Chapter III

Experiment

3.1 Description of Method

From previous research work on rice husk (Chakraverty et al, 1988) the experiment was done by pretreatment of rice husk with inorganic chemicals. Beside this, a study on plant physiology encouraged the use of an enzyme as a help to digest organic matrix. This "soft" technology is expected to result in an amorphous silica with its natural nanostructure preserved.

Methods can be separated in those related to rice husk ash preparation and those related to characterization (of any step of treated husk and ash).

Rice husk was prepared in 9 different ways according to the flow chart given on the next page.

In detail, the following ways were chosen:

1. No chemical treatment (except for washing)
2. NaOH 1 molar, 24 h, room temperature
3. HCl 1:4, boiling 3 h
4. NaOH treatment, then HCl treatment
5. H_2SO_4 1:4, boiling 3 h
6. HNO_3 1:4, 3 h, room temperature
7. Enzymatic treatment
8. Enzymatic treatment, then HCl treatment
9. Enzymatic treatment, then H_2SO_4 treatment

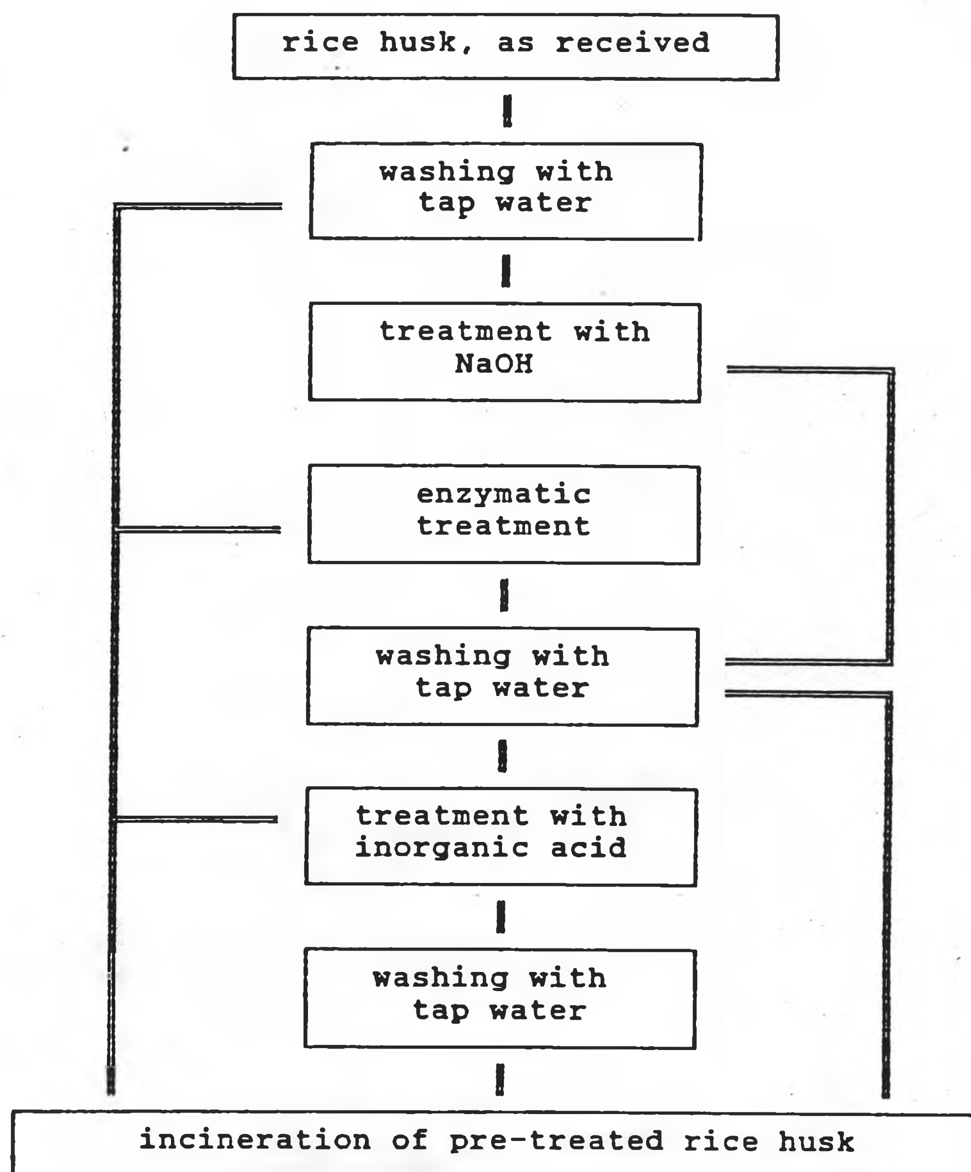

Fig. 9. Treatment of rice husk prior to incineration, flow chart

When planning the procedure, the economy of a future industrial process was considered. Therefore, ordinary tap water was used (instead of deionized water). Moreover, a ratio of 460±5 g husk per 5 l of acid was applied. This ratio may not give highest purification effect, but avoids extensive use of mineral acid.

3.2 Method and Equipment

3.2.1 Rice husk ash preparation

3.2.1.1 Washing method

Before starting the experiment, small pebbles and unsuited plant material (leaves, stem) were selected out by hand from rice husk, because these parts cannot be washed out by a washing machine. Then, rice husk was washed in a washing machine by tap water. In precursor tests with small amount of rice husk, different washing procedures had been tried, e.g., washing on a cloth sieve. After several trials, the most suitable way to wash rice husk in large amounts was spinning it in a finite volume. This encouraged the use of an ordinary washing machine.

Washing equipment is a commercial washing machine Mitsubishi model CW 224E. An amount of 460 g of rice husk was strongly stirred for 5 min, then the water was exchanged, then the husk was softly stirred for 15 min, and the water was drained. Then the husk was filled in a cloth bag and spin-dried, flushed 1-2 times with water and spinned again until completely drained (3-4 min). The rice husk was dried over night at 110°C.

