions was going up. By adding 3 % of additives into
the RDF, the SO₂ emissions was reduced till a level of 70 - 80 mg/Nm³.

The emission of HCl was at a level of 300 - 370 mg/Nm³. By adding paper and straw into the RDF,
the emissions were higher. By adding chips and additives into the RDF, the emissions was reduced.
The lowest emission for HCl, was 225 mg/Nm³ at 11 % O₂ with moving grate.

In figure 15, the emissions is compared with emissions measured in UK and Finland.

For CO, a level of 50 mg/Nm³ is no problem.

For NOₓ, the emissions with coal, peat and straw, is between 340-470 mg/Nm³. By adding RDF into
peat, the NOₓ is reduced. The emission with chips, is 130 mg/Nm³. A NOₓ level of 70 mg/Nm³, is not
a normal level.

For HCl, the emissions from coal is 320 mg/Nm³, and this is in the same level as RDF. The emissions
from straw, is 170 mg/Nm³. By adding bark, peat and chips into RDF, the HCl emission is reduced.

For SO₂, the emissions from coal, tires and peat is higher than from RDF. The SO₂ emission from
straw, is in the same level as RDF. By adding bark and chips into RDF, the SO₂ emissions is reduced.

CONCLUSIONS

The operating conditions from the Norwegian trials show that the excess air ratio is higher in the FB
than in the moving grate. Further we see that the excess air increases by mixing chips into the RDF
in the FB. The variation in the excess air ratio is higher in the FB than the moving grate.

Regarding the temperatures, the primary temperature in the moving grate always is lower than the bed temperature and low free board temperature in FB. The primary temperature in the moving grate can be reduced if wanted, but the bed temperature must be held on a constant level above 820 °C.

The secondary temperature in the moving grate is equal to the medium freeboard temperature in FB.

By adding chips into the RDF, the primary and secondary temperature level is reduced in both levels in the two combustion systems.

Regarding the emissions, a good combustion control is achieved in both FB and moving grate with all the tested RDF-qualities. The NO\textsubscript{x} level can be reduced by changing the operating conditions in the moving grate, and the NO\textsubscript{x} level is reduced by changing the particle size of the RDF. The emissions of the acid gases SO\textsubscript{x} and HCL depend primarily on the composition of the waste, and not so much on the combustion conditions. The emissions of SO\textsubscript{x} and HCl is reduced by adding additive into the RDF. The emission of mercury is rather low. The emission of particles is much higher for FB than moving grate.

The trials shows that to burn 100 % of RDF in a modified biomass combustion system is possible. It is possible to keep the required

- CO - level at 100 mg/Nm\textsuperscript{3}
- secondary temperature above 850 °C
- unburned in ash under 3 %
- emission of Hg under 0.05 mg/Nm\textsuperscript{3}
- emission of SO\textsubscript{x} under 300 mg/Nm\textsuperscript{2}

To meet the emission standard regarding HCL and particles, a cleaning system for HCL and a filter system for particles is necessary.
REFERENCES


Figure 1 - RDF-processing system
Figure 2: Principle of a RDF processing system in Norway
Figure 3
Figure 4
Figure 5
STABILITY BY STORING

Figure 7
Figure 8

Composition [%]

- Paper
- Organic
- Plastic
- Unorganic

Position
Figure 10: The principle of 500 kW FB
A modified biomass moving grate reactor.

Figure 11
### FUEL COMPOSITION

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<th>RDF/ Straw</th>
<th>RDF/ 3%ad</th>
<th>RDF/ 6%ad</th>
<th>RDF/ Plastic</th>
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*a 45 - 50% Briquette piece.  
*b 25 - 45% Loose.  
*c 10 - 25% Extract.  
*d 1 - 10% Fine particle.

A Huddle.  
B Huddle/Loose material.  
C Fine particle.

Figure 12
COMPARISON OF TEMP. & O2 LEVEL FOR COMBUSTION OF DIFFERENT SOLID FUELS IN FB & MG

Figure 13
COMPARISON OF EMISSION LEVEL FOR COMBUSTION OF DIFFERENT SOLID FUELS IN FB & MG

Figure 14
COMPARISON OF EMISSION LEVEL FOR COMBUSTION OF DIFFERENT SOLID FUELS IN FINLAND, UK AND NORWAY

Figure 15
INFLUENCE OF AERODYNAMICS ON COMBUSTION EFFICIENCY AND EMISSIONS

R. Smith, ETH Zurich
AERODYNAMIKENS INFLYTANDE PÅ
FÖRBRÄNNINGSVERKNINGSGRAD OCH NOₓ - EMISSION

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SAMMANFATTNING

Utvecklingen av förbränningsstekniken har i dag målen att minska den negativa miljöpåverkan, sänka energiförbrukningen och göra billig energi tillgänglig. På längre sikt är målet att ersätta kol, olja och natursgas med förnyelsebara energikällor. Dessa mål kräver på kort sikt utveckling av nya förbränningsprocesser, på längre sikt utveckling av nya omvandlingsprocesser. Innan dessa processer utvecklats så långt att de är kommersiellt tillgängliga, måste emellertid befintliga processer utvecklas vidare för att höja deras verkningsgrad och minska emissionen av sot, svavel- och kväveoxider. som utveckling av nya typer av ugnar och pannor.


Förf. har, under sin tid som chef för institutionen för Värme- och ugnsteknik utvecklat en modelleringsteknik och tillämpat den i industriella projekt. Metoden innebär en kombination av försök i anläggningar, i isoterma och heta modeller samt matematisk modellering. Metoden presenteras och illustreras med resultaten från två projekt rörande förbränning av avfall.
INNEHÅLLSFÖRTECKNING

SAMMANFATTNING 2
INLEDNING 4
METODER FÖR MINSKNING AV NOX EMISSION 5
MATEMATISK KONTRA EXPERIMENTELL MODELLERING 6
PRAKTIKFALL 7
  Försök i pannan 7
  Verifiering av modellförsöken 8
  Verifiering av den matematiska modelleringen 9
  Primär- och sekundärluftens inverkan på strömning och blandning 10
  Kväveoxider 11
MODELLERING AV SYSAVS ANLÄGGNING 11
SLUTORD 15
ERKÄNNANDEN 15
REFERENSER 15
TILLÄMPNING AV MODELLERING VID UTVECKLING AV FÖRBRÄNNINGSPROCESSER

INLEDNING
Utvecklingen av förbränningsstekniken syftar nu till att globalt minska emissionen av luftförureningar, att sänka energiförbrukningen och att göra billig energi tillgänglig. På sikt är målet att helt ersätta förbränning av kol, olja och naturgas med förnyelsebara energikällor. Detta kräver på relativt kort sikt utveckling av nya förbränningsprocesser, på längre sikt utveckling av nya energiomvandlingsprocesser. Innan dessa processer utvecklats så långt att de är kommersiellt tillgängliga måste emellertid befintliga processer utvecklas vidare för att höja deras verkningsgrad och minska deras negativa miljöpåverkan. Denna kortsiktiga utveckling kräver både ombyggnad av befintliga anläggningar och nybyggnad, liksom utveckling av nya typer av ugnar och pannor.

Eftersom miljökraven ständigt stegras, måste F o U - insatserna koncentreras på att uppnå bättre behärskning av förbränningsprocessen. Kinetiken för för bildning och reduktion av kväveoxider är redan nu väl känt. Detta innebär att om n... lägner till temperatur, uppehållstid, och koncentrationer av de viktigaste reaktionsdeltagarna, kan man med relativt stor noggrannhet beräkna hur olika delreaktioner avlöper. För att omsätta dessa kunskaper i utformning resp. styrning av produktionsanläggningar, måste man kunna kontrollera förbränningen och styra den, så att de kemiska reaktionerna följer önskade vägar. De områden som kräver särskild uppmärksamhet är hur turbulensen inverkar, samt blandningen mellan bränsle, luft och rökgaser.

Det brådskar emellertid med att sänka emissionerna av luftförureningar. Nya kunskaper måste därför, allteftersom de kommer fram, tillämpas vid om- och nybyggnad av anläggningar och i utveckling av nya processer. Därför måste även modelleringstekniken för förbränningsanläggningar kontinuerligt utvecklas.

Förf. har under många år deltagit i utvecklingsprojekt i samarbete med industrin, och därvid utvecklat en modelleringsteknik, som visat sig mycket användbar. Metoden är en kombination av försök i produktionsenheter, försök i isoterna strömningsmodeller och matematisk modellering. Som bakgrund genomgås först kväveoxidkemin och de erfarenheter som redovisas i litteraturen. Därefter diskuteras modellförsök och matematisk modellering. Slutligen diskuteras modellering av avfallspannorna i Gärstad och Spillepengen i Malmö, där reburning och ureainjektion för NOX reduktion tillämpats.
METODER FÖR MINSKNING AV NO\textsubscript{X} EMISSION

För begränsning av NO\textsubscript{X} - emissionen från anläggningar genom förbränningstekniska åtgärder, kan man urskilja fyra olika principiella metoder: stegvis lufttillsättning, återföring av rökgaser, stegvis bränsletillsättning och injektion av ammoniak, urea osv. De två första metoderna syftar till att begränsa bildningen av NO\textsubscript{X}, genom att minimera temperaturen och tillgången på syre. Den tredje metoden innebär reduktion av redan bildad NO\textsubscript{X}, genom att upprätthålla en reducerande zon efter den primära förbränningszonen. Den fjärde metoden innebär att man styr om reaktionssvagen genom injektion av ett ämne, som vid lämplig temperatur reducerar NO till N\textsubscript{2}. Hur detta kan gå till, illustreras i fig 1. Figuren visar schematiskt hur kväve omsätts i en förbränningsanläggning \textsuperscript{1}). Beroende på temperatur, uppehållstid och luftfaktor i olika zoner av brännkammaren kan processen följa olika reaktionsvägar.

Kemin är som synes mycket komplex. Ett par detaljer framkommer dock tydligt:-
- Kväve, som tillförs processen både från förbränningsluften och från bränslets koksåterstod, oxideras direkt till NO om temperaturen är tillräckligt hög. (Reaktionsväg 1 - 2 i figuren). Detta är termisk NO\textsubscript{X}.
- Reducering av NO genom reburning (2 - 3 - 4 - 1 i fig 1) kräver närvaron av kolvätteradikaler. Dessa bildas vid förbrännningen av reburningbränslet. Det krävs alltså att syre tillförs i början av reduktionsprocessen. Från punkt 4 i fig 1 kan reaktionerna gå vidare tre olika vägar, varvid det bildas NO, N\textsubscript{2}O, lustgas, eller molekylärt kväve.

I punkten 4 finns ammoniak, som bildats ur bränslekvävet via HCN och NCO. Beroende på temperaturen och tillgången på NO respektive OH radikaler, bildas NO eller N\textsubscript{2}. Om ammoniak injiceras vid lämplig rökgastemperatur, reduceras NO till N\textsubscript{2}. Vid fel temperatur

Fig 1  NO - kemin, schematiskt
bildas i stället NO och dessutom kommer ett överskott av ammoniak att emitteras till omgivningen med avgaserna. Det temperaturområde där ammoniak måste injiceras, är mycket snävt, 100 - 150 °C. Exemplet visar att man i en förbränningsanläggning måste kunna bestämma var ammoniaken skall injiceras och dessutom kunna blanda den effektivt med rökgaserna.

I produktionsanläggningar tillkommer många komplikationer, som gör att man måste förenkla alla matematiska modeller: Strömningen är turbulent, blandningen är svårkontrollerbar, temperaturen varierar både i tiden och rummet, uppehållstiden i olika delar av systemet är olika etc. Man har emellertid i de flesta fall ännu inte kunnat beskriva skeendena matematiskt/teoretiskt, utan tvingats dra allmänna slutsatser om mekanismerna. Däremot har försöksresultaten ofta visat förbluffande god överensstämmelse med försök i driftanläggningar.

MATEMATISK KONTRA EXPERIMENTELL MODELLERING


Försök i strömningsmodeller har fördelen att de återger den verkliga strömningen så länge systemet är isotermt. I ett system med förbränning tvingas man också till förenklingar för att ta hänsyn till de densitets- och temperaturskillnader, som existerar i ett verkligt fall. Här nedan skall dock visas att skillnaden mellan hastighetsfördelningen i ett isotermt fall och i ett fall med förbränning i många fall kan försummas.

Betrakta som ett exempel strålningsdelen i en ångpanna. Temperaturen i flamman är ca 1500 °C, i utloppet till konvektionsdelen ca 1000 °C. Om dynamiska trycket beräknas vid en medeltemperatur av 1250 °C blir felet 8 % mot 1000 °C och 1500 °C. Man gör därför inget större fel om flödesfältet bestäms vid en representativ medeltemperatur, resp. i strömningsmodell.

Själva flamman kan inte behandlas på detta sätt. Denna zon är mycket viktig i studier av NOx-emission, ty det är här förbränningen bildar de kolvåtsradikaler, som är nödvändiga för att bilda prompt NO, NO ur bränslets kväveinnehåll och för att reducera NO i reburningprocessen. Här måste därför matematisk modellering tillgripas.
PRAKTIKFALL

Gärstadsverket utanför Linköping består av 2 pannor på vardera 16 MW. Där bränns huvudsakligen hushållsavfall.

Fig 2 Modellering av förbränningsprocesser, princip

Vår institution genomförde år 1990 till 1991 ett projekt med stöd av STEV 2). Målet var att utveckla en metodik för modellering av anläggningar för avfallsförbränning. Eftersom olika zoner i systemet kräver olika behandling, användes en kombination av försök i produktionsanläggningar, försök i modell och matematisk modellering, Fig. 2. Genom att inbördes jämföra resultaten från den matematiska modelleringen och modellförsöken med mätresultat från pannan, kunde båda modelleringsteknikerna valideras. De användes sedan för att studera inverkan av primär- och sekundärluften på strömning, blandning och temperaturfördelning i pannans fribord.

Försök i pannan

Med sonder över bränslebädden, på de två nivåer och i utloppet till konvektionsdelen bestämdes temperatur och atmosfärens analys. Dessutom avlästes driftsinstrumenten. Ur dessa data kunde sammansättningen av pyrolysgasen som steg upp ur bädden ges i form av \( C_mH_nO_o \). Nedanstående tabell visar sammansättningen vid två tillfällen. den stämmmer relativt väl med amerikanska data för hushållsavfall.
Tabell 1
"Ekvivalent" bränsle

<table>
<thead>
<tr>
<th></th>
<th>1990</th>
<th>1991</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formel</td>
<td>C6H12O3,75</td>
<td>C6H9O3,75</td>
</tr>
<tr>
<td>Fukthalt i %</td>
<td>11</td>
<td>27</td>
</tr>
<tr>
<td>Aska %</td>
<td>37</td>
<td>12,4</td>
</tr>
</tbody>
</table>

Temperaturfördelningen över bädden, nivå 1 och 2 samt omedelbart före konvektionsdelen framgår av Fig 3.

Fig 3 Temperaturer, bestämda i pannan

Dessa data användes som ingångsdata för beräkningar av förhållandena i fribordet. Beräkningar avseende förbränningen i bränslebädden ingick inte i projektet.

**Verifiering av modellförsöken**

Verifiering av den matematiska modelleringen

Dataprogrammet FLUENT användes och beräkningarna genomfördes med de ingångsdata som erhölls vid mätningarna i pannan. Först jämfördes beräkningen av ett isotermt fall med samma data som använts vid modellförsöken. Därefter beräknades hastighetsfördelningen isotermt, och jämfördes med hastighetsfördelningen med förbränning, fig 5.

Fig 5 Beräknad hastighetsfördelning
a) isotermt  b) med förbränning

Fig 6 Jämförelse mellan beräknade och experimentella temperaturer och koncentrationer
Skillnaden mellan de båda hastighetsfälten var obetydlig, vilket stöder antagandet ovan, att hastighetsfältet utan större fel kan beräknas isotermt. Därmed är det också sagt att hastighetsfördelningen med gott resultat kan bestämmas i isotermt strömningsmodell. Slutligen jämfördes de beräknade temperaturerna, CO₂ och O₂ med de värden, som bestämts i utloppet till konvektionsdelen, Fig 6. God överensstämmelse kunde konstateras. Därmed var både modellförsöken och den matematiska modellen verifierade, och kunde användas för att studera inverkan av olika variabler på strömning och blandning i pannan.

Primär- och sekundärluftens inverkan på strömning och blandning

Fig 7 visar koncentrationsfördelningen av oförbränt bränsle för två inställningar av sekundärluft. När 70% injiceras genom portarna i fronten, vänstra bilden, tvingar den luftsträlen från motsatta väggen att vika av, och båda strålarna strömmar tätt intill väggen.

Till vänster utbildas ett stort område med långsamt cirkulerande gas, som får antas innehålla högre halter av oförbrända gaser. Om sekundärluften omfördelas så, att lika mycket kommer från vardera sidan, trycks strålarna från frontväggen tillbaka, och de två strålarna går nu mer mitt i pannan. Vid fördelningen 30/70% tar strålen från bakväggen överhanden, och båda
strålarna kommer att strömma uteefter frontväggen. Det finns alltså stora möjligheter att styra förbrännningen med hjälp av sekundärluft. Ytterligare möjligheter, som inte kunde undersökas, är att ändra på strålarnas riktning, och luftmunstyckenas areor.

Kväveoxider

Som nämndes i inledningen, finns ännu inte någon matematisk modell som möjliggör en tillförlitlig beräkning av NO\textsubscript{X} -konzentrationer i förbränningsanläggningar. En del slutsatser kan dock dragas av de vanliga beräkningarna av flödes- koncentrations-och temperaturfält. Mätningar i pannan visade höga koncentrationer av NO\textsubscript{X} i de recirkulationsvirvlar som modellförövningen påvisade. Temperaturen i plan 1, strax ovanför sekundärluftstrålarna, uppmättes till 872 resp. 977 °C vid två tillfällen. Temperaturen sjönk till 698 resp. 796 °C strax före konvektionsytorna. Dessa låga temperaturer innebär att reburning inte torde vara ett realistiskt alternativ. Av Fig 1 framgår, att NO förmodligen skulle oxideras eller inte alls påverkas av sekundäbränslet. Troligtvis skulle sekundäbränslet inte heller brinna färdigt i strälningsdelen. Den mest realistiska åtgärden bör vara att återföra rökgaserna tillsammans med sekundärlufta för att hålla nere temperaturen och O\textsubscript{2} - koncentrationen och därigenom sänka bildningen av NO. Eventuellt skulle man genom att ändra sättet för sekundärlu tinjektionen kunna förbättra blandningen, så att förbrännningen fördelar sig jämnare i strälningsdelen.

MODELLERING AV SYSAVS ANLÄGGNING

I SYSAVs anläggning i Spillepengen i Malmö har reburning, samt injektion av urea för NO\textsubscript{X} -reducering prövats. Med stöd av STEV/NUTEK genomfördes modellförsök och matematisk modellering parallellt med detta projekt. Pannan är högre och smalare än pannan i Gärstad. Pannan är försett med två injektionsställen för sekundärluft. Portarna i bakväggen är riktade uppåt. Portarna i frontväggen sitter 3,6 m högre upp, och är riktade nedåt. Sekundärluftstrålarnas inverkan på strömningen i pannan är därför något annorlunda. Fig 8 visar arrangemanget vid ureainjektion. De två översta strålarna till höger i Fig 9 visar urean. De två vänstra figurerna visar hur urean smyger sig uteefter strålarna i bakvägen, och strömmar ut i konvektionsdelen utan att blandas med ugnsgasen.

Detta inträffade vid de första försöken i pannan, och resulterade i obetydlig reduktion av NO\textsubscript{X}. Genom att gradvis fördela sekundärluften till allt högre andel genom bakvägen, åstadkoms att sekundärluftstrålarna drog ureastrålarna nedåt. Vid 65 % av sekundärluften genom munstycken i bakvägen, Fig 9 längst ned t.h. blev inblandningen av urea effektiv.
Fig 8 System för tillsättning av urea

Fig 9 Ökat luftflöde genom de bakre sekundärluftportarna ger effektivare inblandning av urea.
Förslaget till reburninginstallation innebar att Naturgas injiceras både vid frontväggen och bakvägg, strax ovanför nivån för sekundärluften på frontväggen. Av ugnens totala bränsleeffekt skulle 23 % utgöras av naturgas. För att uppnå god inblandning skulle 3 % av avgasen återföras och blandas med naturgasen.

Slutförbränningsluft tillföres på en sådan nivå att gasen uppnått cirka 0,5 s uppehållstid i reburningzonen.

Sekundärluft tillföres enbart genom de befintliga dysorna på bakväggen.

Efter installationen av reburningutrustningen genomfördes ett basläggningsförsök. Det visade sig då att de ändrade strömningsförhållanden, som blev följd av att dysorna byggdes om, medförde att förbränningen blev mindre stabil. Kväveoxidemissionen minskade något, men det skedde till priset av mindre stabila förbränningsförhållanden och förhöjd CO-halt i avgaserna. Även här kunde inverkan av sättet för injektion av sekundärluften observeras. I driftsförsöken konstaterades att en god slutförbränning åstadkoms när 9000 m³n/h luft (av totalt ), tillsattes genom de nedre sekundärluftdysorna. Modellförsöken visade hur en mycket stor recirkulationsvirvel utvecklas när frontluftstrålarna dominerar. Fig 10 Genom att successivt överföra mer luft till munstyckena i bakväggen kan denna virvel minskas och om blandningen effektiviseras.

