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Fuels and Chemicals from Rice Straw in Egypt

Abstract

In Egypt rice cultivation in the river Nile Delta produces large amounts of rice straw as residue. Assuming that about 20% were used for other purposes about 2.8 Mt were left on the fields for burning within a period of 30 days to get quickly rid of leftover debris. The resulting emissions give a significant contribution to the air pollution called the "Black Cloud". A suitable technology for the use of rice straw is an important contribution to reduce air pollution and gives a significant contribution to use biomass as renewable energy in Egypt.

Based on that fact rice straw was studied as possible feedstock for the BIOLIQ process. The BIOLIQ process which is under development at the Forschungszentrum Karlsruhe (Germany) is a two-step process for the production of chemicals, fuels or electricity from lignocellulosic biomass with high ash content. In the first step the biomass is liquefied by fast pyrolysis. The pyrolysis char and the pyrolysis liquid are mixed to form a slurry. In the second step the pumpable slurry is used to produce syngas in a pressurised entrained flow gasifier. After gas cleaning and conditioning the syngas is used for the production of fuels, chemicals and electricity as by-product. In this work rice straw is studied as a possible feedstock for fast pyrolysis and slurry preparation.

First the Egyptian rice straw was chemically characterised. Ultimate analysis of rice straw showed an elemental composition of 47,8% C, 6,0 %H and 45,3% O, (daf). According to the elemental composition the HHV was calculated to be about 18,1 MJ/Kg (Dulong) up to 20,5 MJ/kg (Ebeling). Based on the experimental HHV 15,3 MJ/kg (rice straw dry, 18% ash) the HHV on a moisture and ash free basis was calculated to be 18,7 MJ/kg. According to the literature the lignin, hemicellulose and cellulose contents of rice straw were about 12%, 28% and 60%, respectively. The rice straw was chopped and sieved (2 mm sieve) and most of the straw dust was separated before use. The pyrolysis process was studied on laboratory and PDU (process demonstration unit) scale. During pyrolysis lignin gave the main contribution to the char formation. TGA pyrolysis experiments showed about 60% of volatiles, 20% fixed carbon and 20% of ash on the average (dry). These results were very close to the results of fast pyrolysis experiments in a PDU with a twin-screw reactor. The chlorine was focussed in the pyrolysis char up to a temperature of ~500°C. If the pyrolysis temperature exceeded 500°C the chlorine was released and its concentration in the chars decreased. The outside of the rice straw stems was completely covered with silica forming a close protection layer. SEM-studies show that the pyrolysis took place only at the inner sides of the stems. Therefore rice straw had to be chopped very carefully in order to brake up short stem pieces and to split them up. Additionally the SEM pictures confirmed the volatility of chlorine at temperatures above 500°C. Condensate viscosity, char porosity and the particle size spectrum as well as slurry production techniques play an essential role for slurry preparation and result in practicable condensate/char-weight ratio variations between about 3 to 1.3 for worse and unfavourable situations. With a special colloid mixer, a robust tool well known for the preparation of a very homogeneous cement grout it was possible to prepare a pumpable char/tar mixture with a high mixing ratio of almost 50% by weight.

The high ash content in rice straw was retained in the char and increased the amount of solid product. The char to condensate ratio decreased to 1.3 resulting in a slurry with about 43% of char.

Fast pyrolysis was essential to generate sufficient condensate for char suspension, especially for feedstocks with more ash like rice straw and in combination a special colloid mixer was necessary for the generation of slurrries with a high char load containing about 90% of the initial biomass energy.

The results showed that for the total available amount of rice straw in Egypt (~2,8 Mt/year) about 28 fast pyrolysis units each with a capacity of 100.000t/a are necessary. Square bales with ~ 100 kg/m^3 bulk density are the preferred feedstock for compact transport and storage. In the regions of the Nile delta the unused half of the straw harvest amounts to ~ 120 - 250 t per year and km^2. For a capacity for a regional pyrolysis plant of 100.000 t/a a maximum delivery radius of 15 km comprises about 700 km^2 resulting in a throughput of 12 to 15 t/h of airdry rice straw. In-time straw delivery to an intermediate storage facility at the pyrolysis plant must be fixed by contracts with the local farmers, as is known from Danish district heating plants. The straw should be as dry as possible (<15% moisture) when delivered at the plant gate. Low temperature process heat can be used there to reduce the moisture content down to < 5%. Before feeding the straw it must be chopped very carefully. The produced slurry of 2,3Mt/a and can be used to produce about 350 Mt of Fischer Tropsch diesel per year.

Herstellung von Kraftstoffen und Chemikalien aus Reisstroh in Ägypten

Zusammenfassung

Bei der Reiserzeugung in Ägypten fallen jährlich große Mengen an Reisstroh als landwirtschaftlicher Rückstand an. Etwa 2,8 Mt werden jährlich innerhalb einer Periode von 30 Tagen im Herbst auf den Feldern verbrannt. Die damit verbundenen Emissionen tragen maßgeblich zur Luftverschmutzung der sogenannten „Black cloud“ bei. Eine Technologie, die es ermöglicht, Reisstroh zu Chemikalien, Kraftstoff oder Strom zu verarbeiten, würde einen erheblichen Beitrag zur Verbesserung der Luftqualität leisten. Eine Möglichkeit dazu besteht in der Nutzung von Reisstroh als Rohstoff für das BIOLIQ Verfahren. Dieses zweistufige Verfahren zur Herstellung von Chemikalien oder Strom aus trockenen landwirtschaftlichen Reststoffen wird derzeit am Forschungszentrum Karlsruhe erprobt. In einem ersten Schritt wird die Biomasse durch Schnellpyrolyse verflüssigt, indem die bei der Verschwelung bei 500°C entstehenden Produkte Koks und Pyrolysekondensat zu einem pumpfähigen Slurry vermischt werden. In einem weiteren Verfahrensschritt wird dieser in einem GSP-Druckvergaser (Gaskombinat Schwarze Pumpe) zur Herstellung von Synthesegas verwendet. Nach der Reinigung und Konditionierung des Synthesegases werden daraus in einer Syntheseanlage Kraftstoffe, Chemikalien und/oder Strom hergestellt. Im Rahmen dieser Untersuchungen wurde Reisstroh aus Ägypten auf seine Eignung als Rohstoff zur Herstellung von Slurry für das BIOLIQ Verfahren untersucht.

Vor den Versuchen wurde das Material auf eine Partikelgröße < 2mm zerkleinert. Der Wassergehalt des untersuchten Materials schwankte zwischen 8 und 12%. Da eine hohe Feuchtigkeit des Eduktes den Gesamtwirkungsgrad deutlich verschlechtert, muss bei technischen Anlagen auf eine gute Vortrocknung geachtet werden. Die Ultimatanalysen ergaben für den trockenen und aschefreien Zustand (daf) eine Zusammensetzung von 47,8% C, 6,0% H und 45,3% O. Aus dem experimentellen Brennwert von 15,3 MJ/kg berechnete sich der Heizwert (daf) zu 18,7 MJ/kg. Die Pyrolyse wurde im Labor- und Technikumsmaßstab (10kg/h) untersucht. Wie aus der Literatur bekannt, trug der Ligninanteil erheblich zur Menge des gebildeten Pyrolysekokses bei. Begleitende Untersuchungen mit der Thermowaage ergaben einen Anteil von 60% an flüchtigen Komponenten, von 20% Koks und von 20% Asche. Aufnahmen mit einem Rasterelektronenmikroskop zeigten, dass besonders die Außenseite der Reishalme komplett mit einer dichten Silikatschicht bedeckt war. Der pyrolytische Abbau des Materials fand deswegen bevorzugt an der Innenseite der Halme statt. Infolgedessen wurde das Stroh sorgfältig gehäckselt, um die Halme der Länge nach aufzuspalten. Durch die Aufnahmen wurde auch gezeigt, dass sich bei der Pyrolyse besonders Chlorid an der Oberfläche anreichert und sich bei Betriebstemperaturen >500°C verflüchtigt und an kälteren Stellen zu Ablagerungen und Verengungen führt.

Die Viskosität der Kondensate und die Porosität und die Partikelgröße des Pyrolysekokses sind bei der Slurryherstellung von großer Bedeutung. Bei einem Gewichtsverhältnis von Kondensat zu Koks von ~3 lassen sich solche Suspensionen ohne Probleme herstellen. Bei Materialien mit hohen Aschegehalten sinkt dieses jedoch auf 1,3 ab. In diesen Fällen konnten pumpfähige Slurries mit einem Feststoffgehalt von ~45% nur durch Verwendung eines Kolloidmischers hergestellt werden. Diese enthielten ca. 90% der ursprünglichen Energie. Eine Modellstudie ergab, dass ca. 28 Pyrolyseanlagen mit einer Kapazität von jeweils 100.000 t/a notwendig wären, um die im Nildelta anfallenden Mengen zu verarbeiten. Bei einer Strohmenge von 120 – 250 t /km^2 Jahr entspricht dies einem Einzugsgebiet von ca. 700 km^2 oder einem Einzugsradius von 15 km. Die zeitgemäße Anlieferung müsste durch entsprechend Lieferverträge mit den örtlichen Farmern geregelt werden. Aus einer Slurrygesamtmenge von ca. 2,3 Mt/Jahr können so ~350 Mt synthetischer Diesel hergestellt werden.

Preface

This study was prepared as a contribution to the agreement between the Government of the Arab Republic of Egypt and the Government of the Federal Republic of Germany on cooperation in the field of scientific research and technological development signed 1979 and 1981. In the frame of the project ”Environmental Analytical Chemistry” between the Atomic Energy Authority (AEA), National Egyptian Radiation and Environmental Monitoring Network in Cairo and the Forschungszentrum Karlsruhe, Institute for Technical Chemistry – Division of Chemical-Physical Processing (ITC-CPV) the environmental situation in Egypt is studied and characterised. On behalf of the BMBF (Federal Ministry of Education and Research) the International Bureau of BMBF linked to the Forschungszentrum Jülich assists in developing this international cooperation. The focus of the two laboratories research program is on renewable energy techniques and their cost-effectiveness use for the identification, control and prevention of pollution to air, water and its subsurface resources. The research provides solutions to environmental problems by developing and promoting techniques that help to protect and improve the environment by advancing scientific information to support regulatory and policy decisions and providing the technical support and by information transfer to ensure implementations of environmental regulations and strategies at the national, state and community levels. It contributes to an international network of research institutions and the education of the involved scientists on both sides. Many of the leading scientists of AEA have been in Germany during their scientific education a fact that results in a very positive attitude towards Germany. The intensive exchange of young scientists who will be the decision makers in the near future will to help to keep up that tradition and thus contribute to strengthen democracy and economy in the Near East in the future.

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1 Summary

In the river Nile delta (Egypt) the amount of rice straw was estimated to be 3.5+-0.6 Mt per year. Assuming that about 20% were used for other purposes about 2.8 Mt were left on the fields for burning within a period of 30 days to get quickly rid of leftover debris. The resulting emissions give a significant contribution to the air pollution called the “Black Cloud. A suitable technology for the use of rice straw is an important contribution to the reduction of air pollution and gives a significant contribution to use biomass as renewable energy in Egypt.

In order to study rice straw as possible feedstock for the BIOLIQ process 30 t of straw from the Nile delta were collected in 2004 and transported to Germany. The BIOLIQ process which is under development at the Forschungszentrum Karlsruhe (Germany) is a two-step process for the production of chemicals, fuels or electricity from lignocellulosic biomass with high ash content. In the first step the biomass is liquefied by fast pyrolysis. The pyrolysis char and the pyrolysis liquid are mixed to form a slurry. In the second step the pumpable slurry is used to produce syngas in a pressurised entrained flow gasifier. After gas cleaning and conditioning the syngas is used for the production of fuels, chemicals and electricity as by-product.

Table A: Summary of rice straw propereties

Moisture (%)					
	after harvest	**field, dry**	**in laboratory**		
	50-80	**10-15**	**~8**		
Ultimate analysis					
	C	**H**	**O**	**N+S**	**Cl**
dry	**39,2%**	**4,8%**	**36,4%**	**0,6%**	**1,9%**
daf	**46,6%**	**6,2%**	**46,5%**	**0,7%**	
Proximate analysis					
		Volatiles	**Fixed carbon**	**Ash**	
TGA		**60%**	**20%**	**20%**	
FP		**61%**	**FC+ash 39%**		
Structural components (%) , literature					
	Cellulose	**Hemicellulose**	**Lignin**		
	33	**28**	**12**		
HHV (MJ/kg)					
	18%A+8%M	**dry**	**daf**		
	14,1	**15,3**	**18,7**		
Amount of Minerals (%)					
	TGA	**Ashing 815°C**	**100%-Ultimate analysis**		
	20%	**19,6**	**18,3**		
Ash composition (%)					
	SiO2	**K2O**	**Na2O**	**MgO**	**CaO**
	65,7	**15**	**3,1**	**2,1**	**1,7**
Ash flow point temperature, reducing conditions (°C)					
	1390				

In this work rice straw is studied as a possible feedstock for fast pyrolysis and slurry preparation.

First the Egyptian rice straw was chemically characterised. Table A summarises the results.

Fast growing biomass can be described by the empirical composition $C_6H_9O_4$ for moisture and ash free lignocellulose corresponding to an elemental composition of 49,7% C, 6,2% H and 44,1% O. The ultimate analysis of rice straw showed an elemental composition of 47,8% C, 6,0 %H and 45,3% O, (daf) proving to be a very satisfactory average to fit these conditions within the experimental scattering. According to the elemental composition the HHV can be calculated. The results for the empirical composition differ from 18,1 MJ/Kg (Dulong) up to 20,5 MJ/kg (Ebeling). Based on the experimental HHV 15,3 MJ/kg (rice straw dry, 18% ash) the HHV on a moisture and ash free basis is calculated to be 18,7 MJ/kg. The results show that rice straw can be described like other types of biomass as $C_6H_9O_4$ combined with certain amounts of ash and moisture. According to the literature the lignin, hemicellulose and cellulose contents of rice straw were about 12%, 28% and 60%, respectively. The pyrolysis process was studied on laboratory and PDU (process demonstration unit) scale. During pyrolysis lignin gives the main contribution to the char formation. The rice straw was chopped and sieved (2 mm sieve) and most of the straw dust was separated before use. TGA pyrolysis experiments give about 60% of volatiles, 20% fixed carbon and 20% of ash on the average (dry). These results are very close to the results of fast pyrolysis experiments in a PDU with a twin-screw reactor (volatile 61%, char + ash 39%, dry). The chlorine is focussed in the pyrolysis char up to a temperature of ~500°C. If the pyrolysis temperature exceeds 500°C the chlorine is released and its concentration in the chars decreases. To avoid any depositions in the downstream piping or corrosion effects the operation temperature of a technical pyrolysis plant should be at 500°C maximum. The outside of the rice straw stems is completely covered with silica forming a close protection layer. SEM-studies show that the pyrolysis takes place only at the inner sides of the stems. Therefore rice straw has to be chopped very carefully in order to brake up short stem pieces and to split them up. Additionally the SEM pictures confirm the volatility of chlorine at temperatures above 500°C.