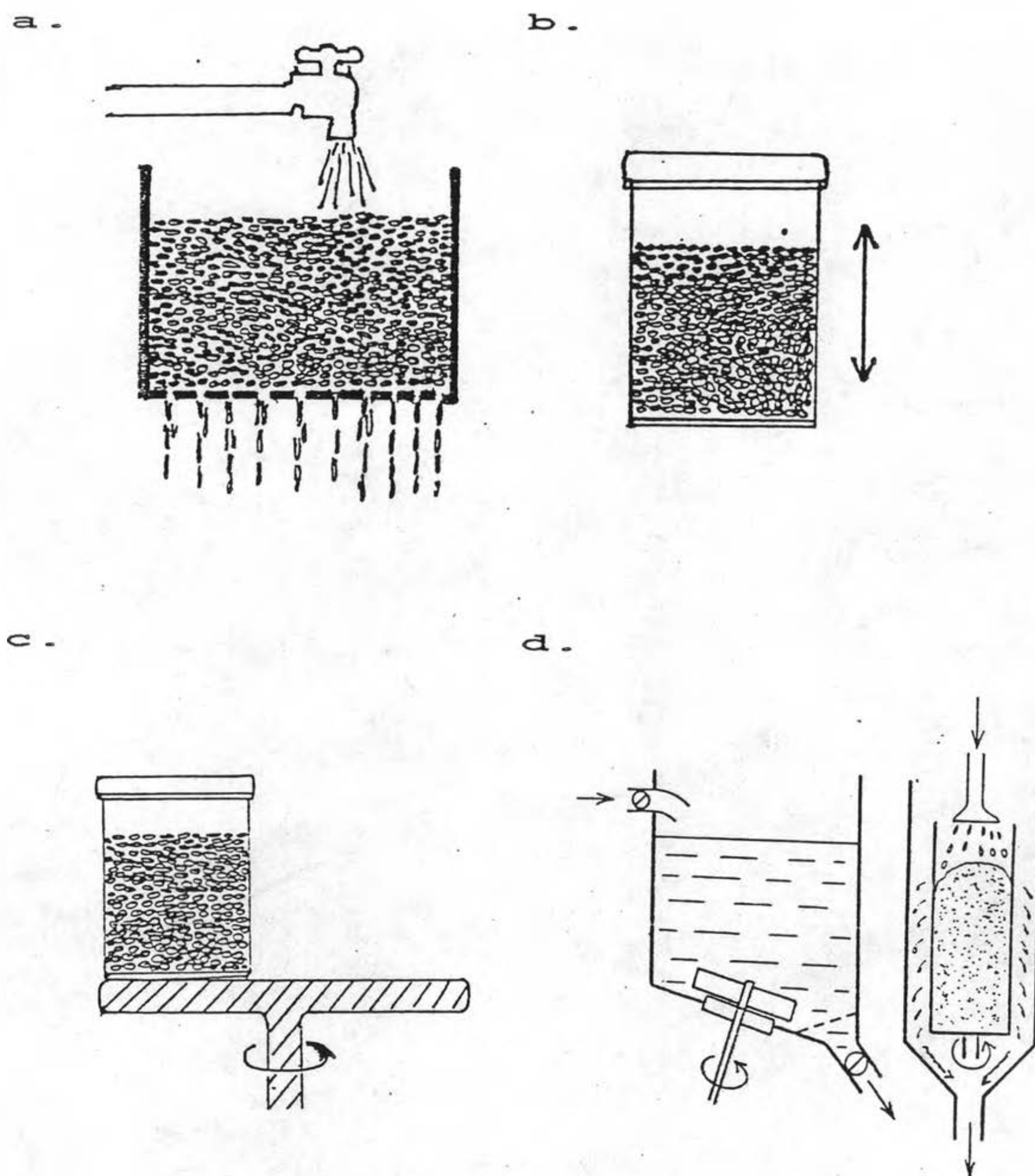

fig. 10. a-d. Illustration of different washing procedures for rice husk;

a: tap water flushing through a sieve;

b: shaking in a finite volume;

c: slinging/spinning in a finite volume;

d: maching washing.

3.2.1.2 Chemical treatment

Two types of chemical treatment were selected, i.e., NaOH treatment and inorganic acid treatment.

NaOH treatment was performed with 25 g rice husk per 350 cm^3 of 1 molar NaOH, 24 h, at room temperature. Rice husk was filled into a plastic bottle, NaOH solution was added until the bottle was full, closed, and shaken strongly to removed trapped air bubbles and make the rice husk sink. After 24 h, the NaOH-treated husk was washed with tap water. The pH value was tested with pH paper until pH $\simeq$ 7 to check for completeness of washing. The treated husk was dried over night at 110°C.

HCl and H_2SO_4 treatment were performed immediately after the washing step because the wet surface of rice husk made the acid permeate through the husk grains. 460 g of rice husk from washing step was boiled in acid solution. Acids were prepared from 1 part of concentrated acid (37 % HCl, and 99 % H_2SO_4 respectively) per 4 parts of tap water to make 5 l solution. After this, the solution was heated up to boil within 30 min, kept boiling for 3 h, and cooled abruptly in a water bath. Acid was washed out with tap water and tested for pH with pH paper until pH $\simeq$ 7. Treated husk was dried over night at 110°C.