I samma projekt studerades även omfordelning av recirkulerade rokgaser, annan dyskonstruktion mm. Det visade sig att man kan förbättra förbränningen och även öka reduktionszonens storlek - dvs uppehållstiden, genom att injicera ett högre flöde av luft och rokgas genom de främre dysorna för slutförbränningsluft- Modellförsöken visade att extra tillsats av rokgas genom luftportarna för slutförbränning i frontväggen samt ökning av strålarnas impuls - minskad portarea -kunde åstadkomma en bättre utformning av reburningszonen, samtidigt som slutförbrännningen förbättrades innan avgaserna lämnade strålningsselen.
Fig 10 En mycket stor recirkulationsvirvel bildas när sekundärluften injiceras endast i fronten. Virveln minskas, och blandningen blir effektivare om luften styrs om till bakväggen.
SLUTORD

För den framtida utvecklingen av förbrännningstekniken behöver vi självfallet öka våra kunskaper om de grundläggande mekanismerna som styr förbränning, blandning, bildning av luftföroreningar etc. Lika nödvändigt är emellertid att vi utvecklar vår förmåga att tillämpa dessa kunskaper i utvecklingen av nya, förbättrade förbränningsprocesser. Med detta avses då modelleringstekniken. Som nämnts ovan har kombinationen av fysisk och matematisk modellering visat sig vara ett mycket kraftfullt verktyg.

Man har kommit mycket långt när det gäller att prediktera NO\textsubscript{X} bildning och NO\textsubscript{X} - reduktion om man kan förutsätta att temperatur, uppehållstid koncentration mm är kända. Här ovan har också visats att man kommit långt när det gäller att beräkna värdet på de variabler som styr dessa parametrar, i verkliga förbrännningssystem. Det fattas däremot modeller som medger direkt beräkning av NO\textsubscript{X} -produktsanläggningar. Förf. har därför bildat en arbetsgrupp för att åstadkomma ett sådant modelleringssverktyg. Verktyget skall baseras på ett kommersiellt, väl utprovat dataprogram, med vilket de sedan vanliga strömnings- förbrännings- och värmeöverföringsberäkningarna kan genomföras. I en postprocessor beräknas sedan NO\textsubscript{X} -bildningen. I de fall kinetiska modeller finns, implementeras de, och "kalibreras" mot resultat från försök i pilot- och produktionsanläggningar. Finns inga modeller, korreleras emissionsdata mot driftsdata från olika anläggningar. Vi ämnar försöka få systemet självlärande i viss utsträckning, och har därför betecknat det som ett expertsystem. Arbetsgruppen sammansätts av forskargrupper med kompetens som sträcker sig från renodlad grundforskning till tillämpning. Medlemmarnas forskargrupper skall fungera oberoende av varandra och söka sin egen finansiering. Samordning skall ske genom regelbundna sammanträffanden och utbyte av informationer. Avsikten är att inom ett år från projektstarten skall systemet ha tillämpats på någon driftsanläggning i Sverige.

ERKÄNNANDEN

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PRESSURIZED BIOMASS COMBUSTION WITH RESPECT OF WOOD FUEL

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PRESSURIZED BIOMASS COMBUSTION
WITH RESPECT OF WOOD FUEL

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ABSTRACT

Today more than ever it is important to recognize that total efficiency is needed to be increased in the electricity and heat production with less emissions including also CO₂. One of the options is to increase the biomass utilization in combustion in forest rich countries.

About 14%, corresponding to 45 TWh/a, of the total primary energy use in Finland will be covered through wood biomass. This amount has already reduced CO₂ emissions 15.5 million tons/a compared to use of fossil fuels.

The goal of this research was to investigate the reactivities of three different wood fuels, particle size less than 500 microns in pressurized entrained flow reactor at VTT in Jyväskylä. The major issues have been; the combustion efficiency related to unburned carbon, risk of slagging, alkali balance and reduction of gaseous emissions like CO, NO, and SO₂.

To optimize the combustion efficiency the tests have been conducted at 800 °C and 1200 °C up to 8.5 bar pressure. The fuel feed was around 190 - 300 g/h. The flue gas oxygen content was kept below 12%.

It was found out that the combustion rate of spruce bark fuel is by far less than pine fuel. Some carbon residue was found in ash at 800°C. However at higher temperature carbon residue disappears. This may be due to thermal decomposition of carbonate so that the combustion was nearly over 99% at 800 °C and nearly 100% at 1200 °C.

The risk of slagging due to mineral content was investigated by determining the ash melting point. One of the tested pine fuels showed an indication to slagg having ash melting at 1267 °C. The other two fuels showed no slagging risks while having the ash melting point above 1400 °C. The wood ash is rich on CaO, especially the tested spruce bark, therefore the sulfur was captured in ash between 50 - 90% depending on CaO content in ash and temperature. The alkali metals, like Na, K, were partly, 30 - 50%, captured in ash and the rest was remaining in gaseous phase and would enter the gas turbine.

In pressurized wood fuel combustion NOₓ, CO and SO₂ emissions can be controlled properly. By increasing the pressure to 3-4 bars the NO emissions decrease at the same temperature about 30%. NO emissions are inversely proportional to square root of the pressure ratio. This investigation has shown that this type of the electricity production as a future method looks promising even though more research and development work is needed.

Key words: Pressurized wood combustion, gas turbine, CO₂ reduction

INTRODUCTION

The Finnish Government has reached an understanding for the taxation of energy at May 28, 1993 in Finland. The following fossil fuels need to pay energy taxes from the beginning of 1994 regarding to their energy and carbon content. Oil, coal and natural gas need to be taxed after their energy and carbon content. Biomass (wood) and wind energy and the energy production using waste material will not put on tax. Peat will be taxed after its energy content. The today's electricity tax will be
removed. Only the electricity produced with nuclear energy will have equal amount of taxes as before.

Today more than ever it is important to recognize that total efficiency need to be increased to achieve an improvement of the electricity and heat production with lower emissions. In 1991 the CO₂ emissions from use of fossil fuels in Finland was about 55 million tons. Already 11 TWh increase on use of biomass (wood) can decrease the CO₂ emissions of 3.8 million tons annually.

One option is to increase the biomass utilization through power generation in forest rich countries like Finland. It has been estimated that the annual use of biomass energy could be increased about 300 - 600 MWₑ. The partial replacement of the fossil fuel use with biomass and optimization in pulp and paper industry could also increase the annual electricity production further about 300 - 600 MWₑ. Taking into account the advanced co-generation alternatives based on pressurized wood fuel combustion and gasification the above mentioned capacity of electricity production in Finland could be doubled during next 10 - 15 years.

The wood fuel fired pressurized combustion in conjunction with gas turbine is most favourable in the capacity range below 5 MWₑ. According to a recent study the available capacity in Finland have been estimated to be 100 - 150 MWₑ (Jaanu, K., 1993). From this about 80% could be replaced until year 2000. The partial replacement of fossil fuel through biomass will help to reduce CO₂ emissions.

Swedish government has made three important decisions (KjäUström, B., 1993).

a) to phase out nuclear power generation before 2010;

b) to protect the main unexploited rivers from hydroelectric power projects;

c) to freeze CO₂ emissions from the energy system at the 1988 level.

This leaves energy conservation, wind power generation and biomass fuelled power generation the most important future possibilities. Closing down the present nuclear power plants means that an annual power generation of 70 TWh must be replaced. Biomass power generation appears to have a significant potential in Sweden according to the Swedish government study SOU 1992:90 "Biofuels for the future", with an estimated fuel potential of 150 - 200 TWh/year.

Studies of the economics of various co-generation alternatives, have identified gas turbines directly fired with wood powder as the potentially most promising option for the capacity range below 5 MWₑ. Gas turbines directly fired by wood are however not commercially available as shown in 1991 completed state of art review (Frediksson J. et al., 1991).

In United States it has been calculated that with proper resource management and through the development of efficient conversion processes, biomass could contribute as much as 20% of current U.S. energy consumption by 2030; i.e., 4 to 5 times today's 3.8 quads, as estimated for the National Energy Strategy. This can only be obtained through the conversion of biomass into efficient secondary energy forms such as electricity and liquid fuels. Biomass already constitutes a significant resource for producing electricity. In 1989, biomass and municipal solid waste powered facilities provided a generation capacity of almost 8.4 GWₑ based on conventional combustion-steam turbine type.

Overall thermal efficiencies across the industry are less than 25% (>14000 Btu/kWh) (Overend, R.P. et al., 1992). The efficiency of power production can be increased using combustion gases directly as a turbine feed, instead of using steam as an intermediate fluid.

Present Status

Wood powder is commercially available fuel in Sweden. There is one production plant in operation (Pulverbränsle AB Ulricehamn), selling the fuel mainly to the district heating plants. Wood powder is also made on site by some users. Production cost from wood sold at 13,86 - 16,63 US$/MWh is reported to be 6,93 - 8.32 US$/MWh, which means that the total fuel price should be of the order of 20,79 - 24,95 US$/MWh for the large users (currency exchange course of 1 SEK = US$ 0,1386).

Use of wood for directly feeding of gas turbines has been tried in several projects. Two of those most recent developments and so far most promising projects are those run by Power Generating Inc.,(Texas) and Aerospace Research Corporation, (Red Boiling Springs), where a turbine giving 1 MWₑ has been run for about 800 hours with oak saw powder as a fuel. No corrosion or erosion damage has been reported. The experiences show however that an inlet temperature above 800 °C gives hard deposits on the turbine blades, which could not be removed with walnut hulls, (Hamrick J.T., 1992). For lower inlet temperatures, ash deposits still occur, but the deposits can be removed by injection of walnut shells. The turbine must nevertheless be stopped for cleaning after
about 200 operating hours. For commercial operation this is clearly not acceptable. Other unresolved problems relate to maintaining accurate control of solid fuel feeding into the pressurised combustion chamber and adaption of standard machines to a different air/gas flow ratio and higher pressure drop over the combustion chamber. No information about the performance of the test turbine in Red Boiling Springs with other wood fuel species is available. The 0.4 MW, PGI-project based on pressurized wood fired gas turbine process as shown schematically in Fig. 1 (McCarroll, R., 1992), should be going in operation in Laramie next year.

Table I Estimated flue gas parameters at the gas turbine inlet (Kjälström, B., 1993)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Acceptable</th>
<th>Presently Expected</th>
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</thead>
<tbody>
<tr>
<td>Particle concentration in gas</td>
<td>&lt; 300 ppm</td>
<td>&lt; 50 ppm</td>
</tr>
<tr>
<td>Particle size</td>
<td>&lt; 2 um</td>
<td>&lt; 2 um</td>
</tr>
<tr>
<td>Na + K content</td>
<td>&lt; 1 ppm</td>
<td>&lt; 1 ppm</td>
</tr>
</tbody>
</table>

According to the above results the gas quality seems to be on an acceptable level except the alkali metal concentrations. However, the solid concentration and some other metal compositions cannot be separated from this point of view, because also other metals causing eutectic with SiO$_2$ which leads to a low ash softening and melting points.

According to the comparison presented in Table II the direct combustion option is by far the most competitive in the small scale units.

Table II Costs and performance data for biomass fuelled co-generation installations with combined cycle in Sweden, (Kjälström, B. 1993).

<table>
<thead>
<tr>
<th>Source</th>
<th>DEMEC AB</th>
<th>STUDSVIK</th>
<th>VÄRNAMO</th>
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<tr>
<td>Electric power (MW$_e$)</td>
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<td>6</td>
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<tr>
<td>Heat supply (MW heat)</td>
<td>8.0</td>
<td>21</td>
<td>9</td>
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<td>Performance:</td>
<td></td>
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<tr>
<td>- total efficiency</td>
<td>0.83</td>
<td>0.84</td>
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<tr>
<td>- electric yield</td>
<td>0.29</td>
<td>0.42</td>
<td>0.33</td>
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<tr>
<td>Specific investment SEK/MW$_e$</td>
<td>11100</td>
<td>14280</td>
<td>27000</td>
</tr>
<tr>
<td>US.$/MW$_e$</td>
<td>1538</td>
<td>1979</td>
<td>3741</td>
</tr>
<tr>
<td>Estimated costs of electricity SEK/MWh$_e$</td>
<td>384</td>
<td>403</td>
<td>795</td>
</tr>
<tr>
<td>US.$/MWh$_e$</td>
<td>53</td>
<td>56</td>
<td>110</td>
</tr>
</tbody>
</table>

Calculations are based on 4000 operation hours, fuel price: 110 and 160 SEK/MWh(fuel), annuity 12%, a credit for heat supply of 235 SEK/MWh$_{hr}$, investment subsidy of 4000 SEK/MWh$_{hr}$.  

Fig. 1 Schematic Description of PGI -Co-generation Process
The goal of the project is to investigate the reactivities of different wood fuel to optimize the combustion efficiency at 7 and 15 bar pressure range and in the temperatures from 800 °C and 1200°C. A fuel feed of 190 - 300 g/h has been used. The excess oxygen content in flue gas has varied from 3 - 11 % O₂. In addition to the combustion optimization alkali metal and gaseous emissions need to be reduced to avoid slagging problems due to low ash softening point in the combustor and deposition on the turbine blades. The investigation is taking place during 1993 and 1994.

EXPERIMENTAL

Main features of a new pressurised entrained flow reactor, and the first result of the evolution and emissions of nitrogen oxides and alkali metal contents of solid samples in the experiments with pulverised wood and bark are presented. The reactor enables controlling of the experimental conditions with high precision. It is possible to carry out experiments under prevailing conditions at the freeboard of a pressurised fluidised bed boiler (T = 800 - 950 °C, p = 5 - 10 bar), and under conditions prevailing at the combustion zone of combined cycle including a pressurised pulverised fuel combustion stage (T = 1000 - 1400 °C, p = 10 - 20 bar).

Test Facilities

The pressurised entrained flow reactor has an effective electrical preheater, by which a gas flow of 48 m³/h can be heated up to 1400 °C. The hot reaction gases are mixed with the fuel in about 10 ms in a conical nozzle, where the particle heating rates are of the order 10⁵ °C/s. The laminar-like flow is then led to the reaction tube (inner diameter 0.06 m, length 2 m), where the combustion occurs. The schematic diagram of the reactor is shown in Figure 2. Three separately controlled heating zones that surround the reaction tube keep the temperature in narrow limits.

The initial oxygen content in the reaction tube can be varied between zero and 20% by mixing nitrogen with the air. The maximum operation temperature of the reactor is 1400 °C and maximum pressure 20 bars. The gas and solid samples are taken with a vertical movable water-cooled probe. In addition, cold nitrogen is introduced at the top of the probe to ensure rapid extinction of gas and particles when sampled at the burning zone. Flue gas are analysed by commercial on-line analyzers and on-line FTIR spectrometer.

The temperature and gas composition reach a balance rapidly after starting the fuel feed. The amount of fuel consumption during the experiments is 200 - 300 grams/h depending on the pressure. One filling of the fuel bin, 12 liters by volume, is good enough for a ten hours test run with wood and bark fuels. The fuel is transferred from the pressurised dosage vessel to the mixing nozzle in nitrogen flow.

The operations of the device are controlled by a computer. A commercial automatization system, code named "Genesis", was used as a frame in the programming work. The automation system works as was planned; the values of several parameters can be simultaneously changed between two experiments. Genesis is used also for logging the data on process parameters and measurements. (Aho M. et al., 1993.)

Properties of the VTT's pressurised entrained flow reactor are given in Figure 2.

Properties of reactor:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate (m³/h)</td>
<td>1 - 2</td>
</tr>
<tr>
<td>Max. res. time (s)</td>
<td>4</td>
</tr>
<tr>
<td>Max. operating T (°C)</td>
<td>1400</td>
</tr>
<tr>
<td>Operating pressure (bar)</td>
<td>1.1 - 20</td>
</tr>
<tr>
<td>Particle heating rate</td>
<td>10³</td>
</tr>
<tr>
<td>Solid/gas mixing time (s)</td>
<td>0.01</td>
</tr>
<tr>
<td>Material of reaction tube</td>
<td>ceramic</td>
</tr>
<tr>
<td>Inner diameter - (m)</td>
<td>0.06</td>
</tr>
<tr>
<td>Length - (m)</td>
<td>2</td>
</tr>
<tr>
<td>Observations port</td>
<td></td>
</tr>
<tr>
<td>Vertically mobile probe</td>
<td></td>
</tr>
<tr>
<td>Computer-control</td>
<td></td>
</tr>
<tr>
<td>Heating</td>
<td></td>
</tr>
<tr>
<td>Number of heating zones</td>
<td>5</td>
</tr>
<tr>
<td>Atmosphere (% O₂ in N₂)</td>
<td>0 - 50 %</td>
</tr>
</tbody>
</table>

Fig. 2 The pressurised entrained flow reactor and its properties.
RESULTS AND DISCUSSION

Three different wood fuels such as spruce bark and two pines, analysis of which is shown in Fig. 3, have been tested in our pressurised entrained flow reactor with respect to the combustion capability, alkali metal output and gaseous emissions like CO, NO, N₂O, NOₓ, SO₂ and particles.

![Fuel analysis](image)

**Fig. 3** Fuel analysis

An example of operation temperature and flue gas measurements with spruce bark fuel is given in Fig. 4 and 5.

![Temperature distribution](image)

**Fig. 4** An example of the test conditions: axial temperature distribution in reactor tube. Trial run with spruce bark fuel at 6 bar and 800 °C.

![Emissions distribution](image)

**Fig. 5** An example of emissions distribution in flue gas at 6 bar and 800 °C by using spruce bark as a fuel

The combustion efficiency

The spruce bark fuel has mainly been burnt after about 400 milliseconds, which was almost twice as long compared to the pine fuel at 800 °C and 6 bar. The principal effect of ambient pressure on flame structure is to change its thickness. Then the thickness of the flame front is inversely proportional to pressure. Depending on the local atmosphere, oxygen rich or poor, around the particle the combustion takes place either on the surface of the wood particle or outside in the gaseous phase while due to oxygen poor zone the pyrolysis reactions are very strong compared to char leading the oxidation into the gas phase. The heterogeneous reactions always go over through pseudo homogenous reaction phase to the homogenous reaction phase. This is the case when the wood particle are burnt down to the particle size less than 50 microns. Then the impact of the pressure on heterogenous combustion will be clear, so that the reaction rate increases rapidly. The effect of pressure on combustion rate of pulvzerized fuel has recently been examined (Saastamoinen, J., 1993).

However, for industrial applications the wood particles may have a particle diameters up to 2 - 3 mm. As a next step of this work the combustion rate of wood fuel for industrial application will be examined.

Ash behavior

One of the important issues in burning wood is the ash softening and melting points. Depending on type of the wood it may vary much due to ash mineral content. According to our earlier tests the ash melting point may vary from 1190 °C to more than 1400 °C. In this work one of the pine wood has shown as low melting point as 1267 °C, which should be too low for direct combustion application, while increasing the risk of fouling. This was due to too high mineral content in ash, especially those of SiO₂, Fe₂O₃ and K₂O, see Fig. 6. The other fuel sample have shown melting points over 1400 °C, see Fig. 7.
Environmental aspects

Under oxidizing conditions (3 - 4% oxygen in flue gas) at 800 °C the carbon monoxide content was varying between 20 - 30 ppm at 3 and 6 bar when using spruce bark as a fuel. Under above conditions all kind of NOx (NO, N₂O and NO₂) emissions were produced, see Fig.8. In both cases N₂O and NO₂ emissions were very small corresponding together to less than 7 ppm. The pressure did not appear to have any major impact on these two components.

The pressure seems to have strong impact on NO emission. Then an increase of the pressure about 3 bar decreases the NO emissions about 30% as shown in Fig. 8 and 9. The impact of the pressure is about inverse of the square root of the pressure ratio, which can be expressed by following equation:

\[ C_{NOy} = C_{NOy_0} \times \sqrt{P_1/P_2} \]

The measured, average NO concentration at the pressure 3 bar and 800 °C was 24 ppm and the empirical correlated value was 25 ppm. The difference is about 4%. However at 1200 °C the impact of the pressure is somewhat less than before. The difference between calculated and measured values increases to 8%. This must be related to partly changing NO-production mechanism from fuel NO mechanism to the fuel NO and thermal NO mechanism. The thermal NO mechanism is a function of the temperature and oxygen partial pressure and not so much of the total pressure.
The capturing of the sulfur in ash and removing it from the flue gas through the separator before the gas enters the gas turbine to prevent alkali sulfate formations on the turbine blades, is an important matter. For instance by using spruce bark as a fuel, above 90% of the sulfur could be removed through ash at 800 °C, as shown in Fig. 11. This is due to high CaO content in fuel as can be seen in Fig. 12. An example of total flue gas emissions at 800 °C and 1200 °C are given in Fig. 13. It indicates that under pressurized operation conditions the emissions can be kept low.

Fig. 11 Balance of some components between spruce bark fuel and ash shown as a remaining part in ash at 800 °C and 6 bar and 3 bar pressure (analyzed by XRF and AAS).

Fig. 12 Some mineral composition of spruce bark fuel (analyzed by XRF and AAS).

CONCLUSIONS

The pressurized combustion of biomass (pine core and spruce bark) for the gas turbine process was studied in pressurized entrained flow reactor. The combustibility of the pine core wood was better than bark. The combustion time was for bark almost twice as long as for pine wood. The CO₂ released by the process, was originally extracted from the atmosphere during biomass growth, so the entire process results no net increase in CO₂ in the atmosphere.

By wood combustion in normal case the ash melting point is around 1400 °C, depending the ash content of wood (biomass) it can be drop below 1270 °C. This temperature, however is too low for direct combustion application. The ash behavior of wood depends on its mineral content, especially oxides of silica, iron, potassium and sodium. It will be very important to analyze the fuel mineral content before purchasing the wood fuel.