For the empirical biomass (without ash and moisture) the char/condensate ratio is 2.5 (1). Under these conditions all the char can be suspended in the own condensates. The high ash content in rice straw is retained in the char and increases the amount of solid product. The char to condensate ratio decreases to 1.3 (2) resulting in a slurry with about 43% of char.

1) 100 Biomass (daf) → 25 gas + 50 condensate + 25 char

2) 100 Biomass → 19 gas + 45 condensate + 36 char
(8% moisture +
18% ash)

Condensate viscosity, char porosity and the particle size spectrum as well as slurry production techniques play an essential role for slurry preparation and result in practicable condensate/char-weight ratio variations between about 3 to 1.3 for worse and unfavourable situations. With a special colloid mixer, a robust tool well known for the preparation of a very homogeneous cement grout it is possible to prepare a pumpable char/tar mixture with a high mixing ratio of almost 50% by weight.

Fast pyrolysis is essential to generate sufficient condensate for char suspension, especially for feedstocks with more ash like rice straw and in combination a special colloid mixer is necessary for the generation of slurrries with a high char load containing about 90% of the initial biomass energy.

For the total available amount of rice straw in Egypt (~2,8 Mt/year) about 28 fast pyrolysis units each with a capacity of 100.000t/a are necessary.

Square bales with ~ 100 kg/m^3 bulk density are the preferred feedstock for compact transport and storage. In the regions of the Nile delta the unused half of the straw harvest amounts to ~ 120 - 250 t per year and km$^{2.}$ For a capacity for a regional pyrolysis plant of 100.000 t/a a maximum delivery radius of 15 km comprises about

700 km^2 resulting in a throughput of 12 to 15 t/h of airdry rice straw. In-time straw delivery to an intermediate storage facility at the pyrolysis plant must be fixed by contracts with the local farmers, as is known from Danish district heating plants. The straw should be as dry as possible (<15% moisture) when delivered at the plant gate. Low temperature process heat can be used there to reduce the moisture content down to < 5%. Before feeding the straw it must be chopped very carefully. The produced slurry of 2,3Mt/a and can be used to produce about 350 Mt of Fischer Tropsch diesel per year.

2 Introduction

Egypt is the largest rice producer in the Near East region. After harvest the fields must then be cleaned and prepared for the next winter cultivation in the end of October. Thus the time available between rice harvest and next crop is about one month. Generally the of straw is burned soon after threshing, which is the quickest way to get rid of it and to prepare the soil for the next crop. In Egypt the uncontrolled burning of huge amounts of rice straw causes a severe air pollution. The combustion products are released to the atmosphere and contribute to the formation of the "Black Cloud" in combination with garbage burning operations and emissions from factories in the north of Cairo. Exhaust fumes from the city's estimated 2 million cars combined with emissions from the area's 20,000 metal smelters are the other major man-made factors contributing to the toxic composition of the cloud.

On the other hand energy will continue to play an important role in Egypt's economy in coming years. Though net exports of crude oil and petroleum products have declined in recent years, higher prices on world markets have pushed Egypt's oil revenues upward. Egypt produced an average of about 594,000 barrels per day (bbl/d) of crude oil in 2004, down sharply from its peak of 922,000 bbl/d in 1996, but only modestly below the 618,000 bbl/d produced in 2003 [70]. Increased production of natural gas liquids, which averaged 114,000 bbl/d in 2004, also has offset some of the decline in crude oil production. A suitable technology to use the renewable energy of rice straw would help to reduce Egypt's dependency on fissile fuels and give a significant contribution to reduce environmental pollution.

The adoption of the two-step pyrolysis-gasification process, which is under development at the Forschungszentrum Karlsruhe, might be a solution for this problem. Rice straw from local farmers is converted to a bio-oil-slurry. In the second the bio slurry us gasified to form syngas. Syngas can be used to get chemicals, fuels or electricity. The gasification step is expensive and not necessary at the beginning. It might be an option for development in the future. Instead of the gasification the slurry is then transported to power stations and used there instead of heavy fuel oil.

3 Objectives

Huge amounts of rice straw residues are burned in the Nile Delta every year to get quickly rid of it but without any use. The main objectives of this study are to:

a) Summarize and provide reliable information about the amount of rice straw;
b) Study the use of rice straw as a potential energy resource in Egypt;
c) Use rice straw as feedstock for the BIOLIQ process;
d) Establish a data basis to identify changes in the near future and give a contribution to upcoming international projects like ProMed [4,5];
e) Train young scientists in different analytical techniques and quality assurance;
f) Enhance the sensitivity for environmental impacts of pollutants.

4 Geography and population

Egypt lies in the north–eastern corner of the African continent between latitude 22° und 32° N und longitude 25° und 35° E. The Egyptian territory is almost rectangular: in the north it is bordered by the Mediterranean Sea with a coastline of 995 kilometres. In the East Egypt is limited by a 265 km long border to Israel and the Red Sea, in the south by Sudan (1280 km) and in the west by Libya (1115km) [1]. From north to south the largest distance is about 1085 km, from west to east about 1255 km. It covers an area of about one million km^2 (land 995450 km^2, water 6000 km^2) and is about 3 times larger when compared to Germany. In 2004, the total cultivated land was about 3,3% of the total area. About 2,7% consist of arable land - land cultivated for crops like wheat, maize, and rice that are replanted after each harvest. The rest is used for permanent crops - land cultivated for crops like citrus that are not replanted after each harvest. The vast majority of Egypt's population inhabit the banks along the length of the Nile river (about 40,000 km^2) and the Suez Canal. Large areas of land are part of the Sahara Desert and sparsely inhabited. The total population is about 70,1 million (2004) of which about 55% is rural, with annual demographic growth estimated at 1,8%. The average population density is ~70 inhabitants/km^2, ranging from 2 inhabitants/km in over 96% of the total area to 1500 inhabitants/km^2 in the Nile Valley and Delta [1].

5 Agricultural situation in 2004

Cropping Pattern

Egypt has a wide variety of crops cotton, wheat, rice and berseem or Egyptian glover account for 80% of crops. Wheat and berseem are the main winter crops. In summer cotton and rice are important cash crops, maize and sorghum the subsidence crops. About 90 percent of the agricultural area is concentrated in the Delta and the rest falls within a narrow ribbon along the Nile between Aswan and Cairo and a strip along the Mediterranean. The level of production is relatively high, compared with other countries with similar agro climatic conditions. The warm weather and fertile soil enable Egyptian farmers to practice double and multiple cropping. The most common practices observed in the delta are guided by a three-year rotation based on cotton, berseem and wheat. These three crops are planted on the same plot once every three years interspersed with broad beans, rice and maize. The dominant cropping pattern is shown in table I.

Table I: Dominant cropping pattern in the Nile Delta

Year	Season	Winter	Summer
1	**1**	**Legume**	
	2		**Cotton**
2	**3**	**Berseem**	
	4		**Rice/Maize**
3	**5**	**Wheat**	
	6		**Rice Maize**

Rice, cotton and wheat are usually grown in large blocks arranged on the village level by the cooperatives. The farmers often own land in each of the major blocks. In regions where the amount of water is available rice replaces maize in the crop rotation. Another reason is that the farmers get more bushels per hectare. During summer rice usually covers over half of the cultivated area.

6 Rice

6.1 General

The United Nations has declared 2004 to be the International Year of Rice [5]. Rice (genus Oryza) is tolerant to desert, hot, humid, flooded, dry and cool conditions and grows in saline, alkaline and acidic soils. In general 23 oryza species are known, two are cultivated: oryza sativa which has its origin in the humid tropics of Asia and oryza glaberrima, from West Africa. The Asian cultivated rice has evolved into three eco-geographic races: India, japonica and javanica. The dominant species of cultivated rice is Asian rice (*Oryza sativa*), which is grown around the world, while cultivation of African rice (*Oryza glaberrima*) takes place largely in West Africa. While rice is a matter of survival for many, the United Nations Food and Agricultural Organization points out that the rice grain has achieved a central cultural status in countries such as Japan, Vietnam, and Egypt. Most of the planted rice varieties in Egypt are japonica (~85%).

6.2 Rice Production in Egypt

Egypt is the largest rice producer in the Near East region. In 2003 the total production of paddy was 5.8 million tonnes [3,2] of which 0,7 million tonnes are exported to the Arabic countries (Appendix C, table VIII). However the international prices for rice have been under strong downwards pressure since about 1998. Rice is a major summer crop in Egypt covering 1.5 million feddan (1 feddan = 0,4047ha,

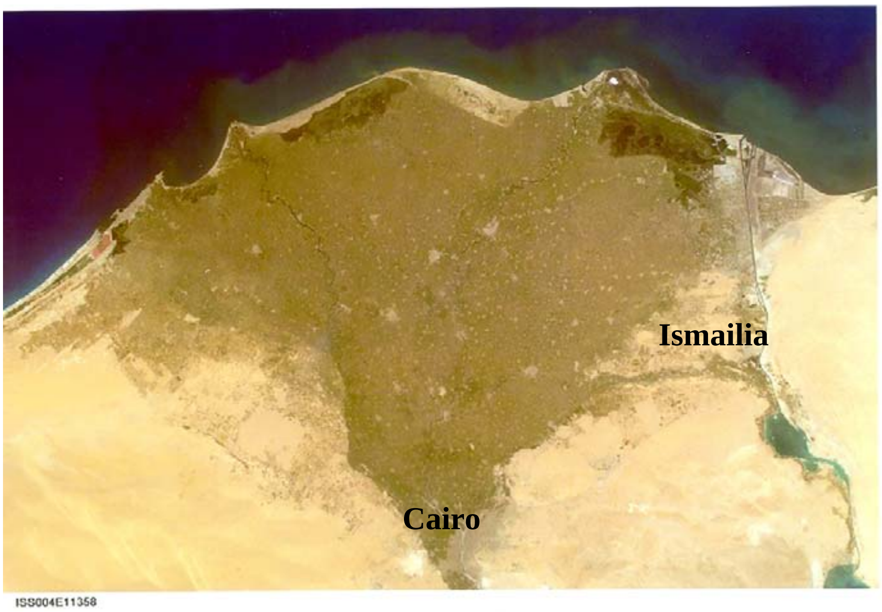


Figure 1: River Nile delta from space, (Nasa, http://eol.jsc.nasa.gov)

615 000 ha) in 2003 out of a total cultivated area of about 7.8 million feddan. In fact, the Egyptian rice yield is one of the highest in the world (9.4 t/ha) [4]); However, due to its high water requirements the rice cultivation is restricted the in the lower valley of the river Nile delta (Fig. 1) with its very intensive irrigation system. Due to the intrusion of seawater about 25% of the land in the lower Nile Valley is affected by different degrees of salinity. Rice areas could be increased, but the problem of water shortage will be a limiting factor.

Rice cultivation is a main source of income. Rice is one of the main source of employment, income and nutrition for a lot of the poor people in rural areas. Many people still have an income after the rice season is over. They work in post harvest activities. Rice has several post harvest activities including threshing, milling, market transport and cooking. There are also people in the rural areas that care for the machinery and tools necessary for harvest and post harvest activities. Thus rice is a substantial crop that helps people in Egypt to make their living.

6.3 Rice Cultivation

The rice plant needs 3-6 months to grow depending on the variety and environment where it is grown. During this time rice completes three growth phases: vegetative, reproductive and ripening. The vegetative phase consists of germination, early seeding growth and tillering and takes about 60 days to complete. The reproductive phase lasts about 30 days and consists of the time before and after heading. The ripening phase last about 30 days. The production of rice is a labour intensive task, which is mainly done by the family – preparing the fields for planting, weeding and harvesting. After harvesting the rice needs to dry, then it goes through threshing, winnowing, drying once again and storage. During our visit to the rice fields in the river Nile delta at Benha and El Mansura we found two species of rice differing in the length of the stalk. The long version had a length of about 122 cm, the short one was about 75 cm long. Harvester-threshers like in Europe were used in a few cases only for the harvest of the short rice species. In this case the straw bales can be formed. Most of the long stalk rice is not in an upright position necessary for machine harvester. About 90% of the rice is hand cut leaving 10 cm high stubbles on the field. The harvest was first left to dry on the field to reduce the moisture content from 30 to about 15%. The rice was then tied into shaves collected and transported to an in-field fix threshing machine. A stationary small threshing machine driven by tractor was generally used. The air blown straw residues form small piles (~ 2m high and 5-8 m in diameter). A small amount was used on the farms as litter for animals. The fields must then be cleaned and prepared for the next winter cultivation in the end of October. Thus the time available between rice harvest and next crop is about one month. Generally the pile of straw is burned soon after threshing, which is the quickest way to get rid of it and to prepare the soil for the next crop. It is also a good way to eliminate rice pests such as Pyricularia Oryzae.

Figure 2: Rice with long and short stalk.

Figure 3: Rice field with short stalks

Figure 4: Rice field of long stalks in the background, bundles drying in the front.

Figure 5: Threshing of rice by local families

6.4 Rice processing

The unprepared rice which is still firmly enclosed in its glumes is called Paddy rice. The seeds of the rice plant are first milled to remove the outer husks of the grain; this creates brown rice. Brown rice is rice which has had its glumes removed but is otherwise unprepared. The majority of the silver skin is still attached to the hulled rice grain. The glumes are removed in the exporting countries by hulling. This process may be continued, removing the germ and the rest of the husk, called bran at this point, creating white rice. The germ is the “heart” of the cereal kernel and a concentrated source of several essential nutrients including Vitamin E, folic acid, phosphorus, zinc and magnesium. Bran (silver skin) is the hard outer layer of cereal grains. Along with germ it is an integral part of whole grains and is often produced as a by-product of milling in the production of refined grains. A mixture of 80% white rice and 20% Paddy rice is provided for maritime transport (Cargo rice).