The equipment for acid treatment consist of a 12 l glass bulb flask with a rubber stopper and a refluxing condensor. Tap water flow cooled the reflux condensor to prevent acid vapor from escaping. By a wet pH paper kept close to the upper part of the condensor, this was varified. Temperature was checked by a thermometer. The flask was heated by a mantle heater.

HNO_3 treatment was performed with wet washed husk, too. An amount of 7 g of husk was treated in 62 cm^3 of solution. Acid solution was prepared at a ratio of 1:4 of concentrated HNO_3 acid (65 % HNO_3) and water. Husk was treated in a glass beaker covered with a thin sheet of plastic preventing evaporation of acid and treated for 3 h at room temperature. Treated husk was washed with tap water and tested for pH until pH $\approx$ 7. Then it was dried over night at 110°C.

3.2.1.3 Enzymatic treatment

Eventually, this treatment was done before acid treatment. "Soft" digestion of cellulose is expected to help the action of acid treatment to extract cations easily from the inner structure of the husk grains, by this preserving the natural nano-structure. Rice husk received from the washing step was charged in a flask. The enzyme solution was prepared in amounts of 5 l, pH 4.5 (HCl) with commercial celluclase enzyme (6 ml). The solution was kept at 60°C in a water bath for 45 h and bubbled with small air pump to increase the efficiency of the enzyme. After 45 h, the solution was drained out and washed thoroughly.