By using wood as a fuel in pressurized combustor NOₓ-emissions can be kept below 50 ppm and CO near to zero. The SO₂-concentration was less than 5 ppm. By increasing the pressure to about 3 - 4 bar at the same temperature level NO emissions can be reduced about 30%.

Depending on the temperature, 30 - 50% of the alkali metals is removed from the gas to the ash. To achieve the acceptable gas for the gas turbine, the alkali metal removal should be as high as 90% when using wood as a fuel. This can be achieved by adding some sorbent to the fuel stream.
According to this investigation the method of co-generation type of electricity production based on pressurized combustion on wood in connection with gas turbine as described by (McCarroll, R., 1992) looks as one of the future technology, although some more research and development work is needed.

NOMENCLATURE

\[ C_{NO_{p_1}} \] NO concentration in ppm at pressure \( P_1 \)

\[ C_{NO_{p_2}} \] NO concentration in ppm at pressure \( P_2 \)

\( P_1, P_2 \) Total operation pressure in bar

LITERATURE


EMPIRICAL MODELLING OF BLACK LIQUOR CHAR GASIFICATION

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EMPIRICAL MODELING OF BLACK LIQUOR CHAR GASIFICATION

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INTRODUCTION

There is growing interest worldwide to develop alternate chemical recovery processes for paper mills which are cheaper, safer, more efficient, and more environmentally sound than traditional technology. Pressurized gasification of black liquor is the basis for many proposed schemes and offers the possibility to double the amount of electricity generation per unit of dry black liquor solids. Such technology also has capital, safety, and environmental advantages.

Little data exists regarding the kinetics of black liquor gasification, particularly under pressurized conditions. Investigations have been made into black liquor gasification with both steam and carbon dioxide at atmospheric conditions. [1-5] Previous studies at Åbo Akademi have investigated separately pressurized gasification of black liquor char with H2O and pressurized gasification with CO2. [6-9] However, no kinetic data exists for a system in which both H2O and CO2 gasification occur simultaneously under pressurized conditions.

The purpose of this study was to investigate the kinetics of pressurized black liquor gasification when both steam and carbon dioxide are used as gasifying agents. Linear regression was used to fit a linear rate expression to experimental data obtained by gasifying black liquor char with a mixture of H2O, CO2, H2 and CO. Based on the resulting expression, trends in the gasification rate and insight into the behavior of a pressurized gasification system were predicted.

EXPERIMENTAL

Experimental approach

The objective of this investigation was to study how the four gases H2O, CO2, H2 and CO affect the gasification rate under pressurized conditions. It was decided to perform all experiments at one temperature but at several different pressures. To investigate separately the effects of pressure and gas composition would require an excessively large experimental matrix. Therefore, a phenomenological approach was chosen. The experimental parameters were all varied between experiments and linear regression was used to fit a rate expression to the experimental data.
A Plackett-Burman algorithm was used to generate the experimental matrix. Four parameters were varied: the total pressure and the concentrations of CO2, H2 and CO. Seven total pressures varying logarithmically between 2 and 30 bar were used. The concentration of CO2 was varied between 20% and 60% and the concentrations of H2 and CO were each varied between 3% and 15%. H2O provided the remainder of the reacting gas, resulting in a concentration range of 10% to 74%. The algorithm generates an experimental plan by minimizing the degree of correlation between experiments, resulting in a matrix which is highly varied yet which covers the ranges of the parameters well. It was found that 30 experiments were necessary in order to achieve a suitable sampling for all parameters.

Sample

The char used in the experiments was produced from a North American hardwood kraft liquor taken from the Weyerhaeuser Paper Company mill in New Bern, North Carolina. It was formed by introducing the liquor into a drop tube furnace under pyrolysis conditions at 900°C and atmospheric pressure. The drop tube furnace and experimental procedure is described in more detail by Clay, et al [10].

Samples of the char used in the experiments (designated char 5) were analyzed for carbon, sodium and sulfur content. No determination was made for hydrogen in this char. However, an earlier batch of New Bern char (char 3) was analyzed for hydrogen. The results of the analyses of both chars, based on their dry weights, are presented in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Char 5, wt. %</th>
<th>Char 3, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>31.47</td>
<td>31.22</td>
</tr>
<tr>
<td>Na</td>
<td>21.70</td>
<td>18.95</td>
</tr>
<tr>
<td>S</td>
<td>4.85</td>
<td>3.99</td>
</tr>
<tr>
<td>O</td>
<td>n/a</td>
<td>38.71</td>
</tr>
<tr>
<td>H</td>
<td>n/a</td>
<td>1.97</td>
</tr>
<tr>
<td>Other (by difference)</td>
<td>41.98</td>
<td>5.16</td>
</tr>
</tbody>
</table>

Table 1 Elemental analyses of New Bern chars, based on dry weight.

Equipment

The gasification kinetics were measured using a pressurized thermogravimetric analyzer (PTGA). A schematic drawing of the apparatus is presented in Figure 2.

The PTGA is capable of operating at pressures up to 100 bar and the reactor has a maximum operating temperature of 1100°C. Up to four gases can be supplied to the reactor. In addition, the apparatus is equipped with a steam generator, thereby making it possible to use water vapor as a reacting gas. The steam and permanent gas lines each have a three-way valve which can be switched either to the reactor or to a bypass line. This makes it possible to stabilize the steam flow in the bypass line prior to the start of gasification, thereby eliminating startup effects associated with the steam generator.
Figure 2 Pressurized thermogravimetric analyzer. 1100°C, 100 bar max.

The reactor consists of a 17 mm i.d. tube wrapped by a heating coil. The sample is suspended in the reactor by a long chain which is connected to a microbalance. The weight signal from the microbalance, as well as the sample temperature, are registered on a data acquisition computer which creates a data file for each experiment.

The PTGA is equipped with a water-cooled, helium-purged sample lock placed above the reactor. The sample is loaded into the device via this lock. By means of a small, electrically-driven winch the sample can be lowered into the reacting chamber once the desired conditions have been established.

**Experimental procedure**

For each experiment, a cylindrical platinum sample holder was loaded with approximately 100 mg of crushed char and placed into the sample lock. The reactor was pressurized and heated to the desired temperature while the steam flow was adjusted and directed through the bypass line. The sample was then lowered into an atmosphere of nitrogen and 10% carbon monoxide.

Figure 3 shows the weight versus time curve for a typical gasification run. In region "a", the sample was in the N₂/CO atmosphere and a sharp weight loss occurred. During this period, moisture in the sample was evaporated and volatile matter not removed during the char formation was pyrolyzed. Also, reduction of sodium sulfate to sodium sulfide may have occurred.

The sample weight stabilized within 100 - 200 seconds. After 400 seconds the gas composition was quickly adjusted to that for gasification and the flow of steam was switched.
from the bypass to the reactor. A sharp decrease in the weight signal was observed, followed by a weight increase (region "b"). The sudden decrease was due to a change in drag force caused by the introduction of the gasification mixture. The rapid weight increase was caused by adsorption of gasifying species onto the sample. Region "c" depicts the weight loss due to the removal of carbon in the sample by gasification.

The sample was gasified until the weight became stable, as in the final 500 seconds of the run shown in Figure 3. The steam flow was then turned off and the sample was lifted into the sample lock. After depressurizing the system, the sample was removed and weighed. The remaining material was usually grey or white in color, since the carbon had been gasified and the residue was composed of inorganic salts.

### Analysis of the gasification data

In order to evaluate the rate of gasification, the gasification section of the weight loss curve was normalized with respect to the amount of gasifiable carbon in the sample. Hence, the rate equation is of the form

\[
\text{rate} = -\frac{1}{m_{ci}} \frac{dm_{c(\ell)}}{dt}
\]

(Eq. 1)

where \(m_{ci}\) is the initial mass of gasifiable carbon in the char, found in preliminary studies to be 18.0 wt% of the initial char. Based on this equation, the units for the rate are \(s^{-1}\).
The rate of gasification was determined by finding the maximum slope of the normalized weight curve. In this study, this was done by first using linear regression to fit a polynomial equation to the weight vs. time data. Correlation coefficients were high, generally above 0.999. By differentiating this equation, an equation for rate as a function of time was obtained. The maximum rate was calculated from this equation, and is hereafter referred to as the gasification rate. The relation between rate and carbon conversion could also be determined from the polynomial equations.

MASS TRANSFER CONSIDERATIONS

In this investigation, the kinetics of the chemical reaction itself was focus of study. Consequently, it is of importance to ensure that film mass transfer and pore diffusion provide such small resistances that their contributions to the overall rate are negligible. Several methods, both theoretical and experimental, exist to determine if this is the case. A brief summary of such considerations is presented here. More detailed analyses can be found elsewhere. [6,7,9,11]

Theoretical determination of the roles of resistances

The Weisz modulus and mass transfer Biot number can be used in combination to determine the influence of film mass transfer and pore diffusion on the overall rate. Frederick and Hupa [7] outline a procedure which employs the Weisz modulus and Biot number to calculate the relative importance of these resistances. Using their procedure, the percentage of the overall rate which is controlled by chemical reaction kinetics was determined for the three fastest experiments in this study, where limitations caused by film mass transfer and pore diffusion would be most likely to occur. In the worst case, film mass transfer and pore diffusion combined account for 0.43% of the total resistance, which is negligible.

A second theoretical method to estimate the influences of film mass transfer and pore diffusion considers the case where either of these processes is the sole rate-determining mechanism. The theoretical time for complete conversion can be calculated for either of these cases, based on known parameters of the system. If the calculated time is close to the observed time for complete conversion, it suggests that the overall rate is controlled by film mass transfer or pore diffusion rather than by chemical kinetics.

Such theoretical calculations, to 90% conversion, were performed for the three fastest runs in the study and compared to the observed time to 90% conversion. In the worst case, the sum of the theoretical times for film mass transfer and pore diffusion is 0.9% of the observed time. Hence, the overall rate of gasification is controlled by chemical kinetics.

Experimental methods to investigate the roles of resistances

Several experimental techniques, such as varying the carrier gas and gas velocity, exist to investigate the role of film mass transfer and pore diffusion in the overall gasification process. Earlier studies performed by Åbo Akademi have included such experimental investigations, and in all cases it was concluded that film mass transfer and pore diffusion provide negligible resistance to the overall gasification process [6-7,9].
RESULTS AND DISCUSSION

Development of the gasification rate expression

The 30 experiments yielded a data matrix which included the partial pressures of H₂O, CO₂, H₂ and CO for each run plus the corresponding gasification rate. Based on this data, the coefficients of linear rate expressions were calculated using a linear regression program. The program optimized the coefficients of the terms in order to minimize the sum of the squares of the residuals. The subroutine could also perform an f-test on each term and remove the insignificant ones so as to simplify the expression. The tested rate equations were chosen with simplicity of the model in mind.

The first model tested was a simple expression of the following form:

$$rate(xl0^*) = Z + Ap_{H_2O} + Bp_{CO_2} + Cp_{H_2} + Dp_{CO}$$  \hspace{1cm} (Eq. 2)

where \( p_i \) is the partial pressure of species \( i \). Upon regression analysis, the resulting rate expression was:

$$rate(xl0^*) = 5.83 + 1.11 p_{H_2O} + 0.616 p_{CO_2} - 3.67 p_{H_2} - 3.91 p_{CO}$$  \hspace{1cm} (Eq. 3)

The correlation coefficient, \( R^2 \), between the predicted and observed rates for this expression is 0.685. Though the closeness of fit is not very good, analysis of each term provides information as to the behavior of the gasification system. The coefficients of the gasifying species H₂O and CO₂ are positive, suggesting that an increase in the partial pressures of these species contributes to an increase in the rate. H₂ and CO, however, have negative coefficients, indicating that they inhibit the gasification reaction. Based on this expression, one would expect that an increase in the partial pressures of H₂ and CO would result in a decrease in the gasification rate. This trend, as well as the positive effect of H₂O and CO₂ have been reported to be true for pressurized black liquor gasification [7,9].

The magnitude of the coefficient for the H₂O term is nearly double that for the CO₂ term, suggesting that it has a larger impact on the rate. Additionally, the magnitude of both the H₂ and CO terms are larger than those of the H₂O and CO₂ terms. This would suggest that, for a particular gas composition, the rate would decrease with increasing pressure. This has been shown to be true for both carbon dioxide and steam gasification of black liquor char. [7,9]

Other forms of the rate expression, including squares, products and inverses of partial pressures were tested and optimized using the regression subroutine. From these models, those terms having the most significance in the expressions were combined into one large expression. This was then analyzed using the regression subroutine and the insignificant terms were removed one by one until an expression containing just six terms remained:
\[ rate(\times 10^4) = 3.312 + 1.157p_{H_2O} + 0.07119p_{CO_2}^2 \]
\[-2.943p_{H_2} - 3.869p_{CO} + 0.6595 \left( \frac{1}{p_{CO}} \right) \]  
(Eq. 4)

It was found that six terms was the least necessary to maintain a high correlation coefficient. For this expression, \( R^2 \) is 0.894, and the correlation between the calculated and observed rates is quite good, as can be seen in Figure 4. This model was chosen to be the most useful due to its simplicity and effectiveness in predicting the gasification rate.

![Figure 4: Calculated vs. observed rate for the rate expression given in Eq. 4](image)

**Prediction of gasification behavior based on the model**

Based on the above expression, trends in the gasification rate can be predicted. One must bear in mind that the conditions at which the rate is evaluated should be within the limits of those for which the model was developed. Specifically, the rate model is only valid for gasification of the New Bern char used in the study at 750°C and with partial pressures of \( H_2O, CO_2, H_2 \) and \( CO \) within the limits of those used in the experiments. However, it is likely that the trends hold true for other black liquors as well.

Figure 5 depicts the gasification rate as a function of total pressure for various gas compositions. Of particular interest is the change in the shape of the curves as the gas composition changes. For the case where the ratio of oxidative species (\( H_2O \) and \( CO_2 \)) to reductive species (\( H_2 \) and \( CO \)) is high, the gasification rate initially decreases with increasing pressure, reaching a minimum at 7 bar, after which it increases. As the percentage of reductive species increases, the minimum on the curve shifts to higher pressures.
APPLICATION OF THE RATE MODEL

The rate expression given in Equation 4 can be used to predict the behavior of a true gasification system. The particular reactor investigated is a hypothetical entrained-flow gasification reactor, shown in Figure 6. Black liquor and air are introduced into the reactor, which is operated isothermally at 750°C. Immediately, the black liquor dries and devolatilizes (zone 1), and the resulting gases come to equilibrium. This gas then completely gasifies the remaining char (zone 2). As the char is gasified, the gas composition changes, which in turn affects the rate of gasification.

![Figure 6 Hypothetical entrained flow reactor for gasification of black liquor](image)

**Figure 5** Gasification rate, based on equation 4, as a function of total pressure
The amount of air introduced into the reactor can be defined in terms of an air ratio, based on the stoichiometric amount required for complete combustion of the black liquor. An air ratio of zero means that no air is fed to the system while an air ratio of 1.0 will result in complete combustion of the black liquor to CO₂ and H₂O. Oxygen present in the black liquor is assumed to contribute to the gasification in the same manner as oxygen in the air supply. Typical gasification systems operate with an air ratio of roughly 0.4. The amount of air introduced into the reactor will affect the equilibrium composition of the gases resulting from zone 1 and will consequently affect the gasification rate.

A typical black liquor with a dry solids composition of C₁₀H₁₂.5O₇Na₂.₄S₀.₃ was used in the calculations. It was assumed that the liquor had been concentrated to 75% dry solids. The composition of the char resulting after pyrolysis, in terms of the original dry solids composition, was C₄.₆₇H₁.₅₁O₄.₅₅Na₂.₄S₀.₁₹₉. In these calculations, sodium and sulfur in the liquor are neglected. It was assumed that the carbon, hydrogen and oxygen contents in the char decreased linearly as a function of conversion and that the char was completely converted to gaseous substances at 100% conversion.

The gasification rate for this reactor has been calculated as a function of the air ratio. Additionally, it has been calculated as a function of char conversion. The equilibrium distribution of gases at a particular conversion was determined based on the composition of the pyrolysis products, vaporized moisture, input air, and gasified char. The gasification rate was then calculated using the partial pressures of these gases.

Figure 7 shows the calculated gasification rate as a function of the stoichiometric air ratio for various pressures. The rates were calculated for the char at 50% conversion. From the figure it can be seen that the gasification rate increases with increasing air ratio. As the air ratio approaches 0.86, the rate approaches infinity. This occurs because the amount of oxygen in the system is sufficient to convert all carbon and hydrogen in the pyrolysis gases to CO₂ and H₂O. The CO partial pressure consequently approaches zero, and due to the \( \frac{1}{p_{CO}} \) term in the rate expression, the rate approaches infinity. The oxygen supplied between air ratio 0.86 and 1.0 will react with the remaining carbon and hydrogen in the char.

Figure 8 shows the predicted gasification rate as a function of char conversion for a stoichiometric air ratio of 0.4. As the char is gasified, the gasifying species are consumed and H₂ and CO are produced (see Figure 9). Consequently, the rate decreases, as seen in the figure.

It must be stressed that the gasification rates given in Figure 8 are predicted from the model, which was developed based on the maximum slope of the weight loss curve, which generally occurred at about 35% conversion. The rate trends shown do not result from a decrease in char reactivity as it is gasified. The figure is of value because it shows the effect of the changing gas composition as the char reacts.
Figure 7 Gasification rate at 50% conversion as a function of air ratio and pressure for the hypothetical entrained flow gasifier. Air ratio is based on complete combustion of the black liquor. Gasification rate is calculated from equation 4.

Figure 8 Gasification rate as a function of char conversion at an air ratio of 0.4.
Figure 9 shows the composition of the gas in the reactor as a function of char conversion for a stoichiometric air ratio of 0.4. It is assumed that the gaseous species remain in equilibrium as the char is gasified. Hence, the equilibrium gas distribution changes with conversion. The concentrations of H$_2$ and CO increase with conversion, as one would expect. Similarly, the concentration of H$_2$O decreases. The CO$_2$ concentration, however, increases slightly. This is due in part to carbon in the char entering the gas phase.

![Equilibrium gas distribution in the reactor as a function of char conversion for a stoichiometric ratio of 0.4.](image)

**CONCLUSIONS**

An empirical rate expression was developed for gasification of black liquor char as a function of the partial pressures of the reacting gas species. The rates predicted by the model correspond well with the observed experimental rates as measured by the PTGA.

The coefficients of the terms in the model provide insight into the gasification behavior. Steam and carbon dioxide both increase the gasification rate with the effect of H$_2$O being roughly double that of CO$_2$. Hydrogen and carbon monoxide both decrease the gasification rate, and their inhibiting effect is stronger than the gasifying effect of H$_2$O and CO$_2$ for a particular partial pressure.

Based on the model, it was found that the gasification rate decreases as a function of pressure at constant gas composition when the ratio of oxidative species (H$_2$O and CO$_2$) to reductive species (H$_2$ and CO) is low (< 2.5:1). At higher oxidative species/reductive...
species ratios, the rate goes through a minimum, beyond which it increases. When the ratio is 16:1, the minimum gasification rate occurs at a total pressure of 7 bar.

The rate expression can be used to predict the behavior of a gasification reactor. The gasification rate increases with as the air ratio increases and as the pressure decreases. As the char is converted, the concentrations of $H_2$ and $CO$ in the reactor increase. This results in a decrease in the gasification rate.

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A COMPUTER MODEL FOR SURFACE COMBUSTION OF STRAW BALES.

N. Bech, Risø, Denmark
ABSTRACT

This paper describes a computer model for the calculation of the steady and non-steady behaviour of surface combusting straw bales. The mathematical formulation is one-dimensional and the flow of gas through the straw bales is described by means Darcy's law for flow through a porous medium.

The model treats important phenomena as:

- Evaporation, condensation and diffusion of water
- Pyrolysis of straw
- Combustion of gas
- Combustion of straw char
- Thermal radiation
- Heat conduction in the straw
- Straw-gas heat transfer
- The straw bale properties such as porosity, permeability and water content may vary with time and the location in the bale.

Numerical experiments show that the results obtained with the model exhibit trends similar to those that would be expected and which have been observed in preliminary experiments.
PREFACE

This paper describes a computer model for the calculation of the steady and non-steady behaviour of surfacecombusting straw bales. Alongside with the theoretical efforts experiments are being carried out with the purpose of measuring temperature and concentration profiles within surface burning straw bales as well as in the furnace room, conf. DTI and RISOE (1992).

The work is carried out by the Department of Combustion Research at Risoe National Laboratory and the Department of Energy Technology at the Danish Technological Institute in Aarhus in cooperation with Voelund A/S.

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1. INTRODUCTION

The principle of surface combustion of straw bales is illustrated in fig. 1.1, taken from Gundtoft (1989).

Fig. 1.1. Surface combustion of straw. Definition of processes and zones.

The straw bales are fed from the left at a rate corresponding to the combusting rate in such a way that the burning bale front remains at a fixed position.

The figure shows the different process areas. Due to diffusion and subsequent condensation of water vapour, a zone may appear of straw with a water content higher than that of raw straw. As the temperature rises, the straw is dried and after that it undergoes pyrolysis. The required heat is transported from the burning surface through thermal conduction and radiation.
When the devolatilization of the straw is finished straw char remains. The burning of the char finally results in a layer of ash or slag.

Primary air is injected for the combustion at the straw surface, while oxygen for the combustion in the furnace room of the remaining gases is provided by a secondary air stream.