6.5 Environmental impacts caused by rice cultivation

The dominance of rice in the cropping pattern causes several problems:

a) The prevalence of rice in the cropping pattern causes problems for water management and drainage. In rice fields, the presence of a subsurface drainage system that was installed for other crops causes substantial water losses through the system and leads to large application of irrigating water [6].

b) Yet Neue (1993) identified rice field methane emissions as a major source of atmospheric methane. In "Methane Emission from Rice Fields: Wetland Rice Fields May Make a Major Contribution to Global Warming," Neue explains that in wetland rice soils, flooding a field cuts off the oxygen supply from the atmosphere, resulting in anaerobic fermentation of soil organic matter. Methane, a major end product of anaerobic fermentation, is released from submerged soils to the atmosphere through the roots and stems of rice plants. Estimates of global methane emission rates from rice fields range from 20 to 100 Tg per year (1 Tg=1 million tons), which corresponds to 6 to 29 percent of total annual anthropogenic methane emission [7,8].

c) A new phenomenon dubbed the "black cloud" which in October or November chokes the population on thick black smoke appeared for the first time in 1999. Farmers are blamed on burning harvest waste products such as rice stalks.

The Egyptian Environmental Affairs Agency (EEAA) had made much progress in helping industry conform to strict Egyptian pollution regulations since environmental laws were first passed in 1994.

7 Rice Straw

7.1 Amount of Rice Straw

For effective utilisation of biomass accurate data on yields and properties are necessary for design purposes. The straw yield and straw to grain ratios for rice straw vary widely and are effected by continent, country, varieties of rice, season, stubble height, equipment losses, etc. . As the total amount of Paddy rice produced in Egypt is well known the amount of rice straw can be calculated if the straw to grain ratio is known. As figure 6 shows the production of Paddy rice has been nearly constant at 2,3 Mt/year in the period 1960 to 1990. Afterwards the production increased up to 5.8 MT per year in 2004. In the same period the harvested hectares increased only from 4 Mha up to 600 Mha in 2004. As a consequence the rice yield (~9,3 t/ha) is one of the highest on world. For the straw to grain ratio Summers reports a ratio 0.7 up to 1.6 [10] for California, USA, effected by cutter high and straw

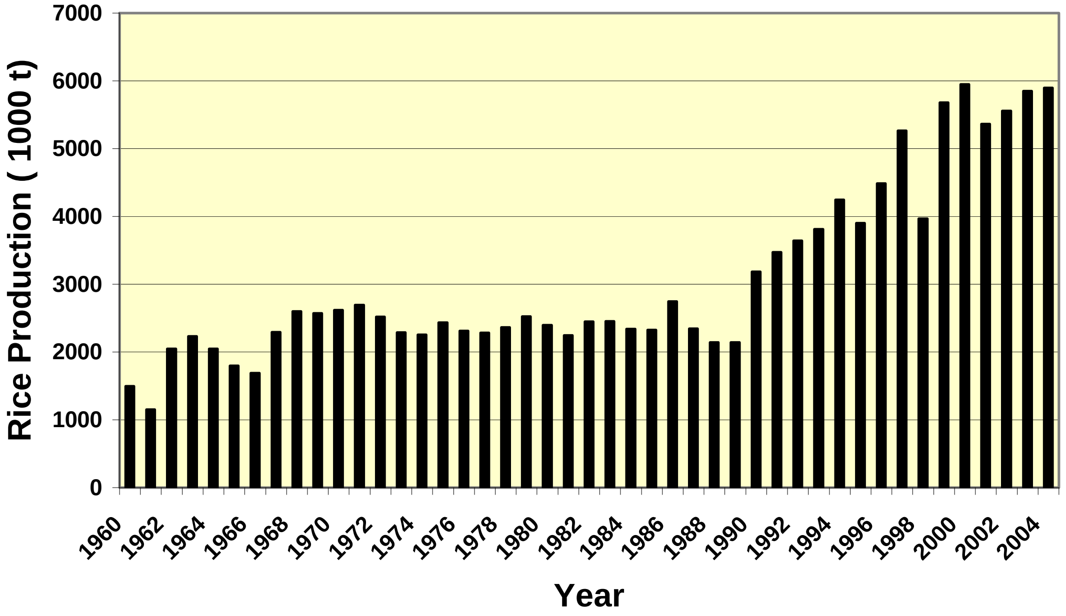


Figure 6: Production of rice (Paddy) in Egypt in the period 1960 – 2002 [9].

variety and more general from 0.89 – 2.29 [11]. Especially for Egypt several amounts of rice straw were reported [Table II]. From these data the average straw to grain ratio in the period 1974 till 2003 was estimated to be about 0.6 for Egypt. In 2003 the corresponding amount of rice straw was calculated to be 3.5+-0.6 Mt per year. Assuming that about 20% were used for other purposes about 2.8 Mt were left on the fields for burning in 2004.

Table II: Rice straw residues in Egypt

Year	Straw Amount (Mt)	Literature Source	Rice Production [9] (Mt)	Straw/Grain ratio
2003	3.29	[13] 1)	5.85	0.56
2001	2.2	[15]	5.2 [15]	0.42
2001	3.48	[16]	5.4	0.64
1998	2.72	[12]	3.97	0.69
1974	1.5	[14]	2.25	0.67
			Average	**0.6 +-0.1**

1) appendix C, table X

7.2 Rice straw burning

When the crop cultivation in Egypt was liberalised the rice production increased because rice is considered by farmers as a lucrative crop. As production increased the agricultural residues also increased and have become unbearable and expensive to store. Burning of the residues and of the standing stubble became the most viable solution for ridding quickly farmers of this burden and making subsequent land preparation easier. Additionally fungal diseases, stem rot and aggregate sheat spot (fungus - Rhizoctonia oryzae) are controlled. Rice straw contains much more silica

(5-8%[17]) and less lignin (6–13%) than other straws which has several consequences:

a) digestibility is reduced

The digestibility of rice straw is reduced and it is not used for feeding. Other types of straw such as wheat straw do not need to be burned because the farmers use them for feeding their animals.

b) burning behaviour

The main part of the silica is placed as silicon oxide on the outside wall of the different stem layers creating an insulation layer which further reduces combustion. The straw in the piles is densly packed, inhibiting oxygen flow to fuel combustion. So the piles tend to char on the outside, creating an additional insulation layer. Inside the pile at temperatures higher than 300°C pyrolysis takes place forming brittle pyrolysis char and pyrolysis gases. Both products are released to the atmosphere and contribute to the formation of the “Black Cloud” in combination with garbage burning operations and emissions from factories in the north of Cairo. Exhaust fumes from the city's estimated 2 million cars combined with emissions from the area's 20,000 metal smelters are the other major man-made factors contributing to the toxic composition of the cloud The situation becomes even worse when there is an isolating layer in the air that is preventing circulation and dispersal of the pollution particles and the wind speeds are lower than normal. The impact of these phenomena on public health is problematic; typical symptoms are soreness or itching in the throat, pains in the eye, itching in the nose, low-grade fever, and sneezing. Then there is a cough, which may come in sporadic attacks that worsen in the evening and at dawn, when the pollution is worst.

7.3 Emissions from rice straw burning

The burning of agricultural wastes and the resulting emissions have been studied in detail [18,19]. Because several factors including the actual amount of dry carbon in the preburned dry matter, the size, shape and moisture content of the sample, and the flaming versus smoldering pattern of the burning process it is very difficult to estimate the emission factors of trace gases from biomass combustion [20] (Table III).

Table III: Emission factors from rice straw burning (kg/t straw, dry matter)

Literature Source	CO_2	CO	CH_4	VOC	NO_x 1)	SO_x	PM10 2)	TPM 2)
[18]	-	35	-	1	3	0.7	3.7	-
[21]	977	79	4	-	-	-	-	-
[22]	1072	29	0.7	-	0.62	-	-	3.2

1) unit in kg N for NO_x 2) for definition see appendix C, table IX

For 2004 within a period of 30 days about 2.8 Mt of rice straw were burned on the fields (i.g. an average combustion rate of ~100000 t per day). Using the emission factors from table III the environmental pollution was calculated per day to be 100.000 t CO_2, 4.800 t CO, 180 t N from NO_x and about 350 t of fine particles with an upper size limit of approximately 100 µm. Soot is the predominating absorbing component within biomass burning aerosols [23]. Haywood showed that black carbon is emitted as chain-like structure close to the combustion source which collapses as time progresses to a more compact structure [24]. Possible silica emissions are not specifically monitored up to now. Numerous studies have linked the particulate matter to aggravated cardiac and respiratory diseases.

7.4 Alternative uses of rice straw

Because of the environmental problems related to rice straw burning several new environmentally friendly technologies are under development to turn agricultural residues into value [27,28]:

Construction:	production of building material [25,26];
Agricultural:	agricultural uses (animal bedding and feed, mushroom cultivation) [26];
Erosion control:	bales, spreading of straw [26];
Paper/Packing:	newsprint, product packing [26];
Chemicals:	production of chemicals by cellulose degradation to levulinic acid and it's derivative conversion products
Fuel:	fuel (ethanol) production [26];
Energy	direct combustion [26];

7.5 Problems using rice straw as feedstock

A number of technologies can convert rice straw to ethanol including acid hydrolysis, enzymatic processes, gasification, steam explosion and solvent process technologies. All of these approaches have been shown to work in converting rice straw to ethanol, but none are commercialised due to remaining technical and economic constraints.

In California rice straw has been used to produce power through direct combustion processes. The most notable problem for using rice straw in combustion processes are the following impacts:

- The low ash sintering temperature creates serious and costly slagging problems in biomass power plant boilers.
- The high silica content of rice straw results in high ash content.
- This ash must be disposed of and reduces the energy efficiency of the biomass boilers.
- There is the risk of possible formation of fine crystalline silica, a potential carcinogen;
- The release of volatile Cl- and K- compounds into the fuel gas causes corrosion, plugging and poisoning of catalysts.

8 The BIOLIQ Process of the Forschungszentrum Karlsruhe

8.1 General

Biomass is expected to substitute gradually a part of the fossil fuels. The EU intends to double the biomass share in its energy mix until about 2010. Firewood contributes most, but biomass residues from agriculture, mainly surplus straw, can make a smaller but significant ca. 5 % contribution to the world primary energy supply and justify a special development. If by a cheap method, biomass is converted to a more uniform liquid fuel with a high energy density, such a secondary fuel might become a commodity on the world market. The bio fuel should be produced on places where biomass is cheap and abundantly available, typically in developing countries. The bio oil production is then de-coupled from its utilisation. It can be transported along existing infrastructure to be used at any desired time, scale or location. It is easy to store, handle and feed, even to pressurised combustion or gasification systems.

8.2 Synfuel production

Compared to all other renewable energy sources like photovoltaics, solar thermal energy, wind, hydropower, tidal, wave or geothermal energy, biomass has the *unique* advantage of being a renewable carbon resource for CH-synfuels and organic chemicals. Biomass utilisation as a carbon resource is inevitable on the very long term after exhaustion of the still cheaper fossil fuels. At present, synfuel from biomass can help to reduce the fossil CO_2 emissions and reduces our dependency from imported oil. For the production of all organic chemicals, mainly plastics like PE, PP, PS etc., a carbon equivalent of only ~ 0.3 Gtoe/y is consumed. Attainable biomass utilisation of 4 Gtoe, exceed the present and probably also the future carbon demand for chemicals production by more than half an order of magnitude. A large scale global biomass use is therefore connected with an energetic biomass use especially for CH-synfuel production. In general gasification is more flexible and superior to simple combustion; it allows a more economic co-production of highly valuable chemicals, synfuel and electric power. Wood gasification in fixed or fluidised beds is commercial practice, technologies for straw are not well developed. Fast growing Biomass gasification is a complex process, with many associated technical problems caused mainly by the widely differing nature of the virgin solid biomass feedstock. Straw and straw like agricultural residues, as all fast growing biomass, contain more ash, alkali and chlorine than wood and are more difficult to handle technically. The main problems are reactor slagging, corrosion, plugging risks and poisoning of catalysts. The common technologies have been analysed and a new two-step pyrolysis/gasification concept for dry biomass has been developed, which considers the special straw properties and the special economical situation in Europe.

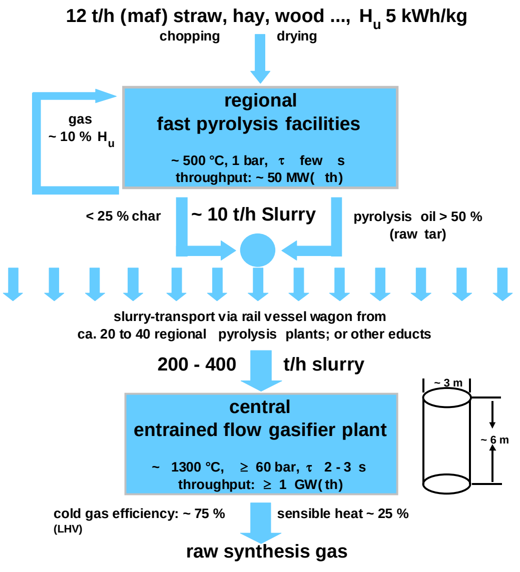


Figure 7: The main characteristic of the proposed concept is fast pyrolysis in many regional plants; slurry transport followed by syngas production in a few central plants.

8.3 Process Concept

At the Forschungszentrum Karlsruhe the BIOLIQ process for the production of fuels and chemicals is under development. [29,30] (Figure 7); In the first step the coarsely crushed dry biomass is mixed with hot sand as a heat source for flash-pyrolysis. The main products are an organic condensate (~75%), the so-called bio-oil, and small quantities of pyrolytic charcoal (~20%) and non-condensable gas (~10%). The charcoal is suspended in the pyrolysis oil to form a slurry. The pyrolysis gas arising is used for inline drying and heating. [31]

A properly operated fast pyrolysis plant will not produce any waste stream. In rural European areas, about half of the cereal straw harvest (~ 50 t/km^2 on the average) is available as an unused surplus. A large delivery radius of > 100 km would be necessary for an economic, large central plant. For straw bales with ~ 100 kg/m^3 bulk density, a maximum delivery distance of 20 or 30 km is at the limits of practicability for the local farmers. Regional fast pyrolysis facilities with ~ 25 km delivery radius are a suitable size. This corresponds to a throughput of 100 000 t/a of air dry straw and straw like biomass residues from 2000 km^2 area. The output is about 10 t/h of pyrolysis oil/char slurry, which can easily be pumped and stored in tanks.