Only for weight loss determinations, a drying step was switched between the individual steps of treatment. Then before the next steps, rice husk was soaked in tap water for 15 min to assure good wettability by the chemicals.

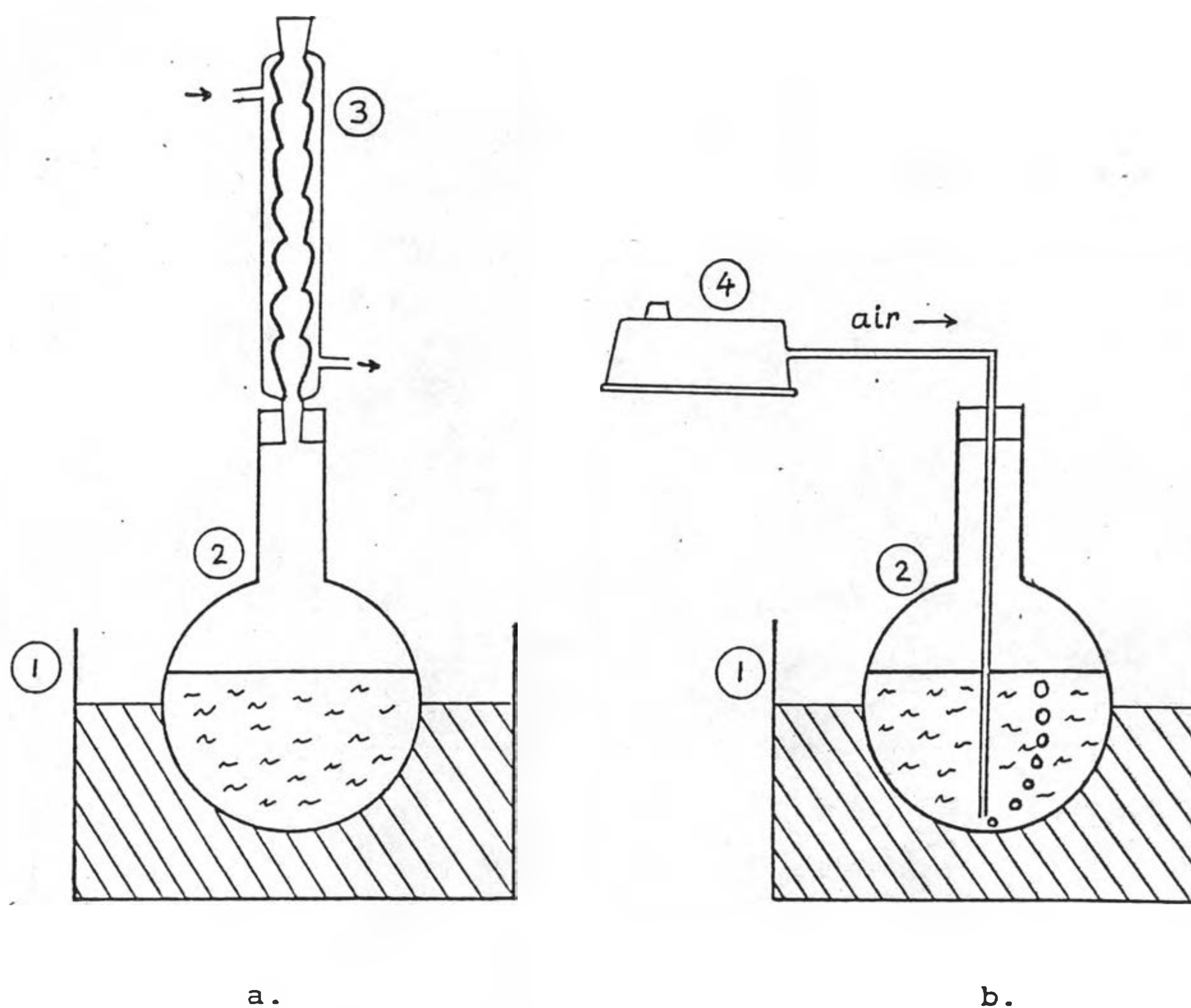

Fig. 11. a-b. Sketch of equipment used for acid (a) and enzymatic (b) treatment of rice husk;

1: mantle heater, or water bath;

2: bulb flask;

3: reflux condensor unit;

4: air pump

3.2.1.4 Incineration

All pre-treated rice husk samples were incinerated in an electric muffle furnace. The husk was incinerated in fused silica crucibles (50 ml, ∅ 7 cm, height 4.5 cm) as a

loosely packed bed of 3 cm height in static air. The furnace was heated up to 600°C. When the temperature in the chamber was constant, the crucibles were put inside at the middle of the chamber for 6 h. After that, the crucibles were pulled out abruptly and cooled down in a desiccator (desiccant silica gel) over night for weight determination.