The work presented in this paper constitutes an initial attempt to model what happens in the straw bales and at the burning surface. The resulting computer model is, in principle, able to predict:

- Flow rate, temperature and composition of the gas as function of axial length and time.
- Flow rate, temperature and composition of gas entering the furnace room as function of time.
- Temperature and composition of the straw as function of axial length and time.

The mathematical formulation is one-dimensional and the flow of gas through the straw bales are described by means Darcy's law for flow through a porous medium.

So far, no comparison has been carried out against experiments. This will, however, be done in the near future. Alongside with the theoretical efforts experiments are being carried out with the purpose of measuring temperature and concentration profiles within surface burning straw bales as well as in the furnace room, conf. DTI and RISGE (1992).
2. MATHEMATICAL MODEL

Some definitions:

"Straw bale": Total bale including air.
"Straw": Biomass only, air not included.
"Straw grid": Biomass only, air not included.

2.1. Assumptions

The following assumptions are made:

1) The system is one-dimensional in space.

2) The cross sectional area of the straw bales is constant.

3) The gas can be described as an ideal gas.

4) The flow of gas through the straw grid can be described by means of Darcy's law for flow through a porous medium.

5) The velocity of the straw grid is constant in the axial direction (but not in time).

6) The porosity and the permeability of the straw grid depends upon time and the location in the bale.

7) Only water vapour diffusion is considered at the moment.

8) Straw-gas and gas-gas thermal radiation is neglected in the straw bales. This means that heat is exchanged between straw and gas by convection only.

9) Combustion takes place at the exit surface only.

2.2. Basic equations

Mass conservation for component no. i in the gas phase:

\[
\frac{\partial m_i}{\partial t} + \frac{\partial}{\partial x} \left( \frac{m_i u_g}{g} \right) = \Gamma^i + S_g
\]  
(2.2.1)

Mass conservation for component no. i in the straw:

\[
\frac{\partial m_i}{\partial t} + u_h \frac{\partial m_i}{\partial x} = - \Gamma^i - S_h
\]  
(2.2.2)
Energy conservation for the gas phase:

\[
\frac{\partial \rho g}{\partial t} + \frac{\partial}{\partial x} \{ \rho g u_g \} = \dot{Q}_g + \sum_i \{ \Gamma_i h^P + s_{inj} h_{inj} \}
\]  

Energy conservation for the straw:

\[
\frac{\partial \rho}{\partial t} + u_h \frac{\partial \rho}{\partial x} = \dot{Q}_h - \sum_i \{ \Gamma_i h^P + \frac{\partial}{\partial x} (r_i h_{inj}) \}
\]

Momentum equation for gas phase (Darcy's law):

\[
u_g = u_h - \frac{K}{\mu_g} \frac{dp}{dx} - g \cos \theta \rho_g
\]

Momentum equation for straw:

\[u_h = \text{constant}\]

Ideal gas law:

\[p = \frac{RT \rho_g}{MW_g}\]

The above equations (2.2.1) - (2.2.7) are used for transient calculations.

During the calculation of the initial steady state the equation system is recast in a different, but equivalent form as shown below:

The mass conservation equations (2.2.1) for the gas phase components are each divided by the molecular weight of the component and summed.

The resulting equation may be written

\[
\frac{\partial}{\partial x} \{ n_g u_g + \sum_i \frac{m_g}{MW_i} \Delta u_g \} = \sum_i \frac{\Gamma_i + s_{inj}}{MW_i}
\]
where, from eq. (2.2.7)

\[ n_f = \sum_{i}^{i} \frac{m_i}{m_f} = \phi_i f_i \sum_{i}^{i} \frac{c_i}{m_f} = \phi_i C_i = \phi_i P \quad \text{(2.2.9)} \]

Equation (2.2.8) is used to compute the initial steady state gas velocity distribution. Equation (2.2.5), the Darcy equation, is rewritten as follows:

\[ \frac{\partial p}{\partial x} = - \left( \frac{u_g - u_h}{\phi} \right) - g \cos \theta f_g \quad \text{(2.2.10)} \]

and used to compute the initial steady state gas pressure distribution.

In other words, during the calculation of the initial steady state, eqs. (2.2.8) and (2.2.10) replaces eqs. (2.2.5) and (2.2.7).

### 2.3: Relationships and constraints

\[ m_g = \sum_{i}^{i} m_i \quad \text{(2.3.1)} \]

\[ m_h = \sum_{i}^{i} m_i \quad \text{(2.3.2)} \]

\[ C_g = \frac{m_i}{\phi} \quad \text{(2.3.3)} \]

\[ C_h = \frac{m_i}{1 - \phi} \quad \text{(2.3.4)} \]

\[ C_i = \frac{m_i}{m_j} \quad \text{(2.3.5)} \]
\[ u_g = u_g + \Delta u_g \]  
(2.3.6)

\[ u_g = \sum_{m_g}^i u_g \]  
(2.3.7)

\[ \Delta u_g = \frac{d}{dx} \phi c_g \]  
(2.3.8)

\[ M_{g} = \sum_{i}^l \frac{c_g}{C_g/MN} \]  
(2.3.9)

\[ c_{\rho_j} = \sum_{j}^i c_j c_{\rho_j} \]  
(2.3.10)

\[ h_g = \frac{e_g}{m_g} \]  
(2.3.11)

\[ h_h = \frac{e_h}{m_h} \]  
(2.3.12)

\[ T_g = \frac{h_g - C_g h_w g}{c_{\rho g}} + T_{ref} \]  
(2.3.13)
\[ T_h = \frac{h_h}{c_p} + T_{ref} \quad (2.3.14) \]

\[ h_p = c_{fh} (T_h - T_{ref}) + \Delta h_p \quad \text{if } \Gamma > 0. \quad (2.3.15) \]

\[ h_p = c_{pg} (T_g - T_{ref}) + \Delta h_p \quad \text{if } \Gamma < 0. \quad (2.3.16) \]

\[ Q_g = Q_{fg} + (1 - \delta) Q_{fh} + Q_{hg} \quad (2.3.17) \]

\[ Q_h = \delta Q_{fh} - Q_{hg} \quad (2.3.18) \]

\[ Q_{hg} = h_{tc}(T_h - T_g)A_{int}/A \quad (2.3.19) \]

The following constraints apply:

\[ \sum_i c_j = 1 \quad (2.3.20) \]

\[ \sum_i \{s_{ij} - s_{ij}^{*}\} = s^{*} \quad (2.3.21) \]
2.4. Evaporation and condensation of water

The water evaporation and condensation rates are computed from the following expressions:

Evaporation:

\[ \Gamma_w^w = k_f^w m_w^w \]  \hspace{1cm} (2.4.1)

\[ k_f^w = A_f^w(T_h^w - T_{water}) \text{ if } T_h^w > T_{water} \text{ else } 0 \]  \hspace{1cm} (2.4.2)

Condensation:

\[ \Gamma_c^w = -k_c^w (m_g^w - m_{g,max}^w) \text{ if } m_g^w > m_{g,max}^w \text{ else } 0 \]  \hspace{1cm} (2.4.3)

\[ k_c^w = \text{constant} \]  \hspace{1cm} (2.4.4)

The max possible water content of the gas phase is calculated as function of straw temperature and pressure as given in Gundtoft (1988)

2.5. Pyrolysis of straw

The rate of formation of gases from pyrolysis of the straw is computed from an Arrhenius type expression:

\[ \Gamma_i^i = k_f^i m_i^i \]  \hspace{1cm} (2.5.1)

\[ k_f^i = A_f^i \exp(-T_f^i/k_h^i) \]  \hspace{1cm} (2.5.2)
2.6. Combustion of gas

The gas phase is assumed to consist of up to four pseudo components:

1) Oxidant
2) Volatiles from the pyrolysis of the straw
3) Water
4) Combustion products

The oxidant consists of oxygen and nitrogen.

In the present version of the code it is further assumed that:

a. The volatiles from the pyrolysis of the straw contains
   1) Carbon dioxide
   2) Water
   3) A combustible fuel pseudo component

      at a fixed a priori specified ratio \\

b. The combustible fuel pseudo component contains:
   1) Hydrogen
   2) Methane
   3) Carbon monoxide

      also at a fixed a priori specified ratio \\

It is the intention to relax these restrictions at a later stage by
incorporating a pyrolysis module which yields composition as well as rate
of formation of the gas formed by pyrolysis of the straw.

The combustion of 1 kg of fuel proceeds as follows:

\[
1 \text{ kg fuel} + S_{FU} \text{ kg oxidant} + \{C_U \text{ kg CO}_2 + C_U \text{ kg H}_2\text{O}\}/C_U \rightarrow \\
\text{CO}_2 \cdot \text{H}_2\text{O} \cdot \text{FU} \\
[1 + S_{FU} + [C_U + C_U]/C_U] \text{ kg products or} \\
\text{a kg H}_2\text{O} + b \text{ kg CO}_2 + c \text{ kg N}_2
\]

(2.6.1)

where
The rate of combustion of the gaseous fuel is calculated from the Arrhenius expression

\[ \text{FU} \quad \text{FU} \quad \text{FU} \]
\[ S = - m^g k_F \]  

\[ \text{FU} \quad \text{FU} \quad \text{FU} \]
\[ k_F = A_F \exp(- T_F / T_K) \]  

Formation of volatiles (which is negative):

\[ \nu \quad \text{FU} \quad \text{FU} \]
\[ S^g = S^g / C_U \]  

Formation of oxidant (which is negative):

\[ \text{OX} \quad \text{FU} \]
\[ S^g = S^g S^g \]  

Formation of products from combustion of gaseous fuel:

\[ \text{PR} \quad \text{FU} \quad \text{FU} \]
\[ S^g = - S^g \{ S^g_F + 1 / C_U \} \]  

Heat production from combustion of gaseous fuel:

\[ \text{FU} \]
\[ Q = - S \Delta h_F^g \]  

\[ \Delta h_F^g = \{ 10.1 C_{\text{FU}}^0 + 121. C_{\text{FU}}^1 \} 10 \]
2.7. Combustion of straw char

The solid matter which is left after complete pyrolyzation, i.e. the straw char, is assumed to consist of two components:

1) Carbon
2) Ash

It is further assumed that the combustion products are

1) Carbon dioxide
2) Carbon monoxide
3) Nitrogen
4) Ash

No NOx model is incorporated at present.

The ratio of carbon monoxide to carbon dioxide formation rate is described by an Arrhenius expression:

\[ r = \frac{CO}{CO_2} = A_r \exp\left\{ - \frac{T_r}{T_{kh}} \right\} \quad (2.7.1) \]

(See, e.g., Smoot and Prat (1979))

Introducing

\[ \frac{1 + r}{1 + r/2} = f_i \quad (2.7.2) \]

the carbon burns according to:

\[ f_i \, C + O_2 \rightarrow 2(\tilde{f}_i - 1) \, CO + (2 - \tilde{f}_i) \, CO_2 \quad (2.7.3) \]

The combustion of 1 kg of carbon proceeds as follows:

\[ 1 \, \text{kg carbon} + f \, \text{kg ash} + S_c \, \text{kg oxidant} \rightarrow f \, \text{kg ash} + d_1 \, \text{kg CO}_2 + d_2 \, \text{kg CO} + e \, \text{kg N}_2 \quad (2.7.4) \]

where
\[
\frac{11(2 - \phi_i)}{3\phi_i} = d_1 \quad (2.7.5)
\]
\[
\frac{14(\phi_i - 1)}{3\phi_i} = d_2 \quad (2.7.6)
\]
\[
E = S_C \frac{N_2}{C_{O_2X}} \quad (2.7.7)
\]
\[
f = \frac{f_{ASH}}{C_{K_i} C_{K}} \quad (2.7.8)
\]
\[
S_C = \frac{8}{3\phi_i C_{O_2X}} \quad (2.7.9)
\]

Following Field et al. (1967) the rate of combustion of the carbon is based on an overall rate constant which is found by combination of the rate constants due to chemical kinetics and bulk diffusion. (See also Wall (1987)):

\[
S_h = - k_c C g \frac{A_{int}}{A} \quad (2.7.10)
\]
\[
k_c = \frac{p}{1/k_d + 1/k_c} \quad (2.7.11)
\]
\[
k_d = \frac{5.10^{-12} T_m}{r \ d_h} \quad (2.7.12)
\]
\[
k_c = A_c \exp\{- r_c / C_{th}\} \quad (2.7.13)
\]
\[
T_m = 0.5 (T_{K_g} + T_{K_h}) \quad (2.7.14)
\]
The formation of oxidant (which is negative) is:

\[ \text{OX} = C \]

\[ S_{h_0} = S_0 - S_h \] (2.7.15)

Formation of products from combustion of carbon is:

\[ \text{PR} = C \]

\[ S_{h_0} = -S_h \{d_1 + d_2 + e\} \] (2.7.16)

Heat production from combustion of carbon:

\[ Q_{Fh} = -S_h \Delta h_{Fh} \] (2.7.17)

\[ \Delta h_{Fh} = \left\{ \frac{(2 - fi) (fi - 1)}{fi} \right\} 10^6 \] (2.7.18)

2.8. Thermal radiation

The finite difference grid which constitutes the basis for the discretization of the differential equations (2.2.1) - (2.2.10) is shown below in fig. 2.1.

---

Fig. 2.1. Finite difference grid.

The straw bales enter from the left and burn on the surface \( N+1/2 \) to the right.
Thermal radiation heat transfer between straw and gas and between the gas in different cells are neglected. Radiation heat transfer occurs only between straw in different cells and between the burning straw at the exit surface and the combustion chamber.

The radiation heat flux between the cells $k$ and $k+1$ is obtained from

$$ q_{k+1} = \frac{E_k - E_{k+1}}{1/e_k + 1/e_{k+1} - 1} $$

(2.8.1)

where

$$ E = \sigma T^4 $$

(2.8.2)

$$ \sigma = 5.67 \times 10^{-8} $$

(2.8.3)

2.9. Boundary and initial conditions

The initial steady state is determined by the specification of the following set of parameters:

1) The feed velocity of the straw bales.
2) The inlet gas velocity.
3) The inlet composition of the straw.
4) The inlet composition of the gas.
5) The inlet temperature (assumed equal for gas and straw).
6) The inlet gas pressure.
7) The exit boundary temperature, i.e. the temperature "seen" by the burning straw surface.
8) The exit boundary emissivity, i.e. the emissivity of the material "seen" by the burning straw surface.
9) The flow rate of air injected towards the burning surface.
10) The temperature of the air injected towards the burning surface.

Transients may be imposed by variation of one or more of the above mentioned parameters determining the initial steady state.
3. EXAMPLE PROBLEM

An example problem has been run with following specifications:

- Feed velocity of the straw bales: 0.00075 m/sec
- Inlet air velocity 0.00075 m/sec
- Inlet temperature 50. C
- Inlet gas pressure 0.1 Pa
- Exit boundary temperature 1000. C
- Exit boundary emissivity 1.
- Rate of air injected at burning surface 0.045 kg/sec
- Temperature of air injected at burning surface 50. C

Other parameters were:

- Porosity of straw bales 0.78
- Water content of straw (weight fraction) 0.01
- Straw-gas heat transfer coefficient 0.25 W/m²/C
- Fraction of heat from char combustion deposited in char: 0.5
- Emissivity of straw 0.9
- Water vapour diffusion coefficient .000026 m²/sec

Results from the initial steady state calculation are shown in figs. 3.1 - 3.4.

It is seen (figs 3.1 - 3.3) that the water in the straw evaporates when the straw temperature reaches 100 centigrade. The water vapour then diffuses backwards towards the inlet and lower temperatures. Consequently, the vapour condenses on the straw and is again moved forward. As a result of this behaviour the water content of the straw exceeds the inlet value at locations just before the point where the straw reaches 100 C.

This movement of the water component around the boiling point is illustrated in fig. 3.3. In the figure the gas and the straw phases are displayed separately. The arrows indicate the direction of water movement.

The pyrolyses of the straw begins when the straw temperature reaches about 200 C and is more or less finished at 550 C. (Conf. fig. 3.2)
Fig. 3.1 Straw and gas temperature distributions.

Fig. 3.2 Mass fraction distributions.
Fig. 3.3 Initial water vapour velocity distribution and sketch of water movements around boiling point.

Fig. 3.4 Initial water vapour velocity distribution.
4. SUMMARY AND CONCLUSIONS

A computer model has been developed for the calculation of the steady and non-steady behaviour of surface combusting straw bales. The mathematical formulation is one-dimensional and the flow of gas through the straw bales is described by means of Darcy's law for flow through a porous medium.

The model treats important phenomena as:

1) Evaporation, condensation and diffusion of water
2) Pyrolysis of straw
3) Combustion of gas
4) Combustion of straw char
5) Thermal radiation
6) Heat conduction in the straw
7) Straw-gas heat transfer
8) The straw bale properties such as porosity, permeability and water content may vary with time and the location in the bale.

So far, no comparison has been carried out against experiments. (This will be done in the near future, conf. DTI and RISOE (1992)).

Numerical experiments show, however, that the results obtained with the model exhibit trends similar to those that would be expected and which have been observed in preliminary experiments. (Wolff (1993)).
5. NOMENCLATURE

a Defined in eq. (2.6.3) (-)
A Cross sectional area of straw bale (m²) or rate constant (1/sec).
A' Internal area of straw grid per unit axial length (m).

b Defined in eq. (2.6.4) (-)

c Defined in eq. (2.6.5) (-)
C Mass fraction (-)
Cp Heat capacity (J/kg/C).

d Diameter (m)
d1 Defined in eq. (2.7.5) (-)
d2 Defined in eq. (2.7.6) (-)
D Water vapour diffusion coefficient (m²/sec).

e Specific energy (J/m³), straw emissivity (-) or defined in eq.(2.7.7) (-).
E \( G^* T^4 \)

f Defined in eq. (2.7.8) (-)
fi Defined in eq. (2.7.2) (-)

h Acceleration of gravity (ra/sec²).

Δh Heat evaluated/consumed at phase transition straw-gas or heat evaluation during combustion(J/kg).
htc Heat transfer coefficient (W/m²/C).

k Reaction rate coefficient (1/sec) or reaction rate (kg/sec/m²).
k Reaction rate coefficient (kg/sec/m²/Pa).
K Permeability of straw grid (m², mD).

L Length (m)

m Specific mass (kg/m³).
MW Molecular weight (kg).

n Number of moles per unit volume (-).
p Gas phase pressure (Pa).
q'' Heat flux (W/m²).
Q Heat production per unit volume (W/m^3).

r Ratio of carbon monoxide to carbon dioxide formation rate (-).

R Gas constant (8315. Pa*m^3/K).

S Mass source in gas equations, mass sink in straw equations (kg/m^3/sec).

t Time (sec).

T Temperature (C).

T Temperature (K).

u Velocity (m/sec).

x Axial coordinate (m).

Greek:

\( \Phi \) Fraction of heat developed during combustion of char deposited in the char.

\( \Delta \) Difference operator

\( \phi \) Porosity of straw grid (-).

\( \Gamma \) Transfer of mass from straw grid to the gas phase per unit volume and time (kg/m^3/sec).

\( \lambda \) Thermal conductivity of straw grid (W/m/C).

\( \lambda_e \) Effective "conductivity" of straw grid which takes into account heat conduction as well as thermal radiation (W/m/C).

\( \sigma \) Stephan Boltzmann constant (5.67E-8 W/m^2/K^4).

\( \mu \) Dynamic viscosity (kg/m/sec).

\( \rho \) Density (kg/m^3).

\( \theta \) Angle between x-axes and vertical (degrees).
Lower indices:

- Condensation
- Carbon
- Diffusion
- "Exit boundary condition"
- Evaporation
- Combustion
- Fuel
- Gas
- Straw or straw grid
- From straw to gas phase
- Injection
- Straw grid internal surface
- Phase index
- Grid cell index
- Kelvin or char
- Average
- Maximal value
- Number of last grid cell
- Oxidant
- Pyrolysis
- Combustion products
- Reference
- Saturation
- Gas formed by pyrolysis (volatiles)
- Water
- Coordinate direction
- Coordinate direction
- Coordinate direction
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MODELLING OF BLACK LIQUOR PYROLYSIS

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ABSTRACT

Model for pyrolysis of black liquor droplets in high temperature atmosphere is described.

INTRODUCTION

Black liquor as a fuel has similarities to different liquid fuels as heavy fuel oil droplet, multicomponent liquid fuel and coal water slurry. Models for heavy fuel oil [1], coal water slurry and multicomponent liquid fuel [2] vaporization and pyrolysis have been presented. The black liquor droplets contain a great amount of water and the drying and pyrolysis occurs partly simultaneously according to calculations based on the present model even when the droplet size is small [3]. The black liquor droplets swell significantly during drying and pyrolysis. The droplet volume increases to a size about 30 times the original size. The model presented here is based on a previous model used for wood particle pyrolysis [4]. The combustion properties of black liquor have recently been studied [5].