In Europe as the second step a gasification of bio-oil for the production of fuels and chemicals is much more promising then direct combustion. The slurry is pumped into a pressurised entrained-flow gasifier (~60bar, 1300°C) [32] to form syn-gas (H_2, CO). After purification the gas is liquefied in a so called "Fischer–Tropsch" reaction, in which carbon monoxide (CO) and hydrogen (H) react and form carbo-hydrogen chains. The resulting paraffin-like liquid is isomerised to increase stability and then distilled or "hydro-treated". In this step, the specifications of the fuel can be fine-tuned to match the requirements of the engines by altering the form or length of the fuel molecules. This fine-tuning is not possible in the currently used standards refining process for diesel or gasoline, hence BTL is also nicknamed "designer fuel".

BTL -Diesel is CO2–neutral as its combustion only releases the CO2 contained in the biomass. Therefore, on a net basis it does not add to the level of greenhouse gasses in the atmosphere. BTL fuel is also free of aromatic components, which can be serious air or water pollutants. BTL is basically free of sulphur. Sulphur in fuel, when it burns is converted to sulphur oxides which are pollutants, contributing to poor air quality and adding to the problem of acid rain.

First calculations of the investment costs for a pyrolysis plant in Europe on a conservative scale have been done at the Forschungszentrum Karlsruhe. The specific plant investments for a 50 MW(th) pyrolysis plant are about 250 €/kW(th) (Input 100.000 t dry straw/year, delivering radius 25 km, output 83.000 t/year of slurry, H_u 22MJ/kg). The thermal energy loss is estimated to be ~10%. The produced slurry corresponds to about 50.000 m^3/year of heavy fuel oil (H_u 43MJ/kg, density 0,85 Kg/L).

9 Rice Straw Sampling

The first step in the BIOLIQ process is a fast pyrolysis to liquefy and concentrate the biomass. In the frame of the experimental work the pyrolysis of rice straw will be studied first with a special focus onto the relatively high ash content.

Sample Collection and Transport

In October/ November 2003 3 t of rice straw were collected on the fields in the river Nile delta. As bales, covered with a plasic bag in spring 2004 the rice straw was shipped to Germany in a container (fig 8,9,10) to Hamburg habour and by rail and

Figure 8: Rice straw in Egypt, ready for transport

Figure 9: Rice straw arrival at FZK, Germany

Figure 10 Storage at FZK

lorry to the Forschungszentrum Karlsruhe. Each bale had a size of 50x35x100 cm and atotal weight of 18kg (density ~ 100 kg/m^3). There at the Institute of Technical Chemistry (ITC-CPV) a simple storage barn for straw bales and diminution machines has been built at some distance from the institute buildings for safety reasons.

10 Chemical Analysis

10.1 Equipment, Methods and Results

10.1.1 Moisture Content

The moisture content of a solid is expressed as the quantity of water per unit mass of the solid as delivered. It is a critical component for collection, transportation, storage and processing which varies considerably. At the time of harvest, rice straw has about 50 to 80% moisture content while after drying on the fields it decreases down to about 10%. At a water content higher than 15% excess losses of dry matter of straw occur because of microbiological activities. Spontaneous ignition of straw baled may also occur. An increase in moisture content decreases its heating value, which reduces the conversion efficiency of the pyrolysis as a large amount of energy is used for the vaporisation of the fuel moisture. Thus a dry fuel material is preferred but a certain amount of fuel moisture has been reported to be beneficial for pyrolysis [41]. In this work the wet basis water content is used which is the ratio of the total mass of moisture in the original sample to the original wet mass of sample.

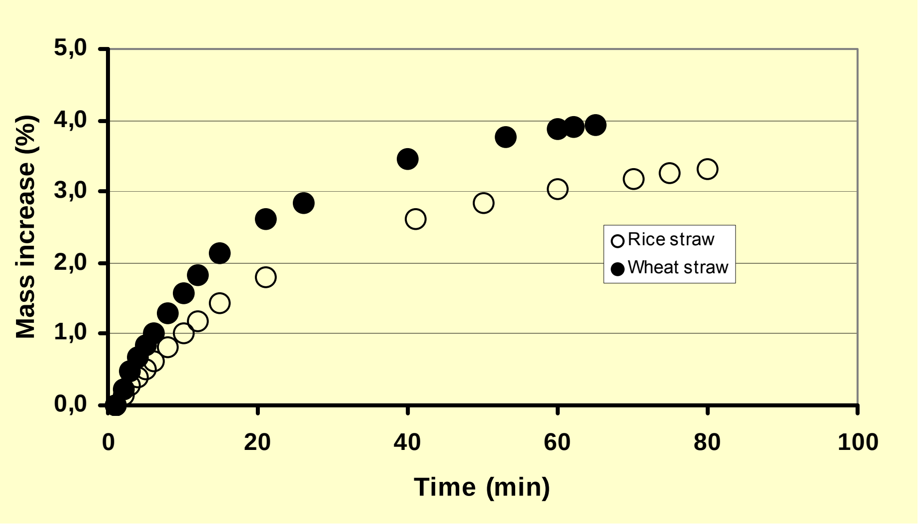


Figure 11: Moisture uptake of dried (105°C, 24 h) biomass, mean particle size 0.12 mm

Water can be determined by different methods. The conventional determination of moisture is drying in an oven in air to constant weight at 105°C. Prolonged drying in the oven can result in loss of volatile constituents due to decomposition, distillation or oxidation of the biomass. Typical initial values extend from ~50% to 10%. The moisture content of a dry analytical sample can change during handling. Rice straw has got about 15 – 10% moisture as delivered. During storage in the laboratory it may decreases down to an equilibrium value of about 5%. Very dry biomass materials are hygroscopic. For most analytical procedures, biomass was milled in a cryo mill (mean particle size ~ 0,12 mm) and completely dried. As figure11 shows these materials show a very rapid uptake of moisture. As a consequence the dried materials were stored carefully in closed vessels. Even short time handling has to be performed in a completely dry atmosphere. Correct handling is precondition for reliable analytical results.

10.1.2 Ultimate Analysis

The ultimate analysis generally reports the elemental carbon (C), hydrogen (H), nitrogen (N), sulphur (S) composition and oxygen (O) very often by difference in the solid fuel. Because of several types of rice plants on different soils in individual countries the results reported differ. Table IV shows the minima, maxima and mean values found in literature, details results are summarised in appendix A table no. I.

Table IV: **Ultimate analysis of rice straw (dry), minima, maxima and mean values of data found in literature.**

	C	H	N	S	O	Cl
Minimum	**34,0**	**4,4**	**0,3**	**0,1**	**34,7**	**0,3**
Maximum	**48,2**	**5,9**	**1,7**	**0,2**	**43,6**	**1,9**
Mean	**39,6**	**5,0**	**0,8**	**0,1**	**37,5**	**0,6**
Stand.Dev.	**4,0**	**0,4**	**0,3**	**0,0**	**3,5**	**0,1**

For the analysis of fast growing biomass samples an instrument (Vario EL) from Elementar GmbH, Hanau, Germany has been used. This systems employs catalytic combustion with pure oxygen to decompose the sample to nitrogen, water, carbon dioxide and sulphur dioxide, which are then determined quantitatively by or thermal conductivity detectors. Every sample was measured at least four times (Tab.V). The absolute standard deviation was 0.5%(C), 0,1%(H), 0,01%(N), 0,1%(S) and 0,5% (O). After modification of the instrument organic bound oxygen was determined

Table V: Ultimate analysis data of dry biomass materials (%, dry)
Typical Values from literature [66,67,68,69] in brackets

	Wheat		**Rice**		**Hay**	**Cotton**	**Wood**
	straw	**bran**	**straw**	**husks**		**stalks**	
C	**45,7 (43,2)**	**47,7**	**39,2 (41,8)**	**44,5 (41)**	**45,9**	**46,6 (39,5)**	**48,6 (50)**
H	**5,7 (5,0)**	**6,4**	**4,8 (4,6)**	**6,3 (4,3)**	**6,0**	**5,6 (5,1)**	**6,1 (6)**
O	**43,3 (39,4)**	**42,0**	**36,4 (36,5)**	**36,9 (36)**	**39,4**	**42,8 (39,1)**	**45,0 (43)**
N	**0,5 (0,6)**	**2,8**	**0,4 (0,7)**	**0,9 (0,4)**	**2,3**	**0,7 (0,4)**	**0,2**
S	**0,3 (0,1)**	**0,3**	**0,2 (0,1)**	**0,6 (0,01)**	**0,3**		
Cl	**0,7 (0,3)**		**1,9 (0,3)**	**(0,1)**	**1,0**	**0,5 (0,1)**	**< 0,1**

directly by catalytic conversion to carbon monoxide – not by difference. In order to avoid confusion and to give a good representation of the fuel itself, the ultimate analysis are performed and reported on a dry basis, because otherwise moisture is indicated as additional hydrogen and oxygen.

For fast growing biomass materials like straw, the determination of chlorine is important, because it represents a possible pollutant and corrosive agent in pyrolysis, gasification and combustion systems. The chlorine content was determined separately after combustion to HCl in a separate analyser. The chlorine content of the Egyptian rice straw (1,9%) is about three times higher than the average chlorine content reported in the literature.

Calculated on a dry and ash free basis the typical composition of woody and herbaceous biomass materials is very similar (Table VI). The organics CHO-composition of lignocellulose like wood or straw is not much different and approximately represented by $C_6H_9O_4$. For quick estimates a more simplified formula is useful: $C_3(H_2O)_2$. It may be viewed at as a mixture of 50wt% carbon with 50 wt% water.

Table VI: Ultimate analysis data of selected biomass materials (m%, dry and ash free)

	Wheat		**Rice**		**Hay**	**Cotton**	**Wood**	**Mean**
	straw	**bran**	**straw**	**husks**		**stalks**		
C	**47,8**	**48,1**	**46,6**	**49,9**	**49,0**	**48,7**	**48,6**	**48,6 +-0,7**
H	**6,0**	**6,4**	**6,2**	**7,0**	**6,3**	**5,9**	**6,1**	**6,3 +-0,4**
O	**45,3**	**42,3**	**46,5**	**41,3**	**41,9**	**44,7**	**45,1**	**44 +-2**
N	**0,5**	**2,8**	**0,5**	**1,0**	**2,4**	**0,8**	**0,2**	
S	**0,3**	**0,3**	**0,2**	**0,7**	**0,3**	**0,0**	**0,0**	

10.1.3 Cellulose, Hemicellulose and Lignin

Carbon, Hydrogen and Oxygen form the lignocellulosic base components: the walls of plants mainly consist of cellulose and hemicellulose, polymers formed by condensation. The cellulose is a polymer of d-glucose of typically 1000 units (wood, up to 3000 units cotton). It is relatively constant in structure compared to other components and therefore the cellulose molecule has been studied more than any other component of biomass. Hemicelluloses are composed of fewer five-and six-membered sugars monomers than cellulose, typically 300 and are often branched and many are attached to other functional units, particularly acetyl units. Lignin is a high polymer compound derivative of phenylpropane and is a principal constituent of the middle lamella and primary cell walls in plants. It occurs also as a sub constituent between cellulose fibrils at the secondary cell walls. It gives stiffness to stems and stalks. In general the amount of lignin in fast growing biomass is lower then in wood. In these cases a part of the lignin is substituted by silica. As the thermal behaviour of each of these components is different their contribution to the thermal degradation is different. The mean results found for rice straw in literature (Table VII) show nearly equal amounts of cellulose and hemicellulose (~30%) and only 12% of lignin (for details see attachment A, table no. III).

Table VII: Amounts of Cellulose, Hemicellulose and Lignine in rice straw; literature data.

	Cellulose	**Hemicellulose**	**Lignin**
Minimum	28	24	10
Maximum	39	36	14
Mean	33	28	12
Stand.Dev.	4	6	1

10.1.4 Proximate Analysis (moisture, ash, volatiles and fixed carbon)

The proximate analysis classifies the fuel in terms of its moisture (M), volatile matter (V), fixed carbon (FC) and ash (A). Literature information on proximate analysis for rice straw shows a broad scattering of the individual results (Table VIII, details see attachment A, table II). For example the fixed carbon content fluctuates from 5,7% up to 19,0%. The thermal behaviour of biomass has been studied by measuring the rate of weight loss of the sample as a function of time and temperature (Thermogravimetric Analysis TGA). The dynamic TGA measurements yield data equivalent to a standardised proximate analysis. In the test procedure the biomass samples (200mg straw or straw like materials) were heated up to 700°C in a thermo balance (STA 409, Netzsch Company, Germany) with different heating rates (0,5 – 50 K/min) in a nitrogen atmosphere (70mL/min) . Further experimental details are given in chapter 11.2.1.

A typical thermodiagram illustrating weight change as a function of both time and temperature as obtained by the Netzsch STA 409 analyser is shown in figure 12 for a rice straw sample. The first part in nitrogen atmosphere shows the loss of moisture and volatiles. The moisture determined represents physically bound water only; water released by chemical reactions during pyrolysis is summarised among the volatiles. Afterwards the decomposition of cellulose, hemicellulose and lignin forming char and volatiles takes place. The pyrolysis yield is representative of that for slow pyrolysis processes; fast pyrolysis techniques employing very rapid heating rates might yield more volatile matter. During the second part of the experiment the fixed carbon is burned in air isothermal at 700°C. The final weight remaining is equal to the total inorganic ash remaining in the sample:

$$\text{moisture} + \text{volatiles} + \text{fixed carbon}_{TG} + \text{ash}_{TG} = 100\ \%.$$

Table VIII: Proximate analysis (wt%) of rice straw, minima, maxima and mean values found in literature; moisture (M) as delivered, rest on dry basis.