3.2.2 Characterization

3.2.2.1 Appearance of rice husk and rice husk ash after treatment

Eight differently prepared samples of rice husk were compared. Color difference, sensation upon touching, and morphology were obsevered. This may help and give some clue to what happen to the rice husk during treatment.

3.2.2.2 Weight loss determination

As explained in 3.2.1.3, every step of treatment was interupted by washing and drying. When such a sample was placed on the balance, it started to absorb moisture from the air again, and the weight increased steadily. In order to determine the weight of the dry* material, the sample weight was recorded as a function of time, and extrapolated to t = 0 by a linear regression.

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* The term "dry" in connection with a porous silica is somewhat ambiguous. Most certainly, chemisorbed water ≡Si-OH was still present. Since the drying agent (blue silica gel) had an extremely high specific surface area (≈ 600 m^2/g), the humidity of the rice husk was force-set to an amount proportional to the vapor pressure above blue silica gel.

Pretests had shown that this procedure resulted in excellently reproducible data.

3.2.2.3 Crystallinity

Ash from every kind of treatment was checked for crystallinity at around $2\theta \simeq 22^o$, because the ash is composed of very high content of amorphous silica. From thermodynamic aspects, amorphous silica tends to form cristobalite or tridymite during heat treatment. Both crystalline phases have their major peak (I_{max}) at somewhere around 22°. (cristobalite: I_{max} peak appears at $2\theta = 22.4^o$, I_{20} at $2\theta = 38.2^o$, and I_{10} at $2\theta = 32.8^o$ (JCPDS No.11-695); tridymite I_{max} peak appears at $2\theta = 22^o$, and I_{90} at $2\theta = 20.8^o$, I_{50} at $2\theta = 23.8^o$ (JCPDS No.18-1170)). A 2θ range of 15° - 30° was chosen. In practice, the peak at $\simeq 22^o$ predominates by far.

For the measurement a Phillips X-ray diffractometer model No. DY 1023 type PW1730/10 was used with a scan velocity of 2°/min.

3.2.2.4 Morphology

Rice husk before, after treatment, and after incineration were inspected by optical microscope and scanning electron microscope (SEM) for changes of morphology. Husk ash and treated husk ash powders were observed by SEM and transmission electron microscope (TEM) to see how they disperse and agglomerate.

To observe morphology changes by SEM; the samples were carefully placed on a brass support by 2-sided adhesive

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JCPDS - Joint Committee on Powder Diffraction Standards

tape. Samples for inspection of cross sections of rice husk were cut by a thin razor blade and stuck to the support by colloidal carbon solution. All samples were kept in a desiccator for a few days before gold sputtering.

For particles observation, rice husk ash and treated-rice-husk ash were ground in an agate mortar and dispersed in ethanol-water solution (1:1) by help of an ultrasonic water bath (15 min), and transferred in amounts of single drops by means of a pipette to a Cu grid (ϕ 3 mm), pre-coated by carbon, and dried. For SEM observation, the grids were placed on the brass supports like above, kept in a desiccator for a few days, and sputtered with Au. For TEM observation, the grids were placed on glass plates and kept until dry; then they were inserted directly into the sample chamber of the TEM.