MODEL DESCRIPTION

The model is based on the solution of the droplet energy equation, which is in spherical coordinates

$$\rho_c \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( \lambda r^2 \frac{\partial T}{\partial r} - \dot{C}'' r^2 T \right) + l_u \dot{\phi}_u + l_v \dot{\phi}_v$$  \hspace{1cm} (1)

where both conduction and convection inside the droplet are included. The combined convection and radiation heat transfer between the surroundings and the droplet surface is described by the boundary condition

$$h(T_s - T_{r=R}) + \varepsilon \sigma (T_s^4 - T_{r=R}^4) = \left( \lambda \frac{\partial T}{\partial r} \right)_{r=R}$$  \hspace{1cm} (2)

The local heat capacity flux consists of the contributions of vapour and volatiles fluxes

$$\dot{C}'' = c_u \dot{m}_u'' + c_v \dot{m}_v''$$  \hspace{1cm} (3)

The pyrolysis occurs in a wide temperature interval. The mass flux of volatiles is
related to the volumetric generation by

\[ m'' = \frac{1}{r^2} \int_0^r \rho_i r^2 dr \] (4)

The evaporation is assumed to occur on a spherical receding wet core. The mass flux of steam is related to this core and the heat flux by

\[ \dot{m}'' = -\rho_d \mathcal{N} \left( \frac{R}{r} \right)^2 \frac{dR}{dr} = -\frac{\lambda}{l_u} \left( \frac{R}{r} \right)^2 \left( \frac{\partial T}{\partial r} \right)_{r=R_u} \quad \text{when } r>R_u \] (5)

\[ = 0 \quad \text{when } r<R_u \]

The pyrolysis is treated as successive evaporations of different components at different temperature levels. Then the kinetics is assumed to be infinitely fast, but the different evaporation temperatures are taken into account. The 'evaporation temperatures', which are described by a continuous function \( m(T)/m_0 = e(T) \), are obtained as mass \( m(T) \) measured with a thermobalance for a small initial sample \( m_0 \) in inert atmosphere by using a slow heating rate. Then the transient local density and local generation of volatiles inside the particle are described by relations

\[ \rho_u(T) = \frac{\rho_0 e(T)}{\beta}, \quad \dot{\rho}_v = -\frac{\partial \rho_d}{\partial T} = -\frac{\rho_0 e'(T)}{\beta} \frac{\partial T}{\partial t} \] (6)

The validity of this assumption for rapid heating is questionable. In future development, an Arrhenius type rate equation for the local generation for volatiles will be considered. Grid-heater pyrolysis results obtained by Åbo Akademi for black liquor will be analyzed and utilized.

A model for particle swelling during pyrolysis has been presented for a swelling coal [6], but the swelling behaviour of black liquor is different and much greater compared to coal. The swelling in the model calculations is not based on a physical swelling model so far, and the droplet swelling is accounted for by using experimental correlation of Frederick [7]. The equations (1)-(5) apply to a non-swelling case, but are also used to the swelling case by replacing \( r \) with a stretched coordinate \( r_s \). The swelling is assumed to take place linearly so that \( r_s/R = 2R_s/R \), where \( r \) and \( R \) are the coordinate and the droplet radius for non-swelling case (droplet initially) respectively. \( 2R_s \) is the droplet diameter that is increasing during drying and pyrolysis due to swelling and calculated by using the experimental correlation. The calculation method will be refined and generalized in the future to non-linear swelling cases.

The droplet contains some liquid water almost at the end of the pyrolysis. The drying time in next calculations denotes the time, when 90% of moisture initially in the droplet has been released.
CALCULATION RESULTS

The effect of particle size on the droplet drying (90%) and pyrolysis time is presented in Table 1.

<table>
<thead>
<tr>
<th>d (μm)</th>
<th>10</th>
<th>100</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying time, ms</td>
<td>0.27 (0.27)</td>
<td>22 (25)</td>
<td>1500 (2000)</td>
</tr>
<tr>
<td>Pyrolysis time, ms</td>
<td>0.42 (0.42)</td>
<td>37 (39)</td>
<td>2900 (3300)</td>
</tr>
</tbody>
</table>

Table 1. Drying and pyrolysis times for different droplet sizes, when gas and wall temperatures are 1000°C and dry solids content is 60%.

Values in brackets have been calculated without the effect of radiation. It is seen that the contribution of radiation increases, when the droplet size is large. Constant slip velocity 0.5 m/s is assumed in the calculations. The effect of slip velocity on the heat transfer coefficient increases with increasing droplet size. If the slip velocity were zero, then the drying and pyrolysis times would be proportional to diameter power two, when the effect of radiation is neglected. Now the exponent is smaller due to slip velocity.

The droplet heating rate is mostly affected by the droplet size. This is shown in Figure 1 for temperatures $T_g = T_s = 800-1200°C$ for droplets with dry solids content 60%. It should be noted that the droplet swells significantly.

The value of the heat of pyrolysis is not known, and the value 610kJ/kg is used in the calculations. The dry mass/volume in the droplet is assumed to be 650kg/3 and the amount of volatiles is 51%.

Figure 1. The time derivative of the average (mass average without water) droplet temperature $dT/dt$ at time instant, when 50% of the volatile matter has escaped the droplet.

The heating rates are very high, when the droplet size is small and the use of low heating rate $tg$-curve $e(T)$ is questionable. There probably exists a critical droplet size. The pyrolysis of larger droplets than the critical size is controlled by heat transfer and equation (6) can be applied.
The effect of gas temperature on the droplet drying (90%) and pyrolysis times is shown in Figure 2. In this case temperatures $T_g = T_s = 1000^\circ C$. The effect of dry solids content on drying and pyrolysis is shown in Figure 3.

Figure 2. The effect of gas temperature on the drying and pyrolysis times.

Figure 3. The effect of dry solids content on drying and pyrolysis times.
ANALYSIS OF RAPID PYROLYSIS IN A GRID-HEATER

Rapid heating measurements in inert atmosphere are required in order to obtain the parameters for the chemical kinetics of pyrolysis. A fast heating rate can be achieved by using an entrained-flow reactor, drop tube furnace and a grid-heater. The measurements do not directly give the parameters of the chemical kinetics of devolatilization, but the heat transfer and possible mass transfer effects must be analysed in order to find out the kinetical effects.

As far as the author is aware, an entrained-flow reactor or a drop tube furnace has not been used to examine the fast pyrolysis of black liquor, which may be difficult due to liquor properties. The droplets may adhere to walls. The grid-heater is more easy to be used for black liquor. In the following the rapid heating of a sample in a grid-heater is analysed.

The heat transfer is approximated with one-dimensional Fourier equation

\[ \rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left( \lambda \frac{\partial T}{\partial x} \right) \]  

(7)

The boundary condition on the wire heater side is

\[ \frac{a}{m_r}[T_h - T_{x=0}] + (1 - \alpha)[h_0(T_g - T_{x=0}) + \varepsilon \sigma (T_s^4 - T_{x=0}^4)] = \lambda \left( \frac{\partial T}{\partial x} \right)_{x=0} \]  

(8)

where \( m \) is the contact heat transfer resistance between the heater and the sample. The heater and the sample are not necessary in direct thermal contact, but a narrow gas gap may exist or be formed through which heat is transferred by conduction and by radiation. The boundary condition (8) is averaged. It is weighted by surface areas. Part of the sample (100*\( \alpha \% \)) is heated by the heater and the rest of the surface emits heat to surroundings by radiation and convection. The heat losses from the upper surface of the sample is presented by the boundary condition

\[ h_1(T_{x=d} - T_g) + \varepsilon \sigma (T_{x=d}^4 - T_s^4) = -\lambda \left( \frac{\partial T}{\partial x} \right)_{x=d} \]  

(9)

In more exact analysis the heat conduction in the sample should be treated two-dimensionally. In the following simplified examples, the thermal properties (density 650kg/m³, specific heat 2 kJ/kgK, heat conductivity 0.5 W/mK and surface emissivities 0.8) of the sample are assumed to remain constant during the heating and pyrolysis. The gas gap between the wire and the sample is assumed to be 10\( \mu \)m. Most of the heat losses are transferred by radiation, the convection heat transfer coefficient is assumed to be 20W/m²K.

The calculated surface temperatures and average temperatures of the sample are shown in Figure 4 for a case, in which the heating rate is 1000 K/s and the average sample temperature for different sample thickness is presented in Figure 5. It is seen that the heater temperature that is measured ann controlled clerly differs from the sample temperature. The pyrolysis kinetics depends on temperature by an exponential function, and the knowledge of the real sample temperature is important in the determination of the kinetic parameters. The error can be decreased by decreasing the sample heat losses.
by constructing the heater for example so that it consists of two grids between which the sample is placed. The error can also be decreased by correcting the sample temperatures according to calculations.

Figure 4. Temperature of the grid-heater and calculated surface and average temperatures of the sample, heating rate 1000K/s, thickness of layer 0.5 mm.

Figure 5. Temperature of the heater and average temperatures of sample with different sample thicknesses.
CONCLUSIONS

A model for pyrolysis of black liquor based on a previous pyrolysis model for wood particles has been developed by including the droplet swelling in the model.

To improve the model, further refinements are required with respect to the treatment of the local devolatilization inside the droplet especially in rapid heating conditions. Also in the present case, the swelling behaviour is not predicted by model calculations, but it is included by using experimental results for the measured droplet diameter. Now swelling of the droplet is averaged throughout using a constant local radius ratio. In reality, it is probable due to temperature propagation that at first the droplet surface layer swells, and the swelling is propagated towards the droplet centre causing further stretching of the droplet outer layer.

The better understanding of the local swelling inside the droplet is especially important in the estimation of the local effective heat conductivity. Both the pore size and the local averaged density have an effect on the effective local heat conductivity inside the droplet. The increase in the pore size increases the radiation heat flow. The decrease in the density decreases the contribution of conduction heat flow.

The model will later be compared to experimental results presented in the literature for large droplet sizes. There is a lack of experimental results for small droplets.

The rapid pyrolysis kinetics of black liquor can be studied by using a grid-heater, but the sample temperature may differ significantly from the temperature of the heater, which should be accounted for in the determination of the Arrhenius parameters.

ACKNOWLEDGEMENTS

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LITERATURE


NOMENCLATURE

Symbols

- $C^*$ heat capacity flow rate/area, W/m$^2$K
- $c$ specific heat, J/kgK
- $d$ thickness of sample layer, particle diameter, m
- $h$ heat transfer coefficient, W/m$^2$K
- $k_a$ dry solids content, %
- $l_v$ heat of vaporization of water, J/kg
- $l_p$ heat of pyrolysis, J/kg
- $m_0$ initial sample mass, kg
- $m(T)$ sample mass as function of temperature of sample
- $m_r$ contact thermal resistance, m$^2$K/W
- $R$ radius, m
- $r$ coordinate from centre of droplet, m
- $T$ temperature, K
- $t$ time, s
- $x$ coordinate from the lower surface of sample upwards, m
- $\alpha$ surface area ratio
- $\beta$ volumetric swelling ratio
- $\epsilon$ emissivity
- $\lambda$ heat conductivity, W/mK
- $\rho$ density, kg/m$^3$
- $\rho_s$ steam or pyrolysis product generation/volume, kg/m$^3$s
- $\sigma$ = 5.67 W/((m$^2$(100K)$^4$)), Stefan-Bolzmann’s constant

Indexes

- $0$ lower surface of sample, location $x=0$, initial
- $1$ upper surface of sample, location $x=d$
- $a$ average
- $d$ dry particle
- $g$ gas
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Term</th>
</tr>
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<tbody>
<tr>
<td>h</td>
<td>heater grid</td>
</tr>
<tr>
<td>K</td>
<td>upper surface of sample</td>
</tr>
<tr>
<td>ka</td>
<td>dry solids</td>
</tr>
<tr>
<td>s</td>
<td>radiation</td>
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<td>u</td>
<td>evaporation</td>
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<tr>
<td>v</td>
<td>pyrolysis</td>
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EMISSIONS FROM SMALL SCALE BIOFUEL COMBUSTION - RESEARCH NEEDS

M. Karlsson, Sweden
Rapport A 93-207

Emissioner från småskalig biobränsleeldning - forskningsbehov

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Denna rapport ges även ut som Statens Provningsanstalt
Rapport 1993:44
INLEDNING

Emissioner från småskalig vedeldning har uppmärksammats allt mer under den senaste tioårspериoden. De negativa effekterna av emissionerna har främst satts i samband med tyngre kolväten (tjära) och gränsvärden har införts för tjärutsläpp från pannor och kaminer som installeras i tätort. Dessa gränsvärden för tjärutsläpp, 30 mg/MJ och 40 mg/MJ, för miljögodkännande av villapannor resp. kaminer (BFS 1988) har medfört att pannor med betydligt förbättrade emissionsegenskaper vad gäller tjärutsläpp har utvecklats. Tjärutsläppen kunde reduceras med en till två tiopotenser jämfört med tidigare konstruktioner. I takt med att befintliga pannor byts ut mot nya, miljögodkända erhålls därmed en dramatisk förbättring från miljösynpunkt.

Emellertid visar emissionsmätningar (Karlsson och Gustavsson 1992) att även betydande emissioner av flyktiga organiska ämnen (VOC, Volatile Organic Compounds) och kväveoxider (NO\textsubscript{x}) förekommer. Kväveoxidemissionerna är normalt mycket högre än vad som tolereras från större anläggningar och VOC är oönskade pga diverse negativa miljöeffekter.

Samtidigt som man konstaterar att emissionerna från småskaliga biobränsleledade anläggningar är högre än vad som tolereras som utsläpp från större pannor är kunskapen om förloppen i små anläggningar betydligt mycket mindre än om motsvarande i stora anläggningar. Överhuvudtaget har, även internationellt sett, endast obetydlig uppmärksamhet riktats mot förbränning av biobränslen. Det finns alltså anledning att diskutera vad som behöver göras för att förbättra kännedomen om förbränning av biobränslen, främst trä, i småskaliga förbränningsanordningar. Detta är ämnet för föreliggande rapport som skall behandla anordningar mindre än 10 MW, alltifrån pannor för uppvärmning av enstaka hus till pannor för större byggnader, industrier och fjärrvärmesystem. Storleksbegränsningen 10 MW har valts i enlighet med propositionen 1992/93:179.

DEFINITIONER OCH UTGÅNGSPUNKTER

Emissioner

Med tjäror menas tyngre kolväten eller organiska föreningar med kokpunkter vid höga temperaturer. Hit hör också polycykliska aromatiska kolväten (PAH) och

VOC är ett samlingsbegrepp för organiska ämnen som avges i gasfas. I begreppet innefattas en rad ämnesgrupper såsom lättare alkaner, alkener, alkyner, aldehyder, ketoner, aromater och alkoholer. Även enkla halogensubstituerade organiska ämnen räknas in. VOC bidrar till växthuseffekten och är en väsentlig orsak till oxidantbildningen i atmosfären. Vissa komponenter har också direkta hälsoeffekter, t ex bensen.

THC, totalkolväten uttryckt som metanekvivalenter, är en storhet som mäts genom förbränning av rökgas i en speciell analysator. Det är ett samlingsbegrepp som alltså även omfattar det mesta av ovanstående tjäror och VOC.

Kolmonoxid, CO, är den traditionellt använda indikatorn på ofullständig förbränning. CO kan grovt sett korreleras med kolvätena, eftersom huvuddelen av CO liksom kolvätena härstammar från bränslenas flyktiga beståndsdelar.

Om syftet enbart är att karakterisera en anläggnings förbränningsegenskaper räcker det att diskutera emissionerna av CO och THC, båda är mått på ofullständig förbränning.

Kväveoxiderna (NO$_x$) är en betydelsefull emission. Den består praktiskt taget enbart av NO, och andra kväveoxider. NO$_2$ och lustgas N$_2$O, förekommer endast i obetydliga kvantiteter vid förbränning av trä vid atmosfärstryck. I motsats till tidigare nämnda emissioner är kväveoxiderna inte ett resultat av ofullständig förbränning utan en slutprodukt.

Det primära problemet vid biobränsleförbränning i småskaliga anläggningar är att uppnå slutförbränning av de gasformiga bränslekomponenterna. Därför fokuseras intresset främst på dessa. Minskning av kväveoxide blir genomförbart först då förbränningen totalt sett kan kontrolleras eller styras så att oönskade restprodukter i form av tjäror VOC och CO ligger på en för omgivningen acceptabel nivå. Därmed är inte sagt att kväveoxidminskning inte är ett väsentligt arbetsområde.
Luftfaktorn anger hur mycket av den tillförda luften som förbrukas. Luftfaktorn är oändlig om ingen förbränning skett och lika med ett om allt syre i luften konsumerats vid fullständig förbränning. En luftfaktor t ex lika med två innebär alltså att endast hälften av det tillförda syret förbrukats vid förbränningen.

Pannor

En panna består av en anordning för bränslemottagning, en förbränningsanordning och en värmemottagande del. Pannorna kan delas in i satsvis eldade och kontinuerligt eldade. Normalt hör villapannor eldade med styckeved till den första typen, medan de större pannorna ofta är kontinuerligt eldade med något berett bränsle; flis, pellets, briketter eller pulver.

Förbränning är torkning, avgasning och slutförbränning av koks och gaser och förbränningsanordningarna är mer eller mindre konstruerade enligt denna princip som tydligare visas i figur 1.

![Princip för förbränningsanordning](image)

Figur 1  Princip för förbränningsanordning

Ideellt skall primärluften bara förbränna så mycket bränsle som behövs för att värma det tillförda bränslet så att det torkar och avgasas samt för att förbränna eller eventuellt förgasa koksåterstoden.
Sekundärluft tillsätts för slutförbränning men utnyttjas även för att skapa omrörning.

I många pannor är de olika stegen i figur 1 tydligt skiljda från varandra vilket ger möjligheter att påverka förbränningen mer än om stegen är blandade. Vid villapannor med undre avbränning, exempelvis, är de olika förbränningsstegen separerade ungefär så som visas på figuren. I vissa fall t ex i större pannor sker de första stegen efter varandra på en rost och gasen förbränns ovanför rosten i förbränningsrummet.

Emissionsproblemet består i att slutförbränna gaserna i gasförbränningssteget. Primärsteget är indirekt viktigt genom att det kan skapa störningar i tillförseln av gas, vilket i sin tur kan ge upphov till oförbränd gas.

Bränslet

Bränslets utseende påverkar förbränningsanordningens konstruktion och bränslets egenskaper och dess funktion och därigenom påverkas emissionerna.

Bränslets utseende: Helved, flis, pellets, briketter, pulver.
Bränslets egenskaper: Fukthalt, kvävehalt och askans sammansättning.

Eldningssättet

Stora förbränningsanläggningar sköts av speciellt utbildad och för ändamålet avsedd personal, medan mindre anläggningar, och särskilt villapannor, inte med säkerhet handhas med intresse och omsorg; eldning och skötsel av en panna är sannolikt en lågt prioriterad sysselsättning. Därför kan, av sådana skäl, av samhället önskade emissioner uppstå. Denna aspekt tas inte upp här utan istället antas att alla förbränningsanordningar handhas så som avsetts av tillverkaren.
TIDIGARE UNDERSÖKNINGAR


Däremot finns inte så mycket publicerat om emissioner från småpannor för biobränsleeldning. Den tidigare verksamheten inom detta område var huvudsakligen inriktad på att förbättra förbränningen med syfte att öka verkningsgraden. De CO-utsläpp som då var av intresse låg betydligt högre än dagens önskemål om mycket låga halter i samband med emissionsminimering.


Ett försök till uppskattning av VOC-emissioner från kaminer har vidare redovisats i Braathen m.fl. 1991. Emissioner från kaminer etc redovisas också i Karlsvik m.fl.

EMISSIONSBILDEN

Befintliga mätningar ger en bild av nuläget vad beträffar emissioner från små helvedeldadade pannor och litet större, mestadels kontinuerligt eldade pannor.

Vedpannor

I det följande avses, om inte annat sägs, emissioner från moderna, miljögodkända, vanligen keramiskt inforrade pannor. Data är hämtade från den undersökning som publicerats av Karlsson och Gustavsson 1992. Jämfört med större pannor är utsläppen av oförbrända gaser höga. Om CO-emissionen tas som jämförelsemått visar mätningar på större fastbränslepannor och olje/gaspannor värden i området 50 till 100 mg/MJ, medan vedpannorna ger 10 till 100 gånger mer CO. De höga CO-utsläppen åtföljs av andra oförbrända ämnen. Uttryckt som totalkolväte är kolväteemissionerna genomgående 50 till 5000 mg CH\textsubscript{4}/MJ. I andra tillämpningar är sådana utsläppsivärden helt oacceptabla. Motsvarande utsläpp av kolväten från större fastbränslepannor och olje/gaspannor är noll eller under alla förhållanden klart under 10 mg CH\textsubscript{4}/MJ.

Emissionerna av oförbränt är ännu högre för traditionella, vattenkylda eldstäder än för modernare, miljögodkända pannor med keramiskt inforrade förbränningsrum, se tabell 1.

Tabell 1 Jämförelse mellan vattenkylda och keramiskt inforrade pannor, medelvärdet (Karlsson och Gustavsson 1992)

<table>
<thead>
<tr>
<th></th>
<th>CO mg/MJ</th>
<th>Tjära mg/MJ</th>
<th>VOC mg/MJ</th>
<th>NO\textsubscript{x} mg/MJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miljögodkända pannor</td>
<td>1300</td>
<td>22</td>
<td>453</td>
<td>116</td>
</tr>
<tr>
<td>Traditionell panna</td>
<td>6200</td>
<td>687</td>
<td>1804</td>
<td>68</td>
</tr>
</tbody>
</table>
Skillnaden är större för de tyngre kolvätena (tjära) än för de lättare (VOC). Observera även NO\textsubscript{x} emissionerna som ändras i motsatt riktning jämfört med övriga emissioner.

Ovanstående emissionsdata är medelvärden över tidsperioder som innehåller störningar på grund av transiente förlopp vid start–stopp, störningar i bränslebädden och andra oregelbundenheter som förekommer vid normal drift av småpannor.