	M %	**A** % dry	**V** % dry	**FC** % dry	**value** MJ/kg dry
Minimum	2,2	2,4	7,9	4,5	12,9
Maximum	15,0	20,5	79,5	20	16,3
Mean	10,2	16,4	56,8	13,8	13,9
Stand.Dev.	4,1	4,8	19,8	5,5	4,1

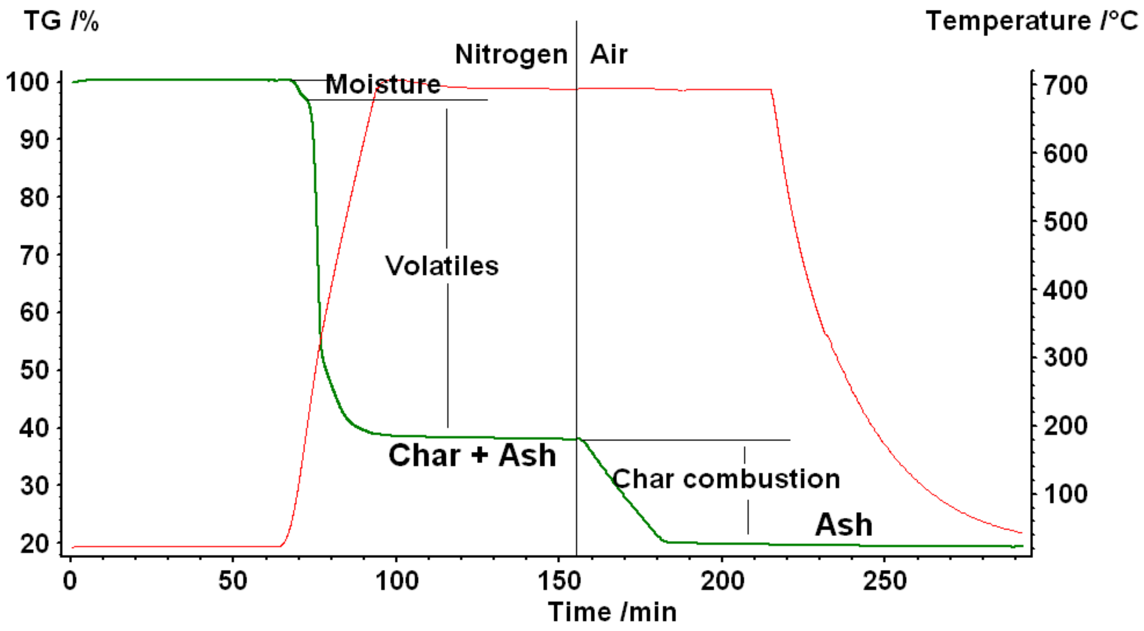


Fig. 12 Thermodiagramm of rice straw, heating rate 20K/min

It is important to note that the resulting ash fraction might not representative for the original mineral content of the biomass because of an oxidation process during the char combustion. A possible weight increase of the ash (formation of oxides) may also influence the amount of the fixed carbon, which in this case will be too low. Therefore in chapter 10.1.7 additional experiments were performed to check this fact. Table IX shows the results of the proximate analysis of several types of biomasses (average results from experiments with different heating rates, details attachment A, table IV).

Table IX: Proximate analysis (t%) of biomass on dry basis (average on TG experiments with different heating rates)

	Rice		Hay	Cotton	Wheat		Wood
dry	**straw**	**husks**		**stalks**	**straw**	**bran**	
Volatiles	**60**	**66**	**65**	**72**	**69**	**70**	**84**
Fixed Carbon	**20**	**17**	**21**	**24**	**23**	**22**	**16**
Ash	**20**	**18**	**14**	**4**	**8**	**8**	**0,3**

Table X shows the same results calculated on a dry and ash free (daf) basis. All the studied fast growing biomass materials show almost identical values for volatiles

Table X: Proximate analysis (%) of biomass on dry and ash free basis (average on experiments with different heating rates)

	Rice		Hay	Cotton	Wheat		Wood
daf	**straw**	**husks**		**stalks**	**straw**	**bran**	
Volatiles	**75**	**79**	**76**	**75**	**75**	**76**	**84**
Fixed Carbon	**25**	**21**	**24**	**25**	**25**	**24**	**16**

(~75 %) and fixed carbon (~25%). For the woody biomass the amount of volatiles/fixed carbon is about 8 % higher/lower.

10.1.5 Calorific Value

The heating value may be reported on two bases. The higher heating value (HHV, cross heating value)) represents the heat of combustion relative to liquid water as the product. The lower heating value (LHV) is based on gaseous water. The difference in the heating value is the latent heat of the product water. For many kinds of coal the gross heating value ranges from 20 to 30 MJ/kg [44]. However, nearly all kinds of lignocellulosic biomass feedstocks show a HHV of 15-19 MJ/kg. The values for most woody materials are 17-19 MJ/kg; for most agricultural residues, the heating values are about 15 – 17 MJ/kg. Because of it's high ash content the mean HHV of rice straw is at the lower limit of 15 MJ/kg.

All heats reported here are HHV on a dry basis. For rice straw various values as reported in the literature are given in the attachment A in table no. II. Table no. XI shows the maxima, minima and resulting mean values. The heating values of biomass feed stock were determined employing an adiabatic bomb calorimeter (Parr Instruments) that measures the enthalpy change between reactants and products at 25°C according to DIN 51900. The dissolved sulphate was calculated during this measurement (by titration) so that the calorific value was corrected for this contribution. Each measurement was repeated 4 times. The resulting average reported was compared with calculations of the theoretical HHV. A common method for estimating heating values of solids is the Dulong-Bertholot equation, which permits estimation from the ultimate analysis. If biomass is considered as $C_6H(H_2O)_3$ with different ash contents the HHV can be calculated according to Ebeling and Jenkins /7/ from the dry and ash free heating value:

Table XI: HHV(MJ/kg) of Rice straw

	HHV MJ/kg
Minimum	**12,9**
Maximum	**16,3**
Mean	**15,0**
Stand.Dev.	**0,9**

$$\text{HHV (kJ/kg)} = K - 271\ A$$

where K is the HHV of lignocelluose (daf 20490 kJ/kg) and A is the percent ash by weight on a dry basis. . Table XII presents the calculated and experimental HHV for selected biomass fuels. The calculated HHV agree within 10% error with the experimental and calculated (Dulong-Bertholot equation) results. For rice straw with an ash content of 19% (dry) the Ebeling equation represents best the experimental result.

Table XII: Experimental higher heating Values (HHV) of different types of dry biomass; Mean values +- 0,2 MJ/kg,

1) HHV= 339 C+1214(H-O/8)+226 H+105 S (Dulong-Bertholot)
2) HHV = 20490 – 271 Ash (Ebeling [50])

	Rice		**Hay**	**Cotton**	**Wheat**		**Wood**
HHV (MJ/kg)	**straw**	**husks**		**stalks**	**straw**	**bran**	
Experimental	**15,3**	**17,5**	**17,1**	**17,4**	**17,8**	**18,3**	**19,0**
Calculated $^{1)}$	**14,7**	**18,6**	**18,2**	**17,4**	**17,2**	**19,0**	**18,4**
Calculated $^{2)}$	**15,3**	**17,6**	**18,8**	**19,3**	**19,3**	**20,3**	**10,4**

The energy density of rice straw (15 MJ/kg) and the density of ~100kg/m^3 result in a volumetric energy density of only 1,5 GJ/m^3. Figure 13 presents the comparison with typical fuels whose volumetric energy densities are about 20 times higher. As a consequence the transporting distance and the plant capacity are limited. In Germany biomass residues can be collected within a distance of 20 to 30 km, corresponding to a catchment area of about 3000 km^2. In rural Europe with about 80 t of wheat straw per km^2 this area is sufficient for a plant capacity of ~ 200 000 t per year.

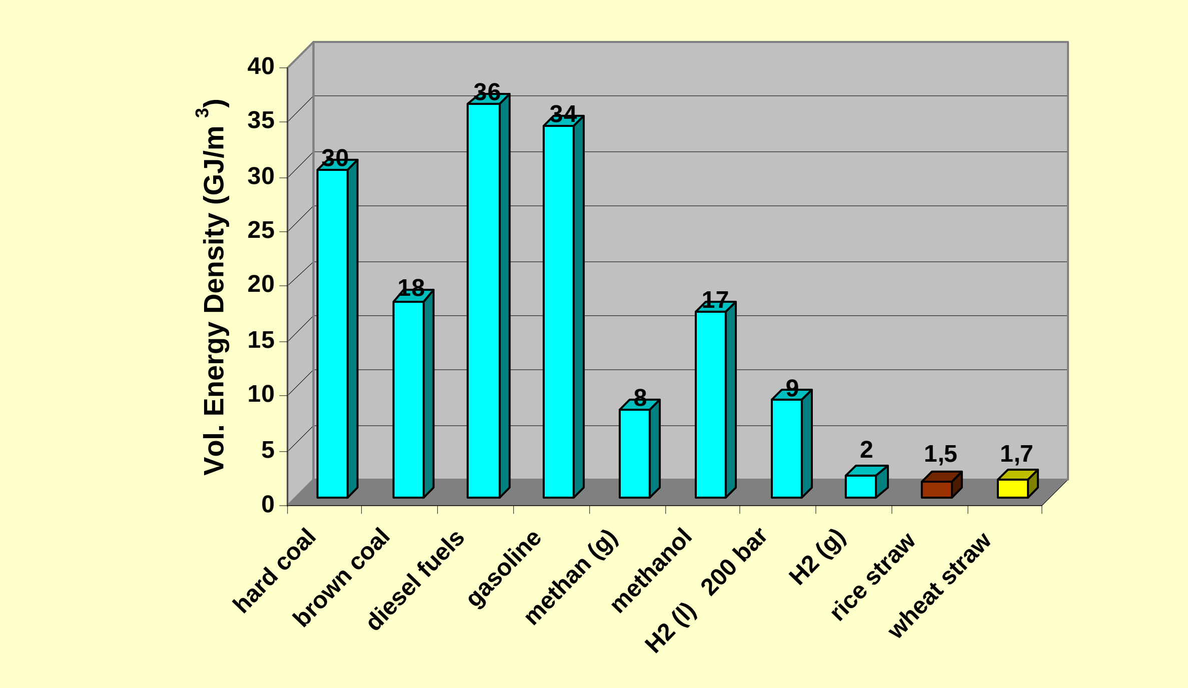


Figure 13: Volumetric energy density of different fuels and straw

For Egypt the production rate of rice straw is higher: A straw to grain ratio of 0,6 and a paddy production rate of 9,4 t/ha result in 560 t/km^2 of rice straw per year. This result is confirmed by the data from Fahmy and Ramadan [13] who give the production rate in 2003 to be 2,18 dry t/acre (1 acre = 4046,9 m^2) which is equal to 520 t/km^2. For California the rate is reported to be 250 t/km^2 up to 620 t/km^2 [46]. As a consequence of the high rice straw production rate of about 400 t/km^2 for a plant capacity of 200 000 t per year the catchment area is only about 500 km^2. This corresponds to a transporting distance of ~15 km which is of big advantage in view of the poorer traffic infrastructure in the rural Egyptian area.

10.1.6 Ash

10.1.6.1 General aspects

The amount of ash and its chemical composition have a great influence onto the process technology used and the resulting operation parameters. Contrary to clean fuel wood, combustion and especially gasification technologies for the poorer herbaceous bio-fuels are not well developed. The high potassium content lowers the ash sintering temperature sometimes to < 700°C. At combustion or gasification temperatures required for a fast fuel conversion, the ash becomes sticky and increases the risk of reactor slagging. Most of the chlorine may be released as HCl into the gas phase. Consequences are corrosion in heat exchangers. Chlorine and sulphur are important elements forming volatile components with potassium that cause fouling on convective surfaces. If the operation temperature is too high even at a pyrolysis plant these problems must be expected.

A certain amount of ash in the feed slurry of the gasification step is necessary to form the protection layer in the entrained flow gasifier. However an increasing amount of ash reduces the heating value of the pyrolysis char and the derived slurries. Slurries with a lower heating value lower than 11 MJ/kg can't be gasified anymore. The amount of ash is normally determined by ashing at 550°C or 815°C. In the literature the amount of ash in rice straw changes from 12,9 up to 21% and a mean value of 17,5% (Tab. VIII). A further detailed study on the ash content of 53 rice straw varieties shows the amount of ash in the range from 15,3 up to 23,8% with a mean value of 18,6% of ash [49]. In this work at 815°C the ash content of the Egyptian rice straw was found to be 19,6% a value close to the upper limit. Due to the formation of oxides it may be to high. The mineral content for dry rice straw calculated by subtracting the amount of C, H, O, N and S is 18,3%.

10.1.6.2 Mineral composition

The inorganic compounds of the biomass are finally left after gasification. Depending on the type of biomass the ash content varies from less than 1% for wood (50-60% Calcium, predominantly as CaO) to as high as 20-25% for rice husk. Ash compromises CaO, MgO, Na_2O, K_2O, SiO_2, Fe_2O_3, Al_2O_3 and P_2O5. The quantity of ash and its melting point are important parameters for processing biomass by pyrolysis and gasification. During pyrolysis the minerals are concentrated in the formed pyrolysis char. High amounts of minerals reduce thus the heating value of the chars. According to the elemental composition the melting temperature of the ash varies over a wide range. During the gasification the melting point of the ash is a limiting factor for reducing the operation temperature of the entrained flow gasifier. For rice straw the range of ash content is reported from 13 up to 21%. In this work the studies rice straw showed an ash content of 19,7+-0,4% (ashing at 815°C in air) and 20+-2% (Thermal analysis). The ash from thermal analysis had a small carbon content of about 0,5%. These results fit to the mineral content of 18,3% as calculated by difference from the ultimate analysis (Table V) because some elements are found as oxides when ashing rice straw in air. Table XIII shows the broad scattering of the mineral composition of rice straw ash found in literature. The high amount of silica and potassium is significant. Own results are presented in appendix C, table VI. The alkali-index is calculated to be about 2 kg/GJ. It is the ratio of the sum of K_2O and Na_2O and the HHV. Jenkins et al. calculate an alkali-index of 1,64 for rice straw with similar concentrations [73]. Values higher than 0,17GJ/kg are considered to cause possibly problems, values exceeding 0,34 kg/GJ almost certainly cause problems concerning slagging and fouling. Another index is the molar ratio between potassium and chlorine which gives an indication of how volatile the potassium is. The ratio of

Tab. XIII: rice straw ash, mineral composition from literature (appendix C, tab. VI)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5
Minimum	3,4	0,03	0,26	0,82	0,23	0,30	3,15	0,23
Maximum	73,5	0,19	0,55	1,84	1,83	0,91	12,95	1,38
Mean	38,5	0,11	0,40	1,33	1,03	0,61	8,05	0,81
Stand.Dev.	49,6	0,11	0,20	0,72	1,13	0,44	6,93	0,81

2,3 for rice straw indicates that there is enough chlorine to make the potassium volatile. These results indicate that at higher temperatures volatile KCL will be a significant contribution to fouling effects. The chlorine study in chapter 11.2.9 and 11.3.3 confirm these facts.