3.2.2.5 Particle size distribution and particle size estimation

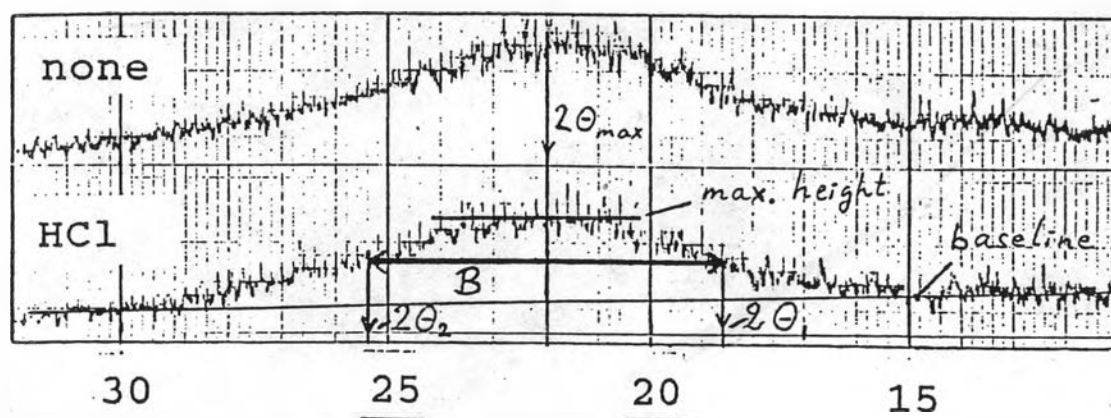

Fig. 12. X-ray peak broadening B for XRD graphs of rice husk ash at $2 \cdot \theta \simeq 22^{o}$; untreated husk ash and HCl treated husk ash.

Particle size distribution was performed in three different ways, i.e., by from TEM micrographs for secondary* particles, from SEM micrographs for low-degree agglomerates, and by light scattering during sedimentation (by gravitation and centrifugation - Shimadzu centrifugal particle size analyser Model SA-CP2). In addition to this, particle sizes of primary particles were estimated from XRD graph peak broadening using Scherer´s formula (see also figure 12)

$$d_o = 0.9 \cdot x/(B \cos\theta)$$

where $x = 0.154$ nm (wavelength of Cu K_α)

$$B = 1/2 \cdot (2\theta_2 - 2\theta_1)\pi/180 \simeq 0.0175\ (\theta_2 - \theta_1)$$

3.2.2.6 Chemical analysis

Rice husk ash and treated husk ash are composed of more than 90 % SiO_2. Therefore, analysis for total silica was the predominant requirement. Gravimetry was the most suited method. Because of the high specific surface area of the product, adsorption of moisture occured all the time at remarkable velocity and at high amounts. So, for reasons of accuracy and precision, the weight was recorded as a function of time, as mentioned in 3.2.2.2. Traditional gravimetry for silica requires removal of alkali prior to weight determination in order to avoid errors due to alkali sulfate formation. For a high specific surface silica, however, this procedure would yield unacceptably high loss silica, much larger than the expected alkali

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* At first, TEM micrographs were misunderstood to display the primary particles, but after consulting other methods (see 5.1), it became obvious that the secondary particles were displayed.

error. Therefore, a simplified way of analysis was chosen: ash was reacted with HF acid in a Pt crucible, according to the equation:

$$SiO_2 + 4HF\ (H_2SO_4) \longrightarrow SiF_4 + 2H_2O\ (H_2SO_4)$$

The sulfuric acid, although not participating in the reaction, is required to bind the released water, thus preventing the HF molecules from becoming associated with H_2O molecules. This would result in H_2SiF_6 formation, and hence, to a less favourable course of volatilization of silica. For the chemical analysis, deionized water was used. Everytime two parallel samples (two Pt crucibles) were used, the weights were measured on a 5-decimal electric balance.

The gravimetric method was done as describe below:

1. The clean Pt crucible was weighed 5 times to determine the starting weight at high precision.

2. Approx. 0.2 g of ash were weighed into the Pt crucible, then heat treated at 1000°C, 15 min to remove adsorbed water.

3. Pt crucible was cooled abruptly, kept in a desiccator for 15 min, as a function of time (see 3.2.2.2); the weight was extrapolated to t = 0.

4. The ash was made wet with a few drops of H_2O; 1 ml of H_2SO_4 (1:1) and 5 ml of HF (40 %) were added. The crucible was kept on a sand bath. The temperature was slowly raised from 95 to 150°C until the majority of the liquid was removed. Then the temperature was raised to 350°C, until all SO_3 smoke had disappeared.