Störningarna i emissionsbilden vid transiente förlopp märks tydligt vid dellasteldning av fläktstyrd panna, figur 2. I exemplet i figur 2 är fläkten i drift under de tre perioderna med låga emissioner och en luftfaktor strax under två. Under resten av tiden står fläkten stilla, men ett läckflöde av luft går genom pannan och

![Diagram av emissionsdata](image-url)

**Figur 2** Variationer i emissionerna av CO och THC vid dellasteldning med fläktstyrd panna. Även luftöverskottets variation visas. Det nedre diagrammet är en uppförstoring av det övre diagrammets första timma.

Störningar av transient natur kan också uppstå under kontinuerlig drift på grund av vedtillförsel, genombränning av bränslebädden, valvbildning med påföljande ras i bädden och omrörning i fyren. Två besläktade exempel på de transienta förloppens negativa inverkan är upptändning och vedinlägg på glödbädd. I båda fallen kan emissionerna av oförbränt öka kraftigt. I upptämningsfallet beror detta

![Diagram 1](image1)

![Diagram 2](image2)

**Figur 3** Variationer i emissionerna av CO och THC vid kontinuerlig drift med vedinlägg (ackumulatoreldad panna). Det nedre diagrammet är en uppförstoring av det övre mellan klockan 2:00 och 3:20.
på låg temperatur. Vid vedinlägg tillkommer, förutom en viss avkylning av bränslebädden, även en plötslig avgasning så att slutförbränning inte alltid kan ske.

Figur 3 visar ett exempel på att transenta förhållanden kan spela en roll även under kontinuerlig drift. Man ser av figur 3 att emissionerna ökar när veden börjar att slut, förbränningsintensiteten minskar, luftöverskottet ökar och temperaturen (ej mått) sjunker under tidsperioden strax före vedinlägget vid 3–tiden. Omedelbart efter vedinlägget ökar THC något, men förbränningen förbättras, luftöverskottet sjunker och efter 10 minuter fungerar pannan bra.

Dessa förförs kan bli olika, beroende på bränsle och pannkonstuktion. Även om de är tidsmässigt korta är de betydelsefulla, eftersom de utgör en avsevärd del av de totala emissionerna.


I en fläktreglerad panna är det möjligt att styra lufttillförseln bättre än i en panna med naturligt drag, men i stället ökar antalet start och stopp vid ökande last. Detta får till följd att emissionerna ökar med ökande dellast (i motsats till pannor med naturligt drag). Först då lastnivån nått den för pannan maximala blir emissionsvärdena måttliga (relativt sett). Figur 5 visar emissionsförloppen för en 25 kW fläktstyrd panna vid dellasterna 15, 7 och 3 kW.

Pannan i figur 5 visar samma beteende som den i figur 2. Återigen kan man konstatera att funktionen är bättre under perioderna med lufttillförsel än under stilleståndsslida perioderna. Å andra sidan är gasflödet lågt under stilleståndsslida perioderna, vilket naturligtvis minskar de totala utsläppen. Ett sätt att
Figur 4: Emissioner av några typer av kolväten från en keramiskt infordrad 15 kW panna med naturligt drag. Lasten var 3 kW (timma 0–2), 7 kW (timma 3–5) och 15 kW (timma 6–8). (Karlsson 1992).

Minimera antalet start–stopp samt att låta pannan gå på maxlast under en lång tid är att pannan får ladda en värmeeckumulator som räcker för byggnadens värmebehov under en viss tid, t ex ett dygn. Detta kallas "ackumulatoreldning" i motsats till "direkteldning" då pannan levererar värme direkt efter byggnadens behov.

Kontinuerligt eldade pannor

Med kontinuerligt eldade pannor menas pannor där bränslet tillförs regelbundet i motsats till satsvis eldade. Därmed räknas även stokermatade pannor som kontinuerligt eldade.

I en omfattande undersökning av biobränsleeldade pannor i storleksordningar från 0,5 till 10 MW som utförts av Statens Provningsanstalt (Karlsson m.fl. 1992) erhölls emissionsnivåer som normalt låg betydligt under de bästa som uppmätts för villapannor.
Figur 5 Emissioner från en 25 kW fläktstyrd panna vid dellasterna 15, 7 och 3 kW. Pannan regleras genom på- och avslag
Emissionsförloppens tidsvariationer, varav ett exempel ges i figur 6, visar att en stor del (nästan hela) av kolväteemissionen beror på oregelbundenheter i bränslenheter eller på eldningsanordningen.

Orsaken till variationerna framgår inte av mätningarna, men den bör fastläggas genom nya mätningar, eftersom det kan misstänkas att denna typ av störningar relativt lätt kan åtgärdas genom ändringar i konstruktionen av bränslehanteringssystemet eller i bränsleberedningen.


En annan typ av störning uppträder då pannorna lastregleras genom på- och avslag. På figur 7 visas ett exempel med två stopp vid 2 h och 3,5 h. Särskilt vid

---

Figur 6 Variationer i emissionen av CO och THC från en panna kontinuerligt eldad med träbriketter.
Figur 7 Variationer i emissionen av CO och THC från en fliseldad planrost med förugn under perioder med start och stopp. (Förbränningen representeras av CO₂-koncentrationen.)

påeldning förekommer avsevärda emissions-"spikar" i THC-emissionen som liknar förloppen vid fläktstyrda vedpannor. Liksom visades för andra typer av pannor (se t ex figur 2) uppstår även här kraftiga emissioner under avställningsperioderna.

Kväveoxidemissioner

Kväveoxidemissionerna är i storleksordningen 50 till 140 mg NO₂/MJ. Jämfört med den svenska riktlinjen för maximiemissioner (50 mg/MJ) eller maxvärden för stora anläggningar i städer (Värtan, 30 mg/MJ) verkar de uppmätta värdena för små biobränsleeldade eldstäder vara helt oacceptabla. Även gränsvärdena för oljeeldade villapannor ligger lägre (40 mg/MJ).

Tillgängliga mätresultat är inte sådana att slutsatser kan dras om påverkande faktorer. Flera potentiellt påverkande faktorer har inte mätts eller har sam-varierat.

PÅVERKANDE FAKTÖRER

Ett stort antal mätresultat från ett stort antal anläggningar kan reduceras till en diskussion om inverkan av ett fåtal primärt påverkande faktorer. Här skall främst påverkan på utbrännningen beaktas, kväveoxiderna behandlas separat.
Följande primärt påverkande faktorer skall diskuteras:

1) Förbränningsrummets storlek
2) Luftfaktor
3) Lufttillförsel
4) Omblandning av bränsle—luft
5) Transienta förhållanden
6) Bränslet.

Förbränningsrummets storlek

Förbränningsrummets storlek påverkar förbränningsförloppen på ett flertal olika sätt.

I små förbränningsrum blir begränsningsytan stor i förhållande till volymen, figur 8. Då kan värmeförlusten på grund av strålning till väggarna bli stor om väggarna är kylta och om det brinnande mediet har stor strålningsförmåga, t ex vid koksförbränning och förbränning med lysandeflammor, men inte vid ren gasförrbränning. Om väggarna är okylta kan de ändå ha en negativ effekt, t ex innan de blivit varma. Tjocka väggar bevarar värme under längre tid och tjänar därmed som en utjämnande buffert men tar längre tid att varma.

Figur 8 Yta/volymförhållandet i ett kubiskt rum.
En motsvarande storhet är effekt–volym förhållandet, \( \varphi_{\text{max}} \). Effekten är pannans maximala bränsleeffekt och volymen den del av rökgasutrymmet där huvuddelen av gasförbränningen sker. Förhållandet illustreras med några exempel från kommersiella pannor i figur 9.

Eftersom bränsleeffekten vid givet luftöverskott är direkt relaterad till ett rökgasflöde \( (m^3/s) \) uttrycker kriteriet \( \varphi_{\text{max}} \) även den inverterade medeluppehållstiden \( \tau \) för gasen, \( \varphi_{\text{max}} \sim 1/\tau \). Ju mindre \( \varphi_{\text{max}} \) desto längre uppehållstid har gasen i förbränningsrummet och desto större blir sannolikheten för utbränning.

Slutsatsen är att de små förbränningsrummen principiellt har en svårare förbrännningssituation än de stora, dels på grund av kortare gasuppehållstid, dels på grund av förhållandevis större yta. Det senare förklarar varför effekten av keramikytor för att minska utsläppen av tjära blev så stor; förbränningsrummen

![Diagram](image)

Figur 9 Specifik effekt och specifik yta som funktion av pannstorlek för några av de pannor som undersöks av Statens Provningsanstalt.
var helt enkelt felkonstruerade med alltför mycket kylyta i små rum och keramikytorna ledde till en minskning av den kyliga ytans storlek.

Tre faktorer är betydelsefulla: Yta-volymsförhållandet, gasuppehållstiden och andelen kyliga väggar.

Luftfaktorn


Adiabatisk förbrännningstemperatur

![Diagram](image-url)

Luftfaktor

Figur 10  Adiabatisk förbrännningstemperatur vid olika fuktkvoter u,
Den adiabatiska förbränningstemperaturen uttrycker den maximala temperaturen som kan uppnås vid förbränningen (då ingen värme avges till omgivningen). I en mer eller mindre kyld brännkammare blir temperaturen alltid lägre än den adiabatiska.

En rimlig förbränning kan upprätthållas vid temperaturer över 750°C. Som synes av figurerna 2 till 6 jämfört med figur 10 har luftfaktorn ofta varit för hög för att denna temperaturnivå skulle kunna upprätthålles. Enbart detta räcker för att förklara en stor del av de höga utsläppen som observerats vid emissionsmätningar på småpannor. Slutsatsen är att vare sig pannan är av självdragstyp eller fläktstyrd har lufttillförseln ofta i de undersökta pannorna varit så hög i förhållande till den förbränning som förekommit att förbränningen släckts eller blivit ofullständig.

Lufttillförseln

Förbränningsförloppet kan enklare styras om de olika stegen, som visas i figur 1, separeras. Därvid separeras lufttillförseln i primär och sekundärluft. Primärluftflödet måste vara sådant att en temperatur på åtminstone 800°C kan upprätthållas i primärzonen. Sekundärluften måste tillsättas på ett sådant sätt att omrörning skapas i sekundärzonen. Detta kan vara svårt att åstadkomma i praktiken, t ex i en självdragspanna vid dellast då den tillförda luftens rörelsemängd är liten. Kunskapen om hur lufttillförseln fördelar sig i småpannor är ofullständig.

Omblandning av bränsle och luft

Det finns två typer av omblandning:

- makroomblandning, som sker mellan gas och luft som strömmar i sträck genom gaskanalerna.
- mikroomblandning, dvs normal turbulent omblandning i reagerande gas.

Mikroomblandningen är alltid närvarande och kan behandlas med konventionella statistiska betraktelsesätt. Makroomblandningen är troligen det stora problemet i de aktuella eldstäderna. Det är oklart hur den skall behandlas, men det kan konstateras att i det ovan nämnda exemplet med CFB-pannan åstadkomms makroomblandning i cyklonen, vilket ledde till hög utbrenning av gasen. Mikroomblandningen var ingen begränsande faktor.

Transienta förhållanden

Uppvärmningsbehovet varierar starkt över året. Ett typiskt belastningsdiagram för byggnadsuppvärming och tappvarmvatten är mycket spetsigt, figur 11.

![Diagram](image)

Figur 11  Belastningsdiagram för uppvärming och tappvarmvatten.
En panna som skall leverera värme till en byggnad måste vara dimensionerad för den största värmelasten (vid lägsta dimensionerande utetemperatur, LUT, dvs ett värde som ligger något över den största verkliga relativa värmelasten 1 på figur 11), vilket betyder att pannan så gott som alltid går med dellast. Start och avstängningsförlopp och eventuell reglering av lasten har därmed en stor betydelse för fortsatta studier. Kombinationer med andra uppvärmningssätt för att minska topplasten är också möjliga.

Detta problem blir mindre i stora uppvärmningssystem. Dels är större pannor (det gäller fortfarande pannor mindre än 10 MW) lättare att reglera utan alltför stora olägenheter, dels kan stora system bestå av ett antal pannor som tillsammans tillgodoser de största belastningarna. Dessa enheter kan därmed gå med konstant last under långa tider och problemet med transiter undviks.

Den andra orsaken till transienta förhållanden är satsvis eldning.

Stor ved
Små pannor
Berett bränsle
Storapannor

Störningar i samband med lastreglering visades ovan vara orsaken till mycket stora emissioner av oförbränt från satsvis eldade villapannor. Kontinuerlig eldning är bättre från miljösynpunkt, men även i sådana fall uppstår störningar av transient natur, figur 6.

Problemet kan undvikas genom att använda berett bränsle (pellets, pulver) även i små anläggningar, men uppenbarligen finns andra hinder för en sådan tillämpning; utvecklad teknik, ekonomi.

Bränslet

Olika grad av beredning påverkar förbränningsanordningen och dess funktion:

Helved, huggen – satsvis eldning
Flis – kontinuerlig eldning
Pellets – "
Pulver – "
Vidare har kväveinnehåll, fukthalt och askans egenskaper betydelse.

Bränslenas kvalitet, t ex fukthalten, varierar ofta med tiden. Pannornas tolerans för kvalitetsvariationer bör undersökas.

Kväveoxider

Kväveoxidemissionerna är endast delvis beroende av ovanstående faktorer. Sannolikt är temperaturnivåerna så låga att inga termiska kväveoxider bildas utan kväveoxidernas ursprung ligger i bränslets kväve. Eftersom biobränslen kan innehålla mycket olika halter av kväve är bränslets kväveinnehåll kanske en av de mest betydelsefulla faktorer som påverkar emissionerna (Leckner och Karlsson 1993). Kvävet avgår dels med de flyktiga beståndsdelarna, sannolikt till största delen som ammoniak, och dels från koksförbränningen som kväveoxid. Denna ammoniak och denna kväveoxid kan sedan antingen resultera i mer kväveoxid eller kan ammoniaken bidra till reduktion av befintlig kväveoxid tillsammans med syre och kolmonoxid.

Denna kvalitativa beskrivning kan i första hand ytterligare klarläggas genom gas-koncentrationsmätningar i förbränningsrum och gaskanaler. Därefter kan strategier för NO reduktion diskuteras.

FORTSATT ARBETE

Sonderande verksamhet

En fortsättning behövs av den utvärdering av emissioner från småpannor som redan påbörjats av Statens Provningsanstalt. Det är önskvärt att karaktärisera och jämföra befintliga pannkonstruktioner samt att närmare undersöka pannorna som system bestående av olika komponenter: Bränslematning, torkning, avgasning, gasförbränning, koksförbränning, kylning av förbränningsprodukter och emissioner vid stationära och transienta förhållanden. Inverkan av primär- och sekundärluft bör undersökas. Temperaturer och koncentrationsförlopp bör mätas, både i utloppet och i förbränningsrum och gaskanaler.

Om möjligt bör undersökningarna omfatta både stationära och transienta förhållanden vid olika laster.

En jämförelse mellan befintliga konstruktioner och storlekar bör göras med utgångspunkt från specifika effekter, medeluppehållstider för gasen och andelar kyltor i förbränningsrum och gaskanaler. Dessa kriterier kan knytas an till mätresultat och teoretiska beräkningar, t ex, teoretiskt beräknade utbränningsstider vid olika temperaturer kan jämföras med anläggningarnas medeluppehållstider.

Provningsverksamhet

Denna verksamhet kan omfatta systematiskt upplagda försök i en speciellt byggd försöksanläggning som är lämpad och åtkomlig för detaljerade mätningar. Syftet kan vara att närmare studera olika förlopp på ett mer generellt och renodlat sätt än vad som kan göras vid sonderande försök i en panna. Exempel på väsentliga aspekter och parametrar:

- temperatur
- utbränning av gaser, jämförelse med beräkningar
- omrörning
- inverkan av stegad förbränning (sambel mellan primär- och sekundärluft)
- bildning och reduktion av kväveinnehållande gaskomponenter.
Även inverkan av konstruktionselement kan studeras:

- anordningar för lufttillförsel
- anordningar för omblandning
- inverkan av väggar
- katalysatorer
- reglerutrustning.

Ytterligare en viktig faktor som bör undersökas är inverkan av bränslets utseende och egenskaper.

Vetenskaplig verksamhet

Denna verksamhet bör ihop med ovanstående. Syftet är att skapa baskunskaper i den mån de inte redan finns tillgängliga i litteraturen.


Matematisk modellering

Matematiska modeller (av olika slag) behövs för att analysera förloppen i de småskaliga förbränningsrummen med syfte att tolka mätresultat, kartlägga svaga punkter och föreslå och utvärdera förbättringar.
Modellerna kan utnyttja befintliga datorprogram och befintlig kunskap men måste kompletteras med information angående biobränslen och andra förhållanden som är speciella för den aktuella tillämpningen.

Utveckling av mätteknik

Relevant mätteknik är ett viktigt redskap för undersökningar av förbränningsförlopp. Metoder och utrustning för mätning av temperaturer, gassammansättning och gasflöden i förbränningsrum och gaskanaler finns redan i viss utsträckning tillgänglig. En anpassning och vidareutveckling med hänsyn till bl.a. de aktuella pannornas små dimensioner är emellertid nödvändig. Detta gäller speciellt sonder av olika typer för mätning i eldstaden. Vidareutveckling av mätteknik, t.ex. FTIR, för bestämning av olika mellanprodukter i en complex förbränningsmiljö är angelägen.

En utvärdering av olika metoder för mätning av kolväteemissioner (THC, tjära, PAH, VOC, Priority Pollutants) med hänsyn till bl.a. inbördes samband, relevans och repeterbarhet, bör göras. Detsamma gäller för olika kväveinnehållande ämnen (NOx, HCN, NH3, N2O, HCNO etc) i en kolväster miljö.

Slutfilen bör, som förberedelser för sonderande mätningar, en mall tas fram för hur denna typ av undersökningar bör ske. Mallen bör innefatta principer för försöksplanering, provtagnings- och analyseteknik, dokumentation av anläggningar och försöksbetingelser samt möjlig och standardisering av bränslekvaliteter.

SLUTSATS

Förbättringar av småskaliga pannor för biobränslen har gjorts under 1980-talet, men särskilt för villapannor är fortfarande emissionerna betydligt mycket högre än vad som accepteras för större förbränningsanläggningar.

På grundval av gjorda mätningar går det att kvalitativt gissa sig till orsakerna för höga emissioner av CO, totalkolväten och andra organiska ämnen: Transienta driftförhållanden, otillräcklig ombländning av den producerade gasen med syre och otillräcklig uppehållstid vid tillräckligt hög temperatur. En så enkel slutsats räcker
inte för att lösa problemen och därför föreslås fortsatt verksamhet för att bättre förstå och förutsäga förloppen i en liten panna i anknytning till pannans konstruktionselement. Denna fortsatta verksamhet kan bestå av flera olika delar: Sonderande mätningar, provningsverksamhet, grundläggande kunskapsinhämtande och matematisk modellering.

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APPENDIX

WORKSHOP ON MODELLING OF BIOMASS CONVERSION
MODELLING THE CONVECTIVE FLOW INSIDE LOGS DURING DRYING, PYROLYSIS AND COMBUSTION OF WOOD.
M. Grønli/M. Melaaen, NTH, Norway.

TEST CASES FOR COMPARISON OF DIFFERENT MODELS DESCRIBING PYROLYSING OF THICK WOOD SAMPLES.
M. C. Melaaen, NTH, Norway//B.K. Brockett, University of Washington, USA.

GASIFICATION OF BLACK LIQUOR.
MODELLING ASPECTS.
K. Whittey, Åbo Akademi, Finland

SIMULTANEOUS DRYING AND PYROLYSIS OF BLACK LIQUOR DROPLES.
J. Saastamoinen, VTT, Finland.

MODELLING OF STRAW COMBUSTION.
N. Bech, Risø, Denmark.
MODELLING THE CONVECTIVE FLOW INSIDE LOGS DURING DRYING, PYROLYSIS AND COMBUSTION OF WOOD

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Modelling The Convective Flow
Inside Logs
During
Drying, Pyrolysis and Combustion
of
Wood

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✔ The Macroscopic Structure of Wood
✔ Water in Wood, and a Short Presentation of
A Mathematical Model for the Drying of Wood
✔ The Role of Convective Gasflow to Pyrolysis of Wood
Some Preliminary Results
✔ A Short Presentation of Our Experimental Setup
The Macroscopic Structure of Wood

Wood is a living material which has a typical and very complex structure depending on the species.
In a living softwood tree, there is two main tube systems.

- One system for the transportation of carbohydrates produced from the photochemical processes in the green part of the tree (leaves or needles) to the growth zones. The inner part of the bark is usually utilized for this, and the main growth zone is the cambial zone, the zone between bark and wood.

- A second system for the transportation of water, minerals and dissolved nutrients from the root system. This cells are called tracheids (longitudinally transport) and ray parenchyma cells (radially transport)
There is easy to see the differences between tracheids being produced early and late in the growth season.

The early-wood (spring-wood) fibres are thin-walled with large lumen for efficient water transport during the intense growth in the spring.

The late-wood (summer-wood) fibres are thick-walled with a small lumen for strength purpose.

The ray parenchyma cells serve as storage and transportation of water and food horizontally through the structure.
The mechanism of water transport from the root-system is due to capillary forces in the liquid phase.

The liquid flows from one tracheid to another through the bordered pits, a membrane ("torous") which can move under the effect of the pressure and which can obstruct the passage of the fluids.