The form in which an inorganic element occurs in a solid fuel has decisive influence on its reactivity in pyrolysis, gasification or combustion. Miles et al. (1996) determined the modes of occurrence of inorganics in very different bio fuels in terms of their solubility in increasing aggressive solvents [56]. According to these results Si and Al are in the form of oxides and insoluble. The alkali and alkaline earth elements (K, Na, Ca and Mg) were predominantly in a soluble form. Over 90% of potassium was in a water-soluble or ion-exchangeable form and thus high volatile. Calcium is reported to be largely in an ion-exchangeable or acid soluble form and thus less volatile than potassium. Almost the chlorine was found to be soluble in water too. Own extraction experiments with pulverised rice straw showed that 25% of the total Mg and Ca, 50% Na, 70% K and 95% Cl are extractable in water (Tab XIV).

Table XIV: Mineral components in rice straw and ash (this study)

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5		Sum
Ash: oxides (%)	65,70	0,30	0,10	1,70	2,10	3,10	15,00	0,50		88,50
Straw: oxides (%)	12,94	0,06	0,02	0,33	0,41	0,61	2,96	0,10		17,4
Elements	SiO_2 1)	Al	Fe	Ca	Mg	Na	K	P	Cl	
Ash: element (%)	65,70	0,16	0,07	1,21	1,27	2,30	12,45	0,22		83,38
Straw: element (%)	12,94	0,03	0,01	0,24	0,25	0,45	2,45	0,04	1,0	17,4
Elements in straw (% abs)				0,06	0,06	0,23	1,74		0,95	
water soluable (% rel)				25	24	51	71		95	

1) Si always calculated as oxide

10.1.6.3 Fouling risks

The inorganic constituents are important to the critical problems of fouling and slagging in combustion furnaces and power boilers. As deposition occurs, the cross-sectional area is reduced, which causes an increase in pressure drop across the apparatus The fouling layer has a low thermal conductivity. This increases the resistance to heat transfer and reduces the effectiveness of heat exchangers. Fouling can be very costly in plants since it increases fuel usage, results in interrupted operation and production losses, and increases maintenance costs. Normally the operation temperature of a pyrolysis unit will be lower (~500°C) than in a boiler (~800°C) and consequently the risk of fouling will be lower. But the high amount of alkali and alkaline earth metals in combination with other elements such as silica and chlorine may still cause problems in the pyrolysis unit. A number of indicators have been developed relating composition to slagging and fouling behaviour. One simple index is the alkali index. It expresses the quantity of alkali oxide in the biomass per unit of fuel energy (kg alkali/GJ) and is computed as:

$$(1/H) * F * (Y_{K2O} + Y_{Na2O}) \quad = \text{Alkali index (kg/GJ)}$$

in which H is the higher heating value of the rice straw on dry basis (0,0153 GJ/kg), F is the mass fraction (dimensionless) of ash in the straw (0,18), Y_{K2O} and Y_{Na2O} are the mass fractions of K_2O and Na_2O (0,15 and 0,031) in the ash. For the Egyptian rice straw the alkali-index is calculated to be about 2 kg/GJ. Jenkins et al. calculate an alkali-index of 1,64 kg/GJ for rice straw with similar concentrations [73]. Values higher than 0,17 GJ/kg are considered to cause possibly problems, values exceeding 0,34 kg/GJ almost certainly cause problems concerning slagging and fouling. Another index is the molar ratio between potassium and chlorine which gives an indication of how volatile the potassium is. The ratio of 2,3 for rice straw indicates that there is enough chlorine to make the potassium volatile. These results indicate that at higher temperatures volatile KCL will be a significant contribution to fouling effects. The chlorine study in chapter 11.2.9 and 11.3 confirmed these facts. As a consequence the operation temperature of a pyrolysis unit should be at a maximum of about 500°C. The thermal isolation of the piping system in the hot part of the reactor should be performed very carefully to avoid any cold spots which might act as origin for depositioning.

10.1.7.4 Ash Melting Point

In the gasification step the ash melting is an important parameter for the operation temperature of the pressurised entrained flow gasifier. The special characteristic of this gasifier type is a thin water-cooled radiation screen inside a cooler steel shell designed for high pressure. A molten slag layer drains down on the inner screen walls and protects the SiC-liner from corrosion. A suitable slag viscosity is adjusted with the temperature (O_2-flow). Prediction of ash chemistry is very difficult, particularly since substantial vaporisation of inorganic compounds will occur during gasification. In order to get a high gasification efficiency the operation temperature should be as low as possible at about 100°C above the melting temperature of the slag. The melting behaviour of slags is characterised in four steps[37] :

I) The sintering temperature (TSI) describes the process, where single ash particles stick together. During this process the sample may change its original dimension without showing characteristics typical at the softening point.

II) At the softening temperature (TSO) the sample shows the first signs of softening, e.g. surface changes, the rounding of the edges are complete and the sample starts filling out the gas volume between the particles.

III) The hemispheric point gives the temperature (TH), when the sample takes on the approximate form of a hemisphere. The height of the melted sample is approximate half the length of the base line.

IV) At the flow point temperature (TF) the sample has shrunk to one third of its original height.

The typical ash melting points of the rice straw ash determined under reducing conditions straw are shown in table XV. The ash shows a broad melting range. At about 860°C sintering starts and finally at 1400°C the melting process is finished. Several efforts were done to estimate the melting process of ash based on its Composition. One possibility is to calculate the typical temperatures (°C) based on the mineral content (%) of the original dry biomass [57]:

$TSI = 1159 - 58{,}7\,K + 237{,}9\,Ca - 743{,}8\,Mg$

$TSO = 1172 - 53{,}9\,K + 252{,}7\,Ca - 788{,}4\,Mg$

$TFP = 1369 - 43{,}4\,K + 192{,}7\,Ca - 698\,Mg$

Table: XV. Experimental and calculated [57] melting points of rice straw ash.

	exp.	calc.$^{1)}$	calc.$^{2)}$
TSI	860	886	958
TSO	1010	903	970
TH	1230		
TF	1390	1134	1188

The calculated temperatures are additionally shown in table XV. Only the calculated sintering temperature is close to the observed temperature. The softening and flow point temperatures show greater differences. Even assuming that the potassium content of the ash is 50% lower (case 2) does not improve the results significantly. Another possibility to estimate the slag melting point is to use the phase diagram of the tertiary system K_20-SiO_2-CaO [58]. Assuming that rice straw ash consists only of 75% SiO_2, 21 % K_2O (K2O + Na2O) and 4 % of CaO (CaO+ MgO) the phase diagram in figure 14 shows a low melting point of about 980 °C. Higher melting points are only possible if the potassium content is reduced. For a mixture of 84% SiO_2, 11% K_2O and 4% CaO a more realistic melting point of 1400°C results.

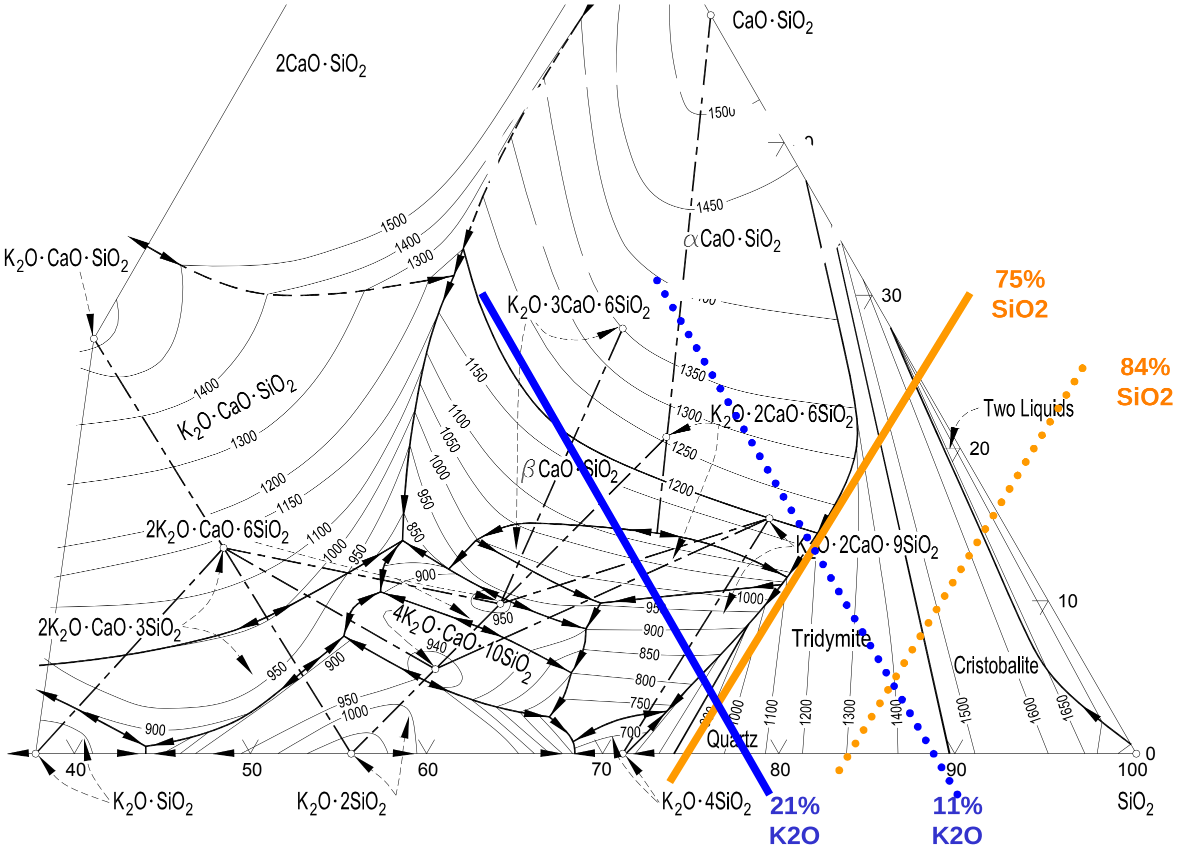


Figure 14: Phase diagram of the system SiO_2*K_2O*CaO [58].

11 Pyrolysis - basics

11.1 Pyrolysis Modes

Pyrolysis or carbonisation is the thermal decomposition of biomass in the absence of air. It yields a mixture of products consisting of varying proportions of solid char, liquid distillate and gases depending on the feedstock characteristics, residence time of the vapours and the heating rate. The product distribution obtained from different modes of pyrolysis are summarised in table XVI [44]. As for the BIOLIQ process the char is suspended in the liquids the fast pyrolysis mode is of particular interest. In order to get a high amount of pyrolysis liquid the vapours have to be separated from the formed char very quickly to avoid secondary cracking reactions. For the characterisation of all kinds of biomass they were first studied by slow pyrolysis in the laboratory.

Table XVI: Typical product yields (dry wood basis) obtained by different modes of pyrolysis of wood (Pynet [44])

Mode	**Conditions**	**Liquid**	**Char**	**Gas**
Fast pyrolysis	moderate temperature, short residence time particularly vapour	75%	12%	13%
Carbonisation	low temperature, very long residence time	30%	35%	35%
Gasification	high temperature, long residence times	5%	10%	85%

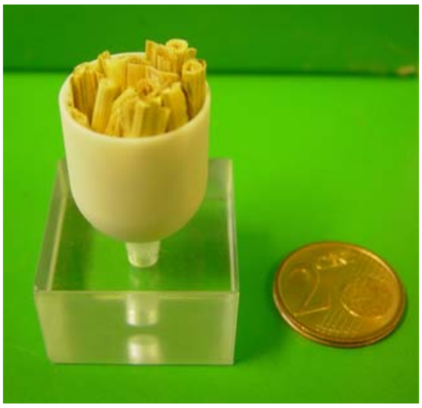


Figure 15 Sample for TGA

11.2 Slow Pyrolysis

11.2.1 Experimental

The thermal behaviour of the biomass was studied by Thermogravimetric analysis (TGA) which records the weight change of a sample as a function of time and temperature in a preset time – temperature program. There is not necessarily an exact relationship between laboratory experiments and the pyrolysis in a technical process demonstration plant (PDU) or a pilot plant. TGA offers a semi quantitative understanding of the pyrolysis process under well-controlled laboratory conditions. About 200 mg of sample were placed as small sticks in Al_2O_3 crucible (Fig. 15) which was placed in the thermo balance onto a thermo couple for temperature control. The non isothermal TG curves were obtained in a Netzsch STA 409 thermobalance in nitrogen atmosphere (70 ml/min). At the end the formed char was burned by switching the gas atmosphere over to air (70 ml/min). All samples were studied under the same conditions given in table XVII - only the heating rate was varied from 0,5 ,1, 2, 5,10, 20, 35 and 50 °C/min. The absolute standard deviation for observed weight losses was 2%. Additionally straw samples were heated up under nitrogen atmosphere with 10 K/min to different final temperatures from 300°C up to 900°C. The resulting char was analysed for its elemental composition and the observed weight losses were used to calculate the amounts of carbon, hydrogen and oxygen which are lost during the pyrolysis.

Table XVII: List of temperature steps

Step	Mode	Temp. °C	HR K/min	Duration hh:mm	Atmosphere
1	isothermal	20	0	01:00	Nitrogen
2	dynamic	700	different		Nitrogen
3	isothermal	700	0	01:00	Nitrogen
4	isothermal	700	0	01:00	Air
5	dynamic	20	40	00:17	Air

11.2.2 Thermal behaviour of Cellulose, Hemicellulose and Lignin

As already mentioned in chapter 10.1.4 the thermal analysis was used for proximate analysis which conveys the moisture content of the sample, the total volatile content, the ash content and the fixed carbon content. The mean results from experiments with different heating rates are listed in table X (p 19). However, the moisture content has been left out because it is dependent of the ambient humidity. The detailed results for different heating rates are given in attachment A, table IV.