5. The crucible was kept at 1000°C for 15 min, and the weight was determined as mentioned in 3.

This procedure yielded the following primary data:

m(1): empty, clean crucible,

m(2): crucible plus ash,

m(3): crucible plus ash after heat treatment (1000°C, 15 min),

m(4): crucible plus residue after HF and heat treatment.

From the data directly determined, the following quantities were calculated:

sample weight	:	m(2) - m(1)
reference weight	:	m(3) - m(1)
silica content	:	m(3) - m(4)
max. impurity level	:	m(4) - m(1)

According to the stability of compounds, alkalis are present as sulfates, alkaline earths as fluorides or oxides, transition metals and group III...V elements as oxides. Thus the quantity m(4) - m(1) is an overestimate of the oxide impurity level.

Then the residue was washed from the Pt crucible by 10 ml of hot conc. HCl and brought to a volume of 100 ml. Standard solutions of K^+ from 10^{-7} to 0.25 mol/l (pH = 2) were prepared, and a calibration curve (mV vs. log concentration) was established by means of a K^+ sensitive electrode. Then the K^+ level of the sample was measured in terms of mV and read as concentration from the calibration curve.

3.2.2.7 Specific surface area determination

The specific surface area, Γ, (given in m^2/g) is a general property of fine powders, which is indirectly correlated to particle size, particle size distribution, and porosity, but directly correlated to active sites or voids which can be occupied by other molecules. For instance, the three differently sized molecules N_2, Ar, and Kr are commonly used to determined the specific surface area. The area which these molecules can occupy depends on their area demand for adsorption (N_2 = 0.162 nm^2, Ar = 0.138 nm^2, and Kr = 0.202 nm^2). So, surface areas referred to the three kinds of molecules are not the same figure, Ar yields the highest figures, and Kr the lowest ones.

The method of determination of the specific surface area was the so-called BET-method (according to Brunauer, Emmet, and Teller). Solid substances have the characteristic property of adsorbing gas molecules on their surface. The dependence of the adsorbed gas quantity on the pressure of a one-component gas at a constant temperature is called adsorption isotherm. From the curve of the isotherm, the number of gas molecules which can form a complete monomolecular layer on the surface area of the solid substances can be calculated. This figure multiplied with the space requirement of the respective gas molecule makes the total surface area of the investigated solid substances.

The equipment for specific surface area determination using N_2 adsorption at the liquidus temperature of N_2 was the single-point differential method according to DIN 66132 (Ströhlein Instruments, Area-meter II). It is sketched in figure 13. The instrument was purchased during the course of the thesis work, and

was delivered as a "brick box" of its individual parts. It was a major task of the present thesis, to assemble the equipment, to purchase the required periphery, to calibrate it, and to demonstrate its accuracy during test runs. Finally, a procedure was developed which gave satisfactorily reproducible and accurate results.

Ash samples were prepared by grinding ash to a powder, then dried at 150°C over night. About 0.1 g were weighed, poured into the sample vessel, and purged with dry N_2 at 150°C, 30 min, to remove any adhering gases other than N_2.

The equipment had two vessels, i.e., a reference vessel and a sample vessel. Both have the very same volume. Before operating the equipment, a N_2 gas flow was lead through the equipment. Every testing series started with a blank test to check that no pressure difference occured between the (void) sample vessel and the reference vessel. Any pressure difference must be calibrated by adjusting the balancing volume (F). After the blank test, a carbon black standard sample was measured (77 ± 2 m^2/g) to check for systematic bias (i.e., accuracy). Then ash samples were measured. When all ash samples were measured, the carbon black standard sample was measured again to check for systematic drifts during the measurement. In order to bring both vessels to thermal equilibrium, a water bath (for room T) or liquid N_2 bath (for $T = T_{liq}(N_2)$) was used. The baths stand on a support which can be moved up and down and fixed to the position to keep the vessels immersed. Sample measurement (or blank test) started when both vessels were in position, and thermally equilibrated at room temperature. Then the operation valves were opened (sequence 4,3,2,1,5) to let N_2 gas flow through the vessels at least for 15 min (for 0.1 g ash sample). Higher sample weight requires longer equilibration time.