This architecture is vital for the life of the trees and plays an important role during the drying process.
Water in Wood

Wood contains water in three forms:

- Bound (Hygroscopic or Adsorbed) Water
- Liquid (Free or Capillary) Water
- Water Vapor
Transport of Fluid Through Wood

**Bulk Flow** of fluids through the interconnected voids of the wood structure under the influence of a static or capillary pressure gradient. The magnitude of the bulk flow of a fluid through a porous structure is determined by its permeability. Permeability is a measure of the ease with which fluids are transported through a porous medium under the influence of a pressure gradient. Darcy's law:

\[
<v_g>_{\text{conv}} = - \frac{K_g K_g^r}{\mu_g} \nabla (<P_g>^g)
\]

where:
- \(<v_g>_{\text{conv}} = \text{Bulk velocity of gaseous mixture}\)
- \(K_g = \text{Intrinsic permeability}\)
- \(K_g^r = \text{Relative permeability of gaseous mixture}\)
- \(\mu_g = \text{Dynamic viscosity of gaseous mixture}\)
- \(\nabla <P_g>^g = \text{Pressure gradient}\)

**Intergas Diffusion** which includes the transfer of water vapor through the air in the lumens of the cells.

\[
J_v = - <p_v>^g D_{\text{eff}}^v \nabla \left( \frac{<p_v>^g}{<p_g>^g} \right)
\]

where:
- \(D_{\text{eff}}^v = \text{Effective diffusivity}\)
- \(\nabla (<p_v>^g/<p_g>^g) = \text{Concentration gradient}\)

**Bound Water Diffusion** which takes place within the cell walls of wood.

\[
<p_B v_B> = - c_{SD} D_B \frac{\partial}{\partial r} <p_B>
\]

where:
- \(D_B = \text{Bound water diffusion coefficient}\)
Three directions of anisotropy have to be taken into consideration:
- longitudinal (l)
- radial (r)
- tangential (t)

Mechanistic modelling (Comstock, 1970)

The ratio of longitudinal to radial permeability is approximately in the range of 100 - 10 000.

Longitudinal: \( K_{ISD} = 5 \times 10^{-13} - 5 \times 10^{-14} \) m\(^2\)
Radial: \( K_{ISD} = 5 \times 10^{-15} - 5 \times 10^{-18} \) m\(^2\)
The theoretical formulation of heat and mass transfer in porous media is usually obtained by a change in scale (Whitaker 1977).

We pass from a microscopic view where the size of the representative volume is small with regard to the pores, to a macroscopic view where the size of the representative volume \( V \) is large with regard to the pores.

The phase average of the quantity \( \psi_i \) associated with the phase \( i \), is noted \( <\psi_i> \) and is defined as follows:

\[
<\psi_i> = \frac{1}{V} \int_{V} \psi_i \, dV = \frac{1}{V} \int_{V_i} \psi_i \, dV
\]

where \( V_i \) is the volume occupied by \( V \) in phase \( i \).

An intrinsic phase average of a quantity \( \psi_i \) is defined as:

\[
<\psi_i>^i = \frac{1}{V_i} \int_{V_i} \psi_i \, dV
\]

The phase average quantity and intrinsic phase average quantity are related by:

\[
<\psi_i> = \epsilon^i <\psi_i>^i
\]
\[ V^s + V^b + V^l + V^g = V \]

\[
\varepsilon^i = \frac{V^i}{V}
\]

where:

\[
\begin{align*}
\varepsilon^s &= \frac{V^s}{V} \quad [m_3/m^3] \\
\varepsilon^b &= \frac{V^b}{V} \quad [m_3/m^3] \\
\varepsilon^l &= \frac{V^l}{V} \quad [m_3/m^3] \\
\varepsilon^g &= \frac{V^g}{V} \quad [m_3/m^3]
\end{align*}
\]

so that:

\[ \varepsilon^s + \varepsilon^b + \varepsilon^l + \varepsilon^g = 1 \]
Dry Solid: (reference volume and density)  
\( \langle \rho_{SD} \rangle = \frac{\text{kg of dry solid}}{\text{total volume}} \) [kg/m\(^3\)]

Cell wall substance  
\( \langle \rho_{SW} \rangle^s = \langle \rho_{SW} \rangle = \langle \rho_{SW} \rangle^f \varepsilon^f \) (kg of cell wall substance/ volume of solid phase) [kg/m\(^3\)]

Liquid Water  
\( \langle \rho_L \rangle^l = \langle \rho_L \rangle = \langle \rho_L \rangle^t \varepsilon^t \) (kg of liquid water/ volume of liquid phase) [kg/m\(^3\)]

Bound Water  
\( \langle \rho_B \rangle^b = \langle \rho_B \rangle = \langle \rho_B \rangle^b \varepsilon^b \) (kg of bound water/ volume of bound phase) [kg/m\(^3\)]

Gaseous Mixture  
\( \langle \rho_G \rangle^g = \langle \rho_G \rangle = \langle \rho_G \rangle^g \varepsilon^g \) (kg of gaseous mixture/ volume of gaseous phase) [kg/m\(^3\)]

Water Vapor  
\( \langle \rho_v \rangle^v = \langle \rho_v \rangle = \langle \rho_v \rangle^v \varepsilon^v \) (kg of water vapor/ volume of gaseous phase) [kg/m\(^3\)]

Gases  
\( \langle \rho_G \rangle^g = \langle \rho_G \rangle = \langle \rho_G \rangle^g \varepsilon^g \) (kg of gases/ volume of gaseous phase) [kg/m\(^3\)]

\[
\varepsilon^s = \frac{\langle \rho_{SD} \rangle}{\langle \rho_{SW} \rangle^s}, \quad \varepsilon^l = \frac{\langle \rho_L \rangle}{\langle \rho_L \rangle^l}, \quad \varepsilon^b = \frac{\langle \rho_B \rangle}{\langle \rho_B \rangle^b}
\]

\[
\varepsilon^g = 1 - \left[ \frac{\langle \rho_{SD} \rangle}{\langle \rho_{SW} \rangle^s} + \frac{\langle \rho_L \rangle}{\langle \rho_L \rangle^l} + \frac{\langle \rho_B \rangle}{\langle \rho_B \rangle^b} \right]
\]
Conservation Equations

Conservation of Species

$$\frac{\partial}{\partial t} <\rho> + \frac{1}{r^a} \frac{\partial}{\partial r} (r^a <\rho> <v>) = \pm <w>$$

Where:

- $<\rho>$: Mass Concentration of Component $i$ [kg of $i$ / m$^3$]
- $<\rho>^j$: Mass Concentration of Component $i$ in phase $j$ [kg of $i$ / m$^3$]
- $<v>$: Velocity [m/s]
- $<w>$: Rate of: (+) Production of Component $i$ [kg of $i$ / m$^3$ s]
- (-) Consumption of Component $i$ [kg of $i$ / m$^3$ s]

$\alpha$: Geometrical Factor: 0 = Infinite Slab
1 = Infinite Cylinder
2 = Sphere

Conservation of Energy

$$\Sigma (<\rho>C_{pi}) \frac{\partial T}{\partial t} + \Sigma (<\rho>^j C_{pi}) \frac{\partial T}{\partial r} = \frac{1}{r^a} \frac{\partial}{\partial r} (r^a K_{eff} \frac{\partial T}{\partial r}) - \Sigma <w> (\Delta h_{i-j}^{o} + h_{i})$$

Where:

- $C_{pi}$: Specific Heat of Component $i$ [J/kg °K]
- $K_{eff}$: Effective Thermal Conductivity [J / m s °K]
- $\Delta h_{i-j}^{o}$: Specific Enthalpy of Formation
  (+) Endotherm Reaction
  (-) Exotherm Reaction [J / kg]
- $h_{i}$: Sensible Heat of Component $i$ [J / kg]

$$h_{i} = \int_{T_i}^{T} C_{i}(T) dT$$
Drying Model

Mass Conservation of Liquid Water

\[
\frac{\partial}{\partial t} \langle \rho_L \rangle + \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a \langle \rho_L \rangle \langle v_L \rangle \right) = - \langle w_{L+B} \rangle
\]

\[<v_L> = - \frac{K_L K_r}{\mu_L} \frac{\partial}{\partial r} <P_L>^1\]

Mass Conservation of Bound Water

\[
\frac{\partial}{\partial t} \langle \rho_B \rangle + \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a \langle \rho_B v_B \rangle \right) = - \langle w_{L+B} \rangle
\]

\[<\rho_B v_B> = - \rho_{so} D_B \frac{\partial}{\partial r} <\rho_B>\]

Mass Conservation of Gaseous Mixture

\[
\frac{\partial}{\partial t} \langle \rho_g \rangle + \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a \langle \rho_g \rangle <v_g> \right) = <w_{L+B} \rangle
\]

\[<v_g> = - \frac{K_g K_r}{\mu_g} \frac{\partial}{\partial r} <P_g>^g\]

Mass Conservation of Water Vapor

\[
\frac{\partial}{\partial t} <\rho_v> + \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a <\rho_v>^s <v_g> \right) = \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a <\rho_v>^s D_{so} \frac{\partial}{\partial r} \frac{<\rho_v>^s}{<\rho_g>^g} \right) + <w_{L+B} \rangle
\]
Mass Conservation of Gases

\[
\frac{\partial}{\partial t} <\rho_g> + \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a <\rho_g>^a <v_r> \right) = \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a <\rho_g>^a D_{eff} \frac{\partial}{\partial r} \left( \frac{<\rho_g>^a}{<\rho_g>^a} \right) \right)
\]

Energy Equation

\[
\Sigma(<\rho_i>C_{pi}) \frac{\partial T}{\partial t} + \Sigma(<\rho_i><v_i>C_{pi}) \frac{\partial T}{\partial r} = \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a K_{eff} \frac{\partial T}{\partial r} \right) - \Sigma <w_i> (\Delta h_{i,j} + h_i)
\]

Thermodynamic Relations

The gaseous mixture is assumed to be an ideal mixture of perfect gases:

\[
<P_i>^g = \frac{<\rho_i>^g RT}{M_i}
\]

\[
<P_g>^g = \Sigma_i <P_i>^g ; \quad <\rho_g>^g = \Sigma_i <\rho_i>^g
\]

where:

- \( M_V = 0.018 \) [kg/mole] Molar mass of water
- \( M_A = 0.029 \) [kg/mole] Molar mass of air
- \( R = 8.3144 \) [J/mole °K] Universal gas constant
The vapor pressure inside the porous wood structure is made up of two parts.

The first part is the pressure that exists when the gas-liquid interface is flat. The Clausius-Clapeyron equation gives the equilibrium vapor pressure in terms of the latent heat ($\Delta h_{L,v}$) of free bulk water surface as:

$$\langle P_v \rangle^e = \langle P_v \rangle^o \exp \left[ - \frac{\Delta h_{L,v}}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right]$$

The second part is the pressure caused by the effect of curvature of the menisci and by using Kelvin's equation, the vapor pressure in a capillary porous system with the hydraulic radius ($r$) can be expressed as:

$$\langle P_v \rangle^s = \langle P_v \rangle^o \exp \left[ - \frac{2\sigma}{\langle \rho_L \rangle^i} \frac{1}{r} \frac{M_v}{R} \frac{1}{T} \right]$$

where $\sigma$ denotes the surface tension in the gas-liquid interface.

$$\langle P_v \rangle^s = \langle P_v \rangle^o \exp \left[ - \frac{2\sigma}{\langle \rho_L \rangle^i} \frac{1}{r} \frac{M_v}{R} \frac{1}{T} - \frac{\Delta h_{L,v}}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right]$$

The partial pressure of the vapor is equal to its equilibrium pressure:

$$M > M_{up} \quad P_v = P_v^{sat} (T)$$

$$M < M_{lp} \quad P_v = P_v^{sat} (T) \ h(M_{lp},T)$$

where $h(M_{lp},T)$ is the relative humidity which is given by sorption theory.

![Graph showing moisture content vs. relative humidity]

The liquid pressure is connected to the gaseous pressure by capillarity:

$$\langle P_L \rangle^i = \langle P_g \rangle^s - P_c \quad \Rightarrow \quad P_c = f(M_L,T)$$
Mathematical Model

One-Dimensional Heating of an semi-infinite slab of wood:

Assumptions:

✓ Thermodynamic Equilibrium between solid phase and gaseous phase
✓ No secondary (cracking) reactions
Property Definitions:

Total Volume: \[ V^s + V^g = V \]
Volume Fraction: \[ \varepsilon^s = V^s / V \]

\[ \varepsilon^s = \frac{V^s}{V} \quad [m^3/m^3] \]
\[ \varepsilon^g = \frac{V^g}{V} \quad [m^3/m^3] \quad \varepsilon^s + \varepsilon^g = 1 \]

The mass concentration of each phase is defined as:

**Dry Solid:**
- \( \rho_{sd} = 500 \) (reference volume and density)
- \( \text{(kg of dry solid/ total volume)} \) [kg/m\(^3\)]

**Cell Wall Substance**
- \( \rho_{sw} = 1500 \) (kg of cell wall substance/ volume of solid phase) [kg/m\(^3\)]
- \( \rho_{sw} = \rho_{sd} = \rho_{sw} \varepsilon^s \) (kg of cell wall substance/ total volume) [kg/m\(^3\)]

**Gaseous Mixture**
- \( \rho_g = \frac{\rho_{g}}{M_g} R T \) (kg of gaseous mixture/ volume of gaseous phase) [kg/m\(^3\)]
- \( \rho_g = \rho_g \varepsilon^g \) (kg of gaseous mixture/ total volume) [kg/m\(^3\)]

\[ \varepsilon^s = \frac{\rho_{sd}(x,t)}{\rho_{sw}^s} \quad \Rightarrow \quad \varepsilon^s = 1 - \frac{\rho_{sd}(x,t)}{\rho_{sw}^s} \]

\[ \varepsilon^s = 0.333 \quad \Rightarrow \quad \varepsilon^g = 0.667 \]
Mass Conservation of Dry Solid

\[ \frac{\partial}{\partial t} <\rho_{SD}> = -<w_{SD->} \]

Mass Conservation of Gaseous Mixture

\[ \frac{\partial}{\partial t} <\rho_{g}> + \frac{1}{r^a} \frac{\partial}{\partial r} (r^a <\rho_{g}> <\nu_g>) = <w_{r-g}> \]

Where:

\[ <\nu_g> = - \frac{K_g}{\mu_g} \frac{\partial}{\partial r} <P_g> \]

Energy Equation

\[ \Sigma(<\rho> C_p) \frac{\partial T}{\partial t} + \Sigma(<\rho> <\nu> C_p) \frac{\partial T}{\partial r} = \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a K_w \frac{\partial T}{\partial r} \right) - \Sigma<w> (\Delta h_{i,j} + h_i) \]
Broido-Shafizadeh’s Reaction Scheme

\[ (1) \quad S \rightarrow A \]
\[ (2) \quad A \rightarrow T \]
\[ (3) \quad A \rightarrow \mu \ C + (1-\mu) \ G \]

Where:

\[ S = \text{Solid} \]
\[ A = \text{Active Solid} \]
\[ T = \text{Tar} \]
\[ C = \text{Char} \]
\[ G = \text{Gases} \]
\[ \mu = \text{Stoichiometric coefficient} \]

\[
\frac{\partial \rho_i}{\partial t} = \pm K_i \rho_i
\]

\[ K_i = A_i \exp\left(-\frac{E_i}{RT}\right) \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( A_i ) (min(^{-1}))</th>
<th>( E_i ) (kJ/mole)</th>
<th>( \Delta H_i ) (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>1,7 ( \times ) 10(^{21} )</td>
<td>242,83</td>
<td>(+) 200</td>
</tr>
<tr>
<td>(2)</td>
<td>1,9 ( \times ) 10(^{16} )</td>
<td>198,04</td>
<td>(+) 200</td>
</tr>
<tr>
<td>(3)</td>
<td>7,9 ( \times ) 10(^{11} )</td>
<td>150,72</td>
<td>(+) 200</td>
</tr>
</tbody>
</table>

\[ \mu = 0,35 \]
One-Step First Order Reaction

\[ S \rightarrow V + C \]

Where:

- **S** = Solid
- **V** = Volatiles (Tar + Gases)
- **C** = Char

\[ \frac{dp_s}{dt} = -(p_s - p_{cm}) A \exp(-E/RT) \]

Shafizadeh and Chin (1977)
Thurner and Mann (1981)
Agrawal (1984)

(1) \hspace{1cm} S \rightarrow \hspace{1cm} G
(2) \hspace{1cm} S \rightarrow \hspace{1cm} T
(3) \hspace{1cm} S \rightarrow \hspace{1cm} C

Where:

- **S** = Solid
- **T** = Tar
- **C** = Char

\[ \frac{dp_i}{dt} = \pm \rho_i A_i \exp(-E_i/RT) \]

(1) \( S \) \( \rightarrow \) \( a_1G_1 + (1 - a_1)H_2O (v) \)
(2) \( S \) \( \rightarrow \) \( T_1 \)
(3) \( S \) \( \rightarrow \) \( a_2C_1 + (1 - a_2)H_2O (v) \)
(4) \( T_1 \) \( \rightarrow \) \( a_3G_2 + a_4T_2 + a_5C_2 + (1 - a_3 - a_4 - a_5)H_2O (v) \)
(5) \( H_2O (m) \) \( \rightarrow \) \( H_2O (v) \)

Where:

\( S \) = Solid
\( G_1 \) = Primary Gases
\( G_2 \) = Secondary Gases
\( T_1 \) = Primary Tar
\( T_2 \) = Secondary Tar
\( C_1 \) = Primary Char
\( C_2 \) = Secondary Char
\( H_2O (v) \) = Water Vapor
\( H_2O (m) \) = Bound (Hygroscopic) Water and Liquid (Free) Water
\( a_i \) = Stoichiometric Coefficients
Effective Thermal Conductivity

\[ K_{\text{eff}} = K_{\text{cond}} + K_{\text{rad}} \]

\[ K_{\text{cond}} = \eta K_{SD0} + (1-\eta)K_{C} \]

\[ \eta = \frac{\langle \rho_{SD}(t) \rangle - \langle \rho_{C} \rangle}{\langle \rho_{SD0} \rangle - \langle \rho_{C} \rangle} \]

\[ K_{\text{rad}} = A \frac{T^3}{\omega(1 - \varepsilon^f)} \]

Where:

- \( K_{\text{cond}} \) - Conduction Term
- \( K_{\text{rad}} \) - Radiation Term
- \( K_{SD0} \) - Thermal Conductivity of Unreacted Solid
- \( K_{C} \) - Thermal Conductivity of Char
- \( \langle \rho_{SD0} \rangle \) - Initial Density of Dry Solid
- \( \langle \rho_{C} \rangle \) - Final Density of Char
- \( A = 9.50 \times 10^{12} \) - Constant \( f(\text{Geometry}) \)
- \( \omega = 0.9 \) - Emissivity
- \( \varepsilon^f \) - Volume Fraction Gaseous Mixture (Porosity)
--- Radiation
--- No Radiation
Spesific Heat

\[ C_{SD} = \eta C_{SD\,0} + (1-\eta) C_c \]

\[ \eta = \frac{<\rho_{SD}>(t) - <\rho_c>}{<\rho_{SD0}> - <\rho_c>} \]

Where:

- \( C_{SD\,0} \) - Spesific Heat of Unreacted Solid
- \( C_c \) - Spesific Heat of Char

Intrinsic Permeability

\[ K_{SD} = \eta K_{SD\,0} + (1-\eta) K_c \]

\[ \eta = \frac{<\rho_{SD}>(t) - <\rho_c>}{<\rho_{SD0}> - <\rho_c>} \]

Where:

- \( K_{SD\,0} \) = Intrinsic Permeability of Unreacted Solid
- \( K_c \) = Intrinsic Permeability of Char
Boundary Conditions

![Diagram of Boundary Conditions]

(1) \[ Q_{\text{flux}} - h_T (T - T_\infty) - \omega_{\text{surf}} \sigma (T^4 - T_\infty^4) = - K_{\text{eff}} \frac{\partial T}{\partial r} \]

(2) \[ P = P_0 \]

Where:

- \( Q_{\text{flux}} = 40.0 \text{ kW/m}^2 \) - External Heat Flux
- \( h_T = 30 \text{ W/m}^2\text{°K} \) - Convective Heat Transfer Coefficient
- \( T_\infty = 298 \text{ °K} \) - Surrounding Temperature
- \( \omega_{\text{surf}} = 0.9 \) - Surface Emissivity
- \( \sigma = 5.67 \times 10^{-4} \text{ W/m}^2\text{°K}^4 \) - Stefan-Boltzmann Constant
- \( P_0 = 1.01325 \times 10^5 \text{ N/m}^2 \) - Surrounding Pressure
Numerical Treatment

The system of presented equations is solved by a method of finite differences based on the notation of control domain (Patankar 1980). The method consists of integrating the conservation equations on the interval $|t, t+\Delta t|$ and on the control domain.

The grid points are placed in the geometric center of the control volumes (Figure below). By this, the value of any physical quantity $\Phi$ at point $P_i$ can be regarded as a good representative value for the control volume. The disadvantage of this formulation is when the control-volume sizes are non-uniform. Their faces will not lie midway between the grid points, which can effect the accuracy when calculating the fluxes across the faces.

The values of the terms of accumulation $(\frac{\partial f}{\partial t})_i$, and the source terms $w_i$ and $w_i (\Delta h^{0}_{i-1}+h_i)$ can be considered as being the averages on the control domain.

The source terms, the terms of convection as well as those of diffusion are evaluated at time $t+\Delta t$ (fully implicit scheme).

Convection in the energy equation is calculated by an upwind scheme.

The different parameters are calculated over the faces of the control domains, their variations can being taken as linear or harmonic.