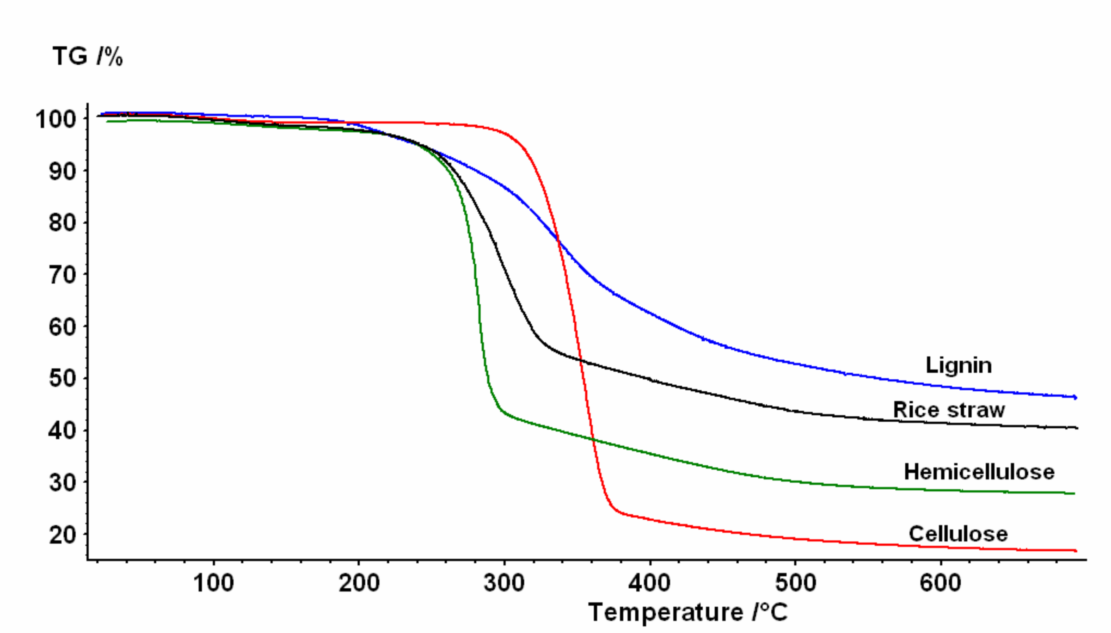


Figure 16 Example of TGA rice straw, lignin, cellulose and hemicellulose, at heating rate 10K/min

As a representative result of the pyrolysis tests, figure16 shows profiles of the mass decrease for rice straw compared to its main chemical components lignin, cellulose and hemicellulose. The thermal degradation of lignin shows that the volatile products are formed over a wide temperature range, beginning from minor decomposition at approximately 200°C. Most lignin pyrolysis occurs at higher temperatures and lasting up to 600-700°C. The observed weight loss of only 50% indicates that lignin is the major source of char contributor during biomass pyrolysis.

Cellulose is stable up to a temperature of 320°C. Then it decomposes in a rather narrow range of about 100°C leaving a char residue of 15%. The dependence of the char yield on the pyrolysis temperature of cellulose is reported by Broido and Nelson [47]: Depending on the temperature and duration of the pre-treatment at about 250°C the char yield varied from 10 to 27%. It seems that the presence of KCl has a strong influence onto the product yields distribution too as for wheat straw it was found that sample washing reduced the char yield by 10% (daf) and increased the tar yield by 30% (daf) which was mainly caused by the decomposition of cellulose and hemicellulose of the biomass [61]. The decomposition of the less stable hemicellulose starts at about 240°C and shows at least two competing reactions. The pyrolysis is finished at about 550°C yielding 30% of char. Table XVIII shows a comparison of the typical temperatures determined from the TG curves at a heating rate of 10 K/min. T_{Start} point is shown as the beginning of the S curve as obtained from the method for determining glass transition temperature. $T_{End\ point}$ is the temperature at the end of the S curve. The point $T_{Maximum}$ shows the temperature at which the maximum rate of reaction occurs.

Table XVIII: Typical temperatures, determined from TG curves at 10 K/min; values in brackets from literature [48]

Component	**Start point T (°C)**	**Maximum T (°C**	**End point T (°C)**
Lignin	**265 (259)**	**327 (331)**	**413 (384)**
Cellulose	**326 (335)**	**355 (351)**	**373 (368)**
Hemicellulose	**271 (244)**	**285 (269)**	**298 (306)**
Rice straw	**262**	**298**	**340**

The pyrolysis result for rice straw consists of two stages, which are a rapid mass decrease on the first stage of cellulose and hemicellulose volatilisation and gradual mass decrease on the second stage as lignin decomposition. In general hemicellulose, cellulose and lignin have decreasing pyrolysis reactivities. During the pyrolysis of rice straw most of the lignin will still be present after the bulk of the first two substances has decomposed.

11.2.3 Volatiles and Char Yield

In order to elucidate the pyrolysis characteristics the amount of char and volatiles formed at several heating rates was determined for rice straw and its main chemical components on a moisture and ash free basis. Fig 17 shows the amount of formed char and volatiles at different heating rates (For details see appendix C, table V). If the heating rate increases up to 50 K/min the char yield decreases significantly for rice straw (5%), cellulose (7%), Hemicellulose (7%) and Lignin (4%) whereas the amount of volatiles increases by the same amount.

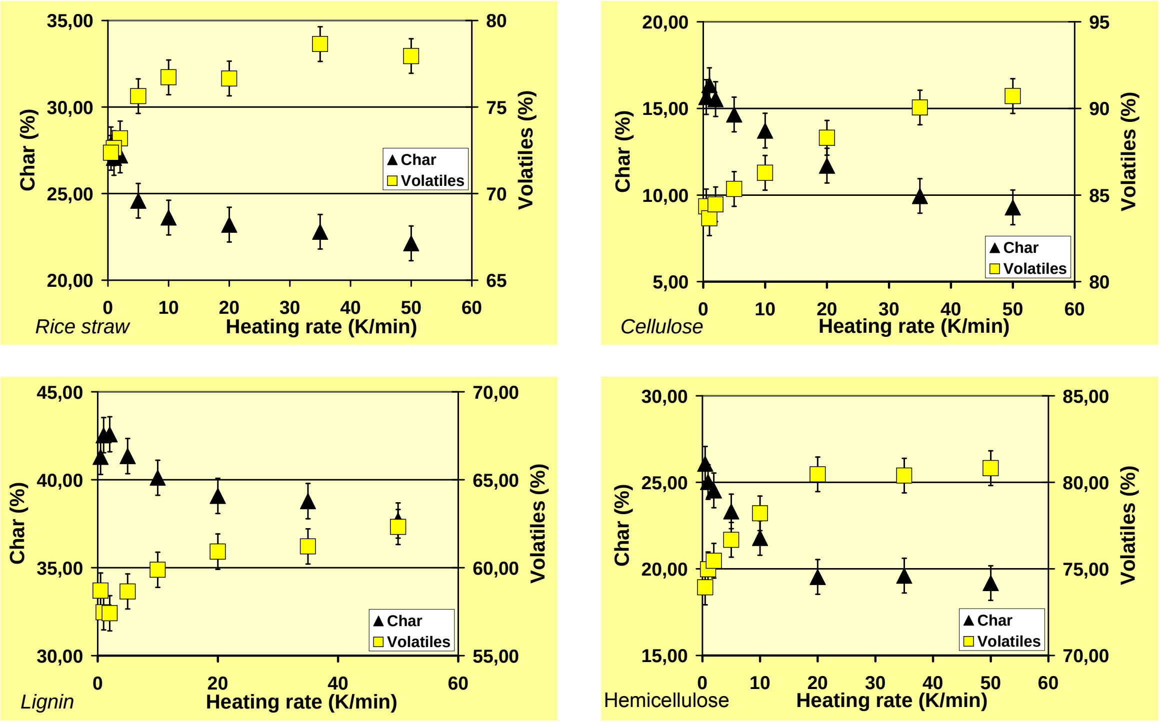


Figure 17: Volatiles and char yield of rice straw, cellulose, lignin and hemicellulose for different heating rates on moisture and ash free basis.

Assuming rice straw as a simulated biomass with an average content of 45% cellulose, 38% hemicellulose and 16% lignin the formed char and volatiles are calculated on an a dry and ash free basis. Figure 18 shows the comparison of the calculated and the observed results for the amount of char and volatiles. In general there is a slight difference of about +4+-1% for char and -4+-1% for volatiles found. This fact may either be caused by inaccurate composition or more likely by the influence of the mineral components. The influence of inorganic materials onto the decomposition of cellulosic materials was found by the work of Tang [54] and confirmed in 1999 by Nassar who examined bagasse and rice straw [55].

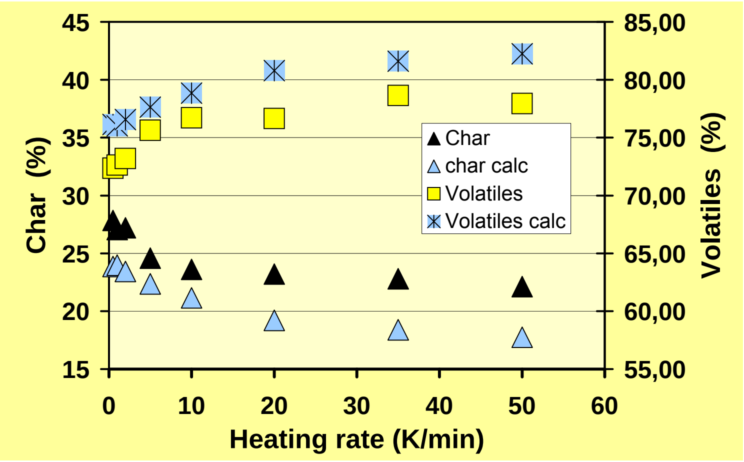


Figure18: Amount of char and volatiles of simulated rice straw for different heating rates on moisture and ash free basis

11.2.4 Kinetic Analysis of Pyrolysis

With increasing heating rate the TG curve is shifted to higher temperatures. The peak temperature of the derived DTG curve was plotted versus heating rate in an Arrhenius type diagram, that is the logarithm of the heating rate versus the reciprocal of the absolute peak temperature. From the slope of the straight lines, the apparent activation energy for different kinds of straw was determined (Tab.XIX). With a similar procedure Mack und Donaldson [63] found for the pyrolysis of cotton 204 kJ/mol and Arsenau [64] for cellulose 190 kJ/mol. Browne und Tang [65] found in 1963 for wood about 150 kJ/mol which is significantly lower. However, present analysis do not predict the variation of char formation with pyrolysis conditions, and this would be useful for operating pyrolysis plants.

type of straw	Activation energy (kJ/mol)
rice	230
wheat	180
rye	160
oats	230
hey	220

Table XIX: Activation energy for pyrolysis of different straw types

11.2.5 Ultimate Analysis of Chars

An increasing pyrolysis temperature leads to an increasing carbon content of the char. Water vapour, CO_2, combustible gases CO, H_2, CH_4 and a complex mixture of organic vapours like organic acids, aldehydes ketones and phenols are produced resulting in an decreasing oxygen and hydrogen content of the char. The details are shown in figure 19 for rice straw and figure 20 for wheat straw. At a pyrolysis temperature above 500°C the elemental composition of the formed rice straw chars do not change any more. In the case of wheat straw still small changes can be observed in that temperature range. Figure 21 shows the C, H, O weight fraction consumed during pyrolysis as a function of pyrolysis temperature for rice straw. At a pyrolysis temperature of 500°C about 87% of the oxygen and 85% of the hydrogen

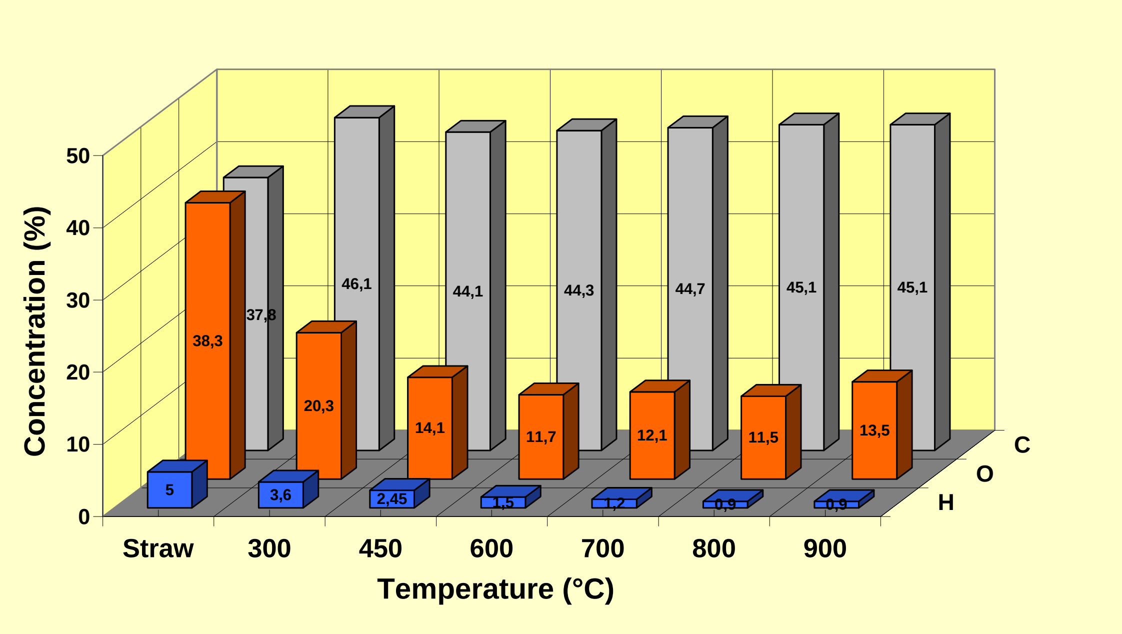


Figure 19: Elemental composition of rice straw and pyrolysis chars produced at different temperatures (dry basis)