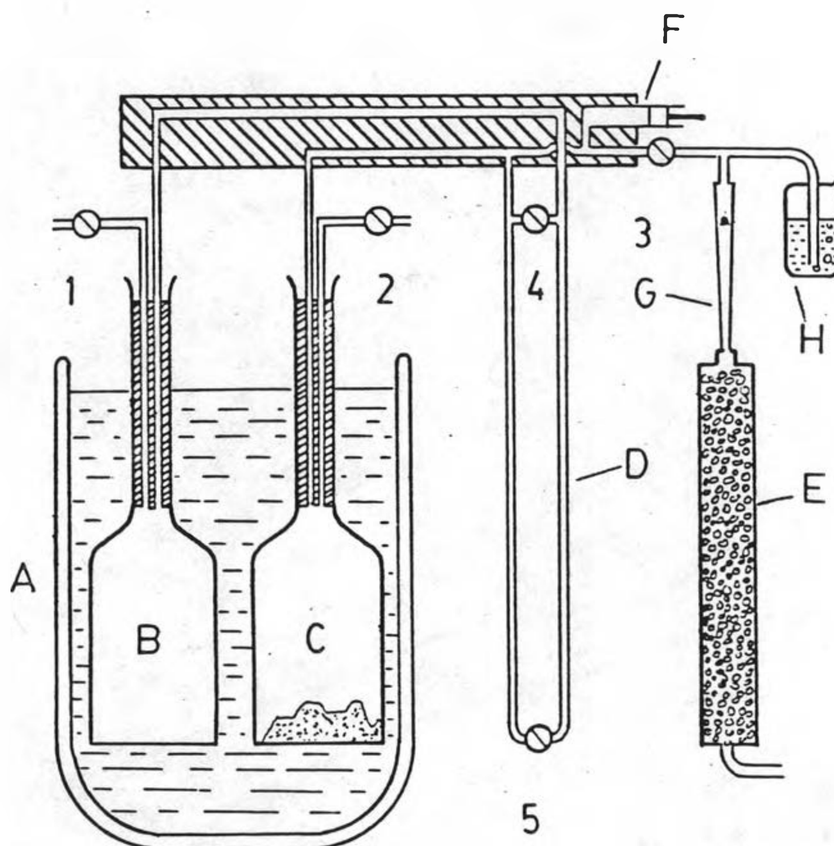

Fig. 13. Sketch of the one-point BET areameter;

1, 2, 3, 4: operation valves	5: manometer valve
A: dewar bath with N_2 (liq)	B: reference vessel
C: sample vessel	D: difference manometer
E: drying column (silica gel)	F: balancing volume
G: flow meter	H: overflow vessel

Otherwise the temperature of the sample vessel will be different from that of the reference vessel, which leads to errors in the value of surface area. Then the valves were closed to stop the N_2 flow, the water bath was removed, and water drops swept away from the vessels. Then the vessels were immersed in the liquid N_2 bath for a while until liquid N_2 stopped boiling (i.e., until $T \simeq T_{liq}(N_2)$). Then valve no. 5 was opened to read the pressure difference (mm) from the difference manometer. The left side of the difference manometer represents the sample vessel pressure and the right side the reference vessel. The pressure difference read from the difference manometer is not a final result yet. It is rather a relative pressure, which has to be converted into a surface area. Because of N_2 adsorption on the surface of the sample, the N_2 gas pressure in the sample vessel is reduced (assuming that the adsorption on the glass surface of sample and reference vessels are equal and can be neglected). When too much weight of sample is used, then the pressure difference is too high to be read from the manometer scale. Another error may occur: When the two vessels are not isotherm, then the pressure from the sample vessel appears to be higher than from the reference vessel. This is because it takes a longer time to transfer heat from a porous sample to the liquid N_2 bath than from a void glass vessel. This problem can be solved by allowing more immersion time in the liquid N_2 bath (longer than 15 min) or by reducing the amount of sample in the vessel. From the pressure difference, the specific surface area can be calculated by

$$\Gamma = (A \cdot \Delta P) / m$$

where Γ = Specific surface area (m^2/g)

ΔP = difference pressure (mm)

m = sample weight (g)

A = coefficient, read from nomogram (see Appendix A)

The application of a more complicated formula, also involving a correction factor B (see Appendix A) was not necessary for the high specific surface areas of rice husk ash.