To attain greater precision without increasing the number of nodes in the grid, adaption of grid is possible.
Dowels of white Fig. 6 - 1.0 cm
H - 13 cm
Heat source ~ Furnace T = 550°C
Pressure ~ Hydraulic needles

Fig. 6. Center-pressure and temperature histories, and flaming record for a 1-in. dowel at a furnace temperature of 550°C. (These curves are average values for several dowels.)

1 psi = 7.0 kPa
≈ 4 psi = 0.28 bar
Lee et al. (1977)

Critical values of maple
D = 2 cm
L = 8 cm

Heat Source: 250 W CO2 Laser
q̇ ≈ 85 kW/m²s

Hypodermic Needle Tubes

Fig. 7. Internal gas pressure histories and pressure profiles for perpendicular "high" heat flux.

1. Wood grain ≈ 0.130 atm
2. Wood grain ≈ 0.003 atm
Thermophysical Properties

✓ Total Simulation Time: 6 Minutes

✓ Thermal Conductivity:
  Virgin Wood  \( K_{SD_0} = 25.50 \times 10^{-2} \text{ W/mK} \)
  Char  \( K_C = 10.51 \times 10^{-2} \text{ W/mK} \)

✓ Specific Heat:
  Virgin Wood  \( C_{pSD_0} = 1500 \text{ J/kg K} \)
  Char  \( C_{pC} = 1100 \text{ J/kg K} \)
  Gaseous Mixture  \( C_{p_g} = 1680 \)

✓ Dynamic Viscosity:
  Gaseous Mixture  \( \mu = 3.0 \times 10^{-5} \text{ kg/ms} \)

✓ Molar Mass:
  Gaseous Mixture  \( M_g = 0.050 \text{ kg/mole} \)

✓ Intrinsic Permeability:

  Case 1:
  Virgin Wood  \( K_{SD_0} = 5.0 \times 10^{-18} \text{ m}^2 \)
  Char  \( K_C = 1000 \* K_{SD_0} \)

  Case 2:
  Virgin Wood  \( K_{SD_0} = 5.0 \times 10^{-17} \text{ m}^2 \)
  Char  \( K_C = 1000 \* K_{SD_0} \)

  Case 3:
  Virgin Wood  \( K_{SD_0} = 5.0 \times 10^{-16} \text{ m}^2 \)
  Char  \( K_C = 1000 \* K_{SD_0} \)

  Case 4:
  Virgin Wood  \( K_{SD_0} = 5.0 \times 10^{-15} \text{ m}^2 \)
  Char  \( K_C = 1000 \* K_{SD_0} \)
3 stk. stykker plassert rundt omkretsen

- 10.3 stuss for transportgass
- 9.1 krave for feste av prøverør aluminium
- 8.1 stuss for pyrolysegasser
- 7.1 stuss for luftstrøm
- 6.1 stuss for trykkmøling
- 5.1 baffle quartz-glass
- 4.2 stuss for transportgass
- 3.1 krave for feste av vindu aluminium
- 2.2 o-ringer
- 1.1 vindu fused-silica

Kunde: VIKING-MJØNDALEN
Prosjektnummer: 150896.00
SINTEF AVD. 15

GLASSREAKTOR FOR TESTING AV GUMMIKOMPOSITOR
TEST CASES FOR COMPARISON OF DIFFERENT MODELS DESCRIBING
PYROLYSING OF THICK WOOD SAMPLES

Morten Chr. Melaaen, NTH, Norway
TEST CASES FOR COMPARISON OF DIFFERENT MODELS DESCRIBING PYROLYSING OF THICK WOOD SAMPLES

BY

MORTEN CHRISTIAN MELAAEN
Division of Thermal Energy
Norwegian Institute of Technology

Test cases selected for testing of the numerical models describing pyrolysing of thick samples. The calculations will be done by Jaakko Saastamoinen, Niels Bech, Barbara Krieger-Brockett, Morten Grønli and Morten Chr. Melaaen.
Assumptions

- Flat plate of wood with thickness 2 cm.
- The dry wood density is 550.0 kg/m$^3$.
- Infinite in y- and z-direction, hence one-dimensional in x-direction.
- Equal boundary conditions on both sides, hence symmetric situation.
- The solid matrix volume is fixed.
The boundary conditions on the surfaces

\[ \pm \hat{\lambda} \frac{\partial T}{\partial x} \bigg|_s = F - H(T_s - T_\infty) - \varepsilon \sigma (T_s^4 - T_\infty^4) \]

Initial conditions

\[ T(x, 0) = 298.0K \]
Cases 1, 2, 3 and 4

Two different sets of boundary conditions:

a:  \[ H = 30.0 \frac{W}{m^2}, \; \epsilon = 0.0, \; F = 0.0 \frac{kw}{m^2}, \; T_{\infty} = 1073.0K \]
b:  \[ H = 30.0 \frac{W}{m^2}, \; \epsilon = 0.9, \; F = 40.0 \frac{kw}{m^2}, \; T_{\infty} = 298K \]

Two different moisture contents:

A:  \[ \text{kg water/kg dry} = 0.0 \]
B:  \[ \text{kg water/kg dry} = 0.3 \]

Totally this will give four different calculations. 
Do the calculations until the pyrolysing is completed.

CASE NUMBER:
1=aA
2=aB
3=bA
4=bB
Cases I, II, III and IV

CASE I:

Constant property case (for analytical solution sent by Jaakko):

\[ c_p = 1500.0 \frac{J}{kgK} \]
\[ k = 0.15 \frac{W}{mK} \]

It is no pyrolysing.

CASE II:
CASE I with pyrolysing, heat of pyrolysing (600 kJ/kg) and convection.

CASE III:
CASE I with moisture.

CASE IV:
CASE II with moisture.

For CASES I to IV we want to find the time to get a temperature of 600°C at surface and centre plane? The boundary conditions is given by (a). The moisture content is given by (B).
GASIFICATION OF BLACK LIQUOR MODELLING ASPECTS

K. Whitty, Åbo Akademi
Gasification of Black Liquor
Modeling Aspects

Kevin Whitty

Workshop on modeling of biomass conversion
Trondheim, Norway
31 August 1993
A history of black liquor combustion and gasification modeling

Black liquor combustion modeling (Frederick & Hupa)
- Physical modeling
- Rate modeling

Black liquor gasification modeling
- Physical modeling (Frederick, Hupa)
- Mechanistic modeling of pressurized CO₂ gasification (Frederick, Hupa)
- Empirical rate modeling of pressurized gasification with H₂O and CO₂ (Whitty, Backman, Hupa)
Mechanistic modeling of CO$_2$ gasification

- Consideration of the catalytic alkali sites in the char
- Development of a mechanistic model
- Determination of the rate limiting step in the mechanism
- Development of a rate expression based on the mechanism
- Optimization of the coefficients in the rate expression by fitting to experimental data
- Validation of the rate expression by comparison with experimental data
5. Deactivation of ox. carbon sites
\[ C(O) + CO \rightarrow C_1 + CO_2 \]

4. Desorption of CO
\[ C(O) \rightarrow CO \]

3. Surface transfer of oxygen
\[ C(O) + * \leftarrow C_1 + *O \]

2. Desorption of CO
\[ *CO_2 \leftrightarrow *O + CO \]

1. Adsorption of CO\(_2\) on catalyst sites
\[ CO_2 + * \rightleftharpoons *CO_2 \]

Catalyzed CO\(_2\)-gasification

- Carbon
- Oxygen
- Catalyst site
CO$_2$-gasification of BL-char

1. \[ CO_2 + * \rightleftharpoons \star CO_2 \]  
2. \[ \star CO_2 \rightleftharpoons \star O + CO \]  
3. \[ \star O + C_f \Rightarrow * + C(O) \]  
4. \[ C(O) \Rightarrow CO + C_f \]  
5. \[ C(O) + CO \Rightarrow C_f + CO_2 \]  

\[ r = \frac{1}{1 - X_c} \left[ \frac{P_{CO_2} - \frac{P_{CO}^2}{K_{eq}}}{\frac{k' P_{CO_2}}{M_c,0} + \frac{k'' P_{CO}}{M_c,0 N_{Na} + K}} \right] \]
Empirical modeling

Parameters:
- Pressure (1-30 bar)
- H$_2$O concentration (20-80%)
- CO$_2$ concentration (20-60%)
- H$_2$ concentration (3-15%)
- CO concentration (3-15%)
- Temperature

Designing experiments to investigate separately the effect of each parameter would result in an enormous experimental matrix.

"Mixing design" approach was chosen, with regression modeling of the resulting data. Plackett-Burman algorithm was used to generate the experimental plan.
More empirical modeling...

Work up to this point has considered only the maximum rate of gasification
- Suitable for predicting the maximum gasification rate under given conditions or for comparing maximum rates between runs
- Unsuitable for determination of gasification behavior in a reactor

Future plans
- Model the rate of gasification during the whole gasification process
- Function of char conversion, gas composition, pressure, temperature.
- Apply this model to a reactor

Even more distant future plans
- Consider black liquor composition
- Model gasification rate as a function of liquor composition
SIMULTANEOUS DRYING AND PYROLYSIS OF BLACK LIQUOR DROPLES.

J.J. Saastamoinen, VTT, Finland
Swedish-Finnish Flame Days 1993
Gothenburg, Sweden, 7-8.9.1993

SIMULTANEOUS DRYING AND PYROLYSIS OF BLACK LIQUOR DROPLETS

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ABSTRACT

Simultaneous drying and pyrolysis of black liquor droplets are examined by model calculations. The droplet size has the most significant effect on drying and pyrolysis times. Droplet solids content and gas temperature have also a great effect. Drying and pyrolysis are locally successive processes inside a droplet, but when considering the droplet as a whole these stages are overlapping. The degree of the overlapping of drying and pyrolysis increases with increasing droplet size and gas temperature.

INTRODUCTION

Black liquor is spent liquor washed from the pulp in the kraft pulping process. It contains both organic matter dissolved from the wood and the spent sodium based inorganic chemicals. Black liquor is typically burned today in Tomlinson-type recovery boilers to recover the organic chemicals in the form of smelt and to convert the combustible materials into usable steam energy. Thus, black liquor is an important source of energy in paper manufacturing countries. For instance in Finland it accounts for about 7% of the total demand of the primary energy.

Black liquor is an aqueous fuel. It is introduced into a recovery boiler as a spray of droplets, typically between the sizes of 0.5 mm and 5 mm. Conventionally it is fired at about 60-70% dry solids content, but with a concentrator technology of today it is possible to reach solids contents in excess of 80% [1].

The combustion behaviour of single black liquor droplets has been experimentally studied at Åbo Akademi [2], and they have divided the combustion process into the following four stages: drying, pyrolysis and combustion of the pyrolysis gases, char burning and reactions of inorganic residue. A characteristic of black liquor is that it swells considerably during drying and especially during pyrolysis. These burning characteristics of liquor droplets determine their trajectories and thus burning profiles in a recovery boiler [3,4].
MODEL DESCRIPTION

The calculation model is based on the numerical solution of the energy equation

\[
p c \frac{\partial T}{\partial t} - \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} - \frac{\dot{C}T}{4\pi} \right) - I_s \rho_u - I_v \rho_v = 0, \quad \dot{C} = 4\pi \int_0^r (c_p \rho_u + c_p \rho_v) r^2 dr \tag{1}
\]

in which local thermal equilibrium between solid, liquid and gas phases is assumed. In addition, a boundary condition and models for the pyrolysis kinetics and the mass transfer of steam and volatiles out from the droplet are required. Steam and volatiles are assumed to escape the particle immediately after their generation due to the great increase in the specific volume. The model has earlier been applied for biomass particles \[5,6\]. The local density and heat conductivity \[5\] inside the droplet decrease due to drying, pyrolysis and swelling. Values 610kJ/kg and 51% are used in the calculations for the heat of pyrolysis and amount of volatiles respectively.

The first term in equation (1) describes the heat storage, the second is due to internal heat conduction and convection. The flow direction of steam and volatiles is towards the surface and opposite to the direction of heat flow, which causes internal mass transfer cooling of the droplet. The last terms account for the energy sinks associated with drying and devolatilization. Vaporization is assumed to occur on a shrinking spherical core. The generation of volatiles is assumed to occur in a wide temperature interval inside the droplet.

So far, the droplet pyrolysis is described by a model, in which the local degree of pyrolysis is defined by the local temperature. It is assumed that the kinetics of pyrolysis is very rapid, but the degree of pyrolysis on the temperature is taken into account \[5\]. The validity of this model for small droplets with fast pyrolysis is questionable. In the future, a model, in which the kinetics is described by two competing reactions of the Arrhenius type will be applied. Such a model has been presented for rapid coal pyrolysis for example by Kobayashi \[7,8\]. The rapid pyrolysis kinetics results in a grid-heater of Åbo Akademi will be utilized.

The convective and radiative heat transfer between the surroundings and the droplet surface is described by the boundary condition

\[
h(T_g - T_{r=R}) + \varepsilon c(T_g^4 - T_{r=R}^4) = \lambda \left( \frac{\partial T}{\partial r} \right)_{r=R} \tag{2}
\]

The heat transfer coefficient is affected by the swelling. It is calculated by using the Ranz-Marshall correlation corrected a coefficient taking into account its reduction due to the Stefan flow. In an oxidative atmosphere with a flame surrounding the droplet, the gas temperature is replaced by the effective flame temperature.

RESULTS AND DISCUSSION

Calculation results are presented in Figure 1 and Table 1 for droplets with 80% dry solids content. The droplet swelling creates an insulative layer around the moist droplet centre core. Then, the real drying time is almost as long as the pyrolysis time, since the
droplet centre is moist almost to the end of the pyrolysis stage. Thus, here when considering the overlapping of the drying and pyrolysis, the drying time is understood as the time required to achieve 90% of moisture removal from the droplet. The droplet diameter has the most significant effect on the drying and pyrolysis times. The drying and pyrolysis times are proportional to square of the droplet diameter, when the particle size is small. The relation becomes $t \propto d^n$, where $n<2$ for larger droplets due to the effect of radiation and forced convection ($Nu>2$). Constant value 0.5 m/s for the droplet slip velocity was used in the calculations.

In the calculations it is assumed that the radiation temperature is the same as the gas temperature, $T_r = T_g$. The radiation heat transfer becomes important, when the droplet size is large and temperature high. The gas temperature and droplet moisture content have also significant effects on drying and pyrolysis time. The effect of the gas oxygen content is similar to that of temperature, since after ignition the combustion of volatiles around the particle increases the temperature.

A greater proportion of volatiles are released during the droplet drying stage with increasing droplet size and gas temperature. Much volatiles are released simultaneously with steam produced in the drying even for small droplets.

![Figure 1. a) Calculated normalized dry droplet mass and mass flow rates escaping the droplets surface. b) Calculated droplet temperatures during drying and pyrolysis.](image)

Decreasing the droplet dry solids content from 80 to 60%, when the dry density is assumed to be constant 650kg/m$^3$ in calculations, increased the total pyrolysis time from 1.5 s to 3.3 s and the degree of overlapping increased from 47 to 50% for 1 mm droplets at 800°C due to increase in the moisture content.

<table>
<thead>
<tr>
<th>d (mm)</th>
<th>$t_d$ (ms) (90% dried)</th>
<th>$t_p$ (ms)</th>
<th>V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_r$ (°C)</td>
<td>800  1000  1200</td>
<td>800  1000  1200</td>
<td>800  1000  1200</td>
</tr>
<tr>
<td>d=0.1 mm</td>
<td>12  10  9</td>
<td>21  16  15</td>
<td>9  17  37</td>
</tr>
<tr>
<td>d=1.0 mm</td>
<td>790  660  640</td>
<td>1500  1300  1200</td>
<td>47  61  68</td>
</tr>
<tr>
<td>d=2.0 mm</td>
<td>2800  2600  2300</td>
<td>5500  5000  4600</td>
<td>55  64  69</td>
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</table>

Table 1. Drying and pyrolysis times at different temperatures for particle sizes 0.1, 1 and 2 mm, and the proportion of volatiles released during the (90%) drying stage.
NOMENCLATURE

Symbols
C  
heat capacity flow rate, W/K

c  
specific heat, J/kgK

h  
heat transfer coefficient, W/m²K

l  
heat of vaporization or pyrolysis, J/kg

Nu  
Nusselt number, -

R  
droplet radius, m

r  
coordinate from droplet centre to surface, m

T  
temperature, K

t  
time, s

V  
proportion of volatiles released during time, when 90% moisture initially
in the droplet has been released, %

ε  
droplet surface emissivity

λ  
heat conductivity, W/mK

ρ  
density, kg/m³

ρ'  
steam or volatiles mass generation/volume, kg/m³s

σ  
Stefan-Bolzmann constant, 5.67 W/(m²(100K)⁴)

Indexes

g  
gas

u  
steam

s  
radiation surface

v  
pyrolysis

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   Devolatilization of Pulverized Coal in Hot Combustion Gases. Sixteenth Symposium
MODELLING OF STRAW COMBUSTION
(Detailed equations)

Nils Bech, Risø, Denmark
BASIC EQUATIONS

Mass conservation for component no. \( i \) in the gas phase:

\[
\frac{\partial m_g^i}{\partial t} + \frac{\partial}{\partial x} \left\{ m_g^i u_g^i \right\} = \Gamma_g^i + S_g^i
\]

Mass conservation for component no. \( i \) in the straw:

\[
\frac{\partial m_h^i}{\partial t} + u_h \frac{\partial m_h^i}{\partial x} = -\Gamma_h^i - S_h^i
\]
BASIC EQUATIONS cont'd.

Energy conservation for the gas phase

\[ \frac{\partial e_g}{\partial t} + \frac{\partial}{\partial x} \left\{ e_g u_g \right\} = Q_g + \sum_i \left\{ \int h_\rho + S_{inj} h_{inj} \right\} \]

Energy conservation for the straw:

\[ \frac{\partial e_h}{\partial t} + u_h \frac{\partial e_h}{\partial x} = Q_h - \sum_i \left\{ \int h_\rho + \frac{\partial}{\partial x} \left\{ \lambda_h \frac{\partial T}{\partial x} \right\} \right\} \]
BASIC EQUATIONS cont'd.

Momentum equation for gas phase (Darcy's law):

\[ u_g = u_h - \frac{K}{\mu_g} \left\{ \frac{dp}{dx} + g \cos \theta \rho_g \right\} \]

Momentum equation for straw:

\[ u_h = \text{constant} \]

PRESSURE EQUATION:

\[ m_g = \phi \rho_g \]
### DISCRETIZATION IN SPACE

A staggered finite difference grid is used:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>k-1</th>
<th>k</th>
<th>k+1</th>
<th></th>
</tr>
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<tbody>
<tr>
<td>i</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>i</td>
</tr>
<tr>
<td>k-(\frac{1}{2})</td>
<td>k+(\frac{1}{2})</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Discretization of convection terms:

\[
\begin{align*}
\int \frac{\partial}{\partial x} \{m_g u_g\}_k & \quad \Rightarrow \quad \frac{i}{i} \quad \frac{i}{i} \quad \frac{i}{i} \\
\left[ m_g u_g \right]_{k+\frac{1}{2}} & = u_g k+\frac{1}{2} \quad m_g k \quad if \quad u_g k+\frac{1}{2} > 0 \\
\left[ m_g u_g \right]_{k-\frac{1}{2}} & = u_g k-\frac{1}{2} \quad m_g k+1 \quad if \quad u_g k+\frac{1}{2} < 0
\end{align*}
\]
PRIMARY EQUATION SYSTEM

\[ \frac{dy}{dt} = f(y, t) \]

\[ y^T = \{(m_i^g, m_i^h), i = 1:NC, \}
\[ e_g, e_h \}, k=1:NV] \]

\[ m_g = \phi g \]

DISCRETIZATION IN TIME

\[ \frac{dy}{dt} \approx \frac{y^{n+1} - y^n}{\Delta t^{n+1}} \]
ALGEBRAIC EQUATION SYSTEM

\[ F(\bar{Y}) = 0 \]

\[ \bar{Y} = [\{(m_g, m_h), i = 1:NC, e_g, e_h, p\}, k=1:NV] \]

NEWTON-RAPHSON SOLUTION

\[ \{J\} \bar{Y}^{(i+1)} + F(\bar{Y}^{(i+1)}) = 0 \]

\[ \bar{Y}^{(i+1)} = \bar{Y}^{(i)} - \frac{F(\bar{Y}^{(i)})}{\{J\} \bar{Y}^{(i)}} \]
BASIC EQUATIONS cont'd.

Steady state gas velocity equation:

\[ \frac{\partial}{\partial x} \left\{ n_g u_g + \int_{i}^{i} \frac{m_g i}{MW} \Delta u_g \right\} = \int_{i}^{i} \frac{\Gamma + S_g}{MW} \]

where

\[ n_g = \frac{\phi P}{RT_{K_g}} \]

Steady state pressure equation:

\[ \frac{dp}{dx} = - \frac{u_g - u_h}{K/\mu_g} - g \cos \theta_{\phi_g} \]
INITIAL STEADY STATE SOLUTION

DO IT = 1, ITMAX

\[ \overline{F}(\overline{Y}_1) = 0, \quad k=1:NV \]

\[ \overline{Y}_1 = \{(m_g, m_h), \quad i=1:NC, \quad e_g, \quad e_h\} \]

\[ \overline{F}(\overline{Y}_2) = 0 \]

\[ \overline{Y}_2 = \{m_g, u_g, \quad k=1:NV\} \]

\[ \overline{F}(\overline{Y}_3) = 0 \]

\[ \overline{Y}_3 = \{e_h, \quad k=1:NV\} \]

ENDDO
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