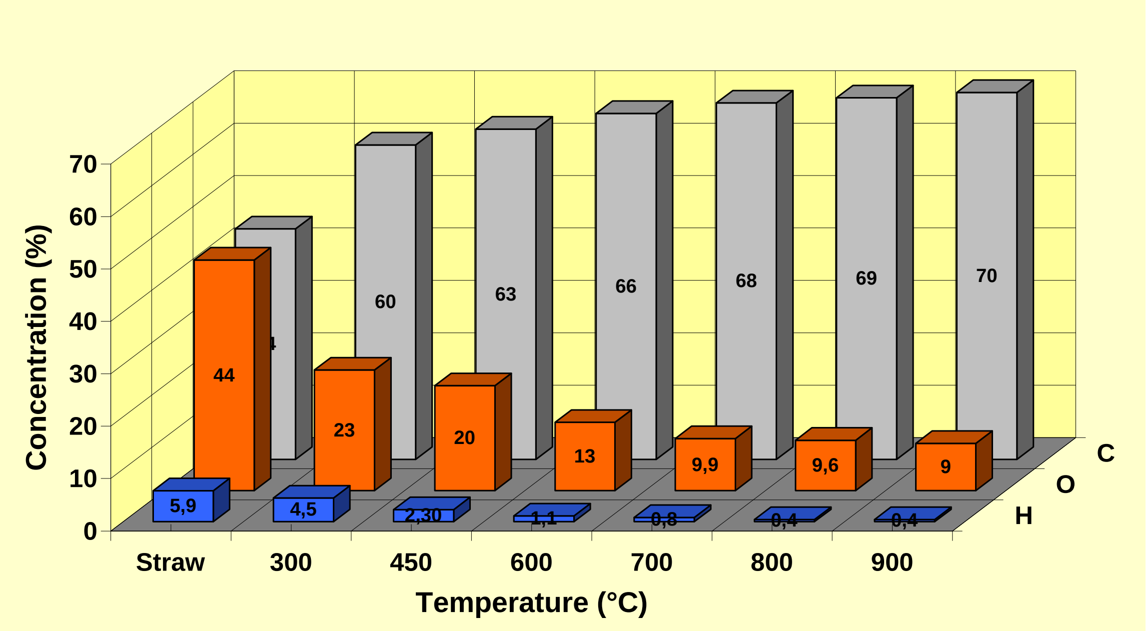


Figure 20: Elemental composition of wheat straw and pyrolysis chars produced at different temperatures (dry basis).

were released along with about 50 percent of the carbon. These parts are forming tar, reaction water and permanent gases mainly CO_2 and CO.

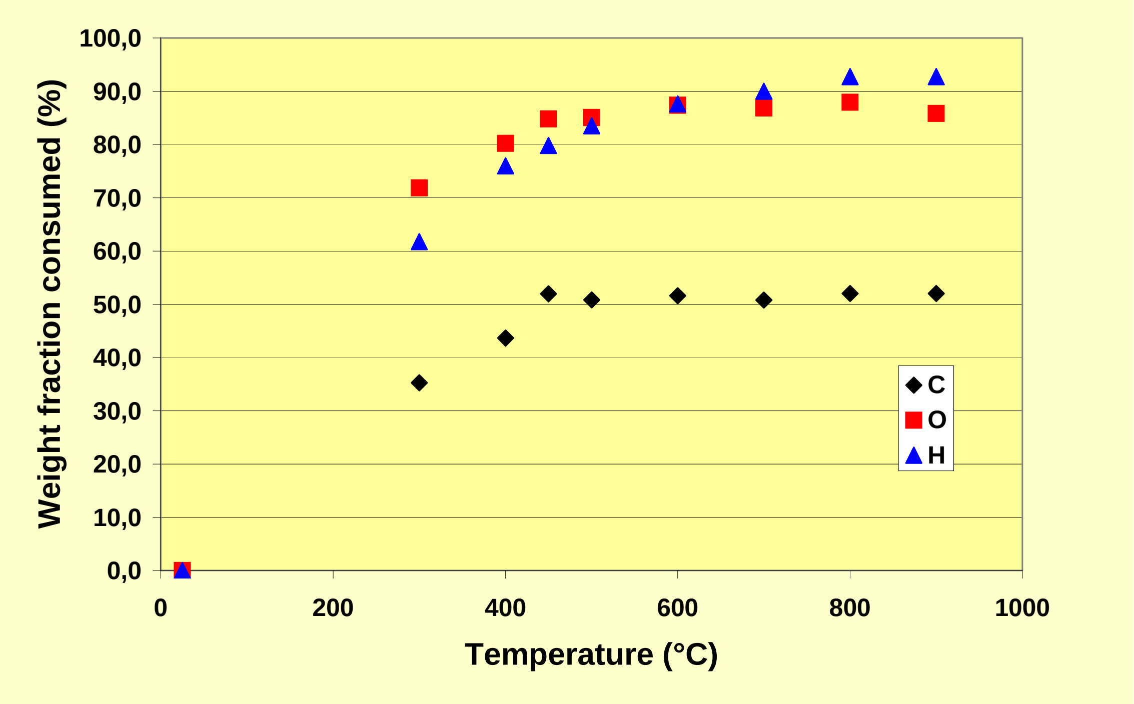


Figure 21: C, H, O weight fraction of rice straw consumed during pyrolysis as a function of pyrolysis temperature.

11.2.6 Ash content of pyrolysis chars

The results of the ultimate analysis of chars produced at different pyrolysis temperatures are summarised in table XX. The amount of minerals are calculated by difference from the ultimate analysis. The mineral content increases from ~ 18% in the original biomass up to 40% when performing the pyrolysis at 900°C. At an operation temperature of about 500°C for the fast pyrolysis plant the ash content of the pyrolysis char is expected to be about 38%.

Table XX: Elemental composition and mineral content of different rice straw chars (% wt) on dry basis.

	Carbon	Hydrogen	Oxygen	N+S	Sum	Minerals as difference
Straw	37,8	5,0	38,3	0,6	81,7	18,3
300	46,1	3,6	20,3	0,7	70,7	29,3
400	46,1	2,6	16,4	0,8	65,9	34,1
450	44,1	2,5	14,1	0,8	61,5	38,6
500	45,1	2,0	13,9	0,8	61,8	38,2
600	44,3	1,5	11,7	0,8	58,3	41,7
700	44,7	1,2	12,1	0,8	58,8	41,2
800	45,1	0,9	11,5	0,8	58,3	41,7
900	45,1	0,9	13,5	0,8	60,3	39,7

11.2.7 Diffuse Reflection Infrared Fourier Transform Spectroscopy (DRIFTS) [71]

Rice straw char prepared at different pyrolysis temperatures was studied with a focus onto the intensity of the C-H stretching vibrations at 2900 and 2940 cm-1. In figure 22 the peak area is shown as a function of the operation temperature. After pyrolysis at 400°C there are still several amounts of C-H bondings detectable. At pyrolysis temperatures higher than 500°C no significant changes were observed. The results confirm the fact that at 500°C the thermal degradation of the organic compounds is nearly finished. As the IR technique can easily adapted it might be an option for an online detection system for the characterisation of the produced char.

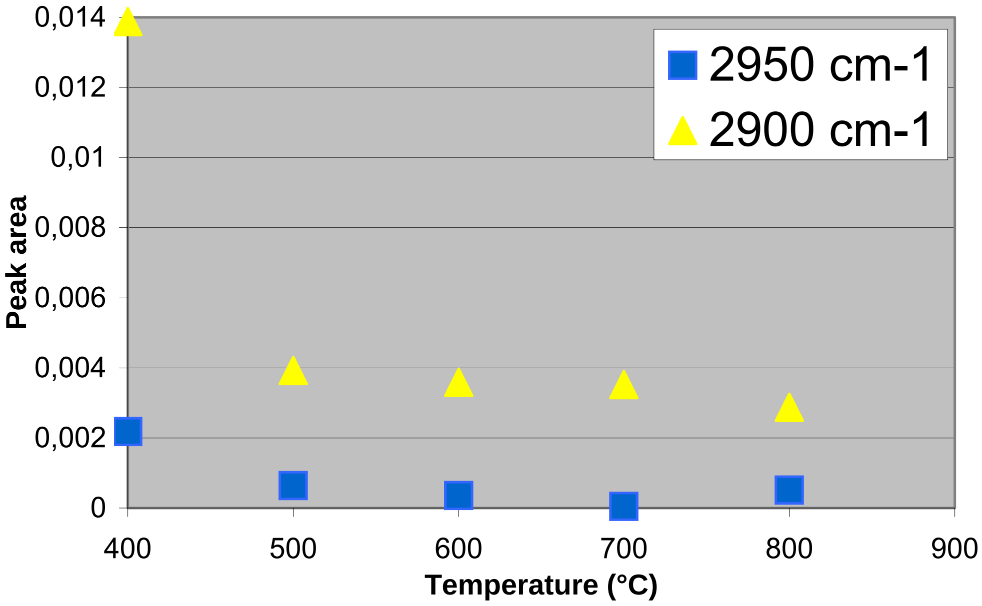


Figure 22: Intensity of C-H stretching vibrations (DRIFTS)

11.2.8 Char, Volatiles and Minerals

From additional dynamic-isothermal thermal analysis experiments the amounts of volatiles (weight loss during pyrolysis) and the amounts of char (minerals plus pyrolysis char formed) were determined. The samples were heated up to several different pyrolysis temperatures with a heating rate of 10 K/min and kept isothermal for 1 hour. Subsequently the char was separated and analysed for its C,H,N,S and O content. The results were summarised and the amount of minerals calculated by difference. These results were finally recalculated to the original biomass as reference using the TGA- results for the amount of char formed. As table XXI and figure 23 show the amount of minerals is nearly constant at about 16,4+-0,7% for all experiments. With increasing pyrolysis temperature the amount of char decreases and the amount of volatiles increases. On a water and ash free basis the amount of char decreases from 45% at 300°C down to 29% at 900°C, whereas the amount of volatiles increases from 56% up to 71%. In the literature char yields of 47% (350°C), 37% (400°C) and 35% (450°C) are reported [59]. On the average at 500°C operation temperature of a fast pyrolysis unit about 25% char together with 16% minerals remain to be suspended during the following slurry preparation step in pyrolysis liquids resulting as a fraction from 60% of volatiles.

Table XXI: Results of Ultimate- and Thermal analysis of rice straw and chars
1) calculated as difference

	Ultimate Analysis of char (dry)		TGA-Analysis of biomass (dry)		Products in % related to biomass (dry)				daf	
Pyrolysis temperature °C	Sum of C,H,N,S,O %	Minerals in char 1) %	Volatiles %	Char + minerals %	minerals %	Char %	Volatiles %	Char + Volatiles %	Char %	Volatiles %
Straw	81,7	18,3								
300	70,8	29,2	46,4	52,6	15,4	37,2	46,4	83,6	44,5	55,5
400	65,9	34,1	53,8	46,2	15,8	30,4	53,8	84,2	36,1	63,9
450	61,5	38,6	58,8	41,2	15,9	25,3	58,8	84,1	30,1	69,9
500	61,8	38,2	57,3	43,8	16,7	27,1	57,3	84,4	32,1	67,9
600	58,3	41,7	58,2	40,7	17,0	23,7	58,2	81,9	29,0	71,0
700	58,8	41,2	58,8	42,3	17,4	24,9	58,8	83,7	29,7	70,3
800	58,3	41,7	59,8	40,2	16,8	23,4	59,8	83,2	28,2	71,8
900	60,3	39,7	59,8	40,2	16,0	24,2	59,8	84,0	28,8	71,2

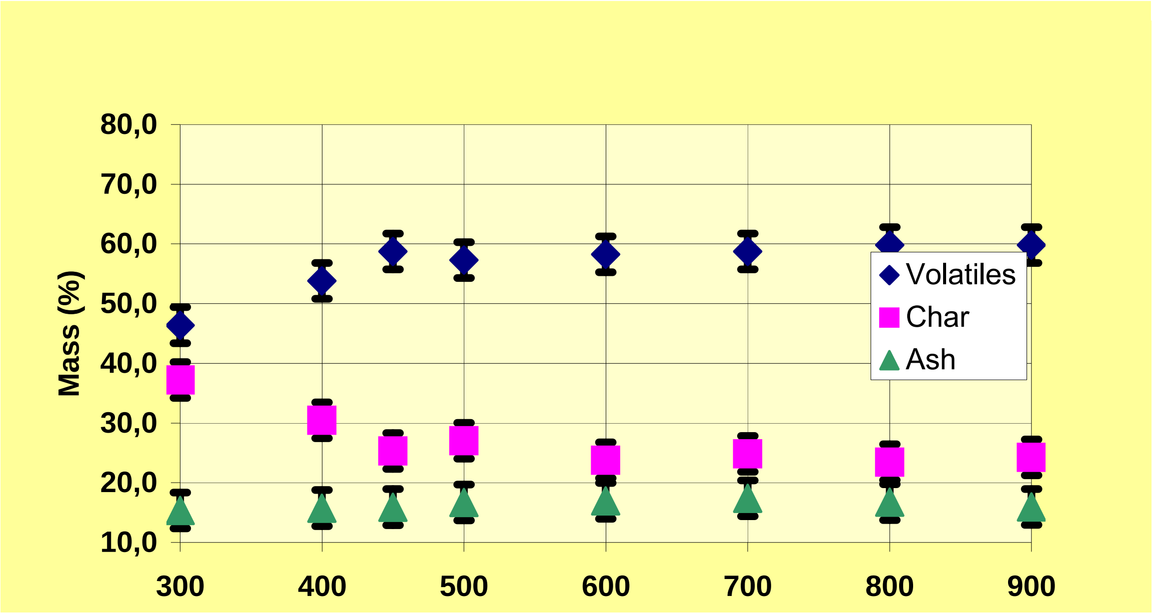


Figure 23: Yields of volatiles, char and ash from Ultimate and thermal analysis

Table XXII: Volatiles and char yield of rice straw at different heating rates (dry)

Heating rate (K/min)	dry Volatiles %	Char %	Ash %
50	62,31	17,69	20,06
35	60,74	17,61	22,76
20	60,72	18,39	20,77
10	60,24	**18,55**	**21,48**
5	59,68	19,43	21,06
2	58,40	21,74	20,18
1	59,27	22,08	18,39
0,5	59,32	22,83	18,02

A comparison to the yields of char and ash formed at the dynamic TGA mode (table XXII; different heating rates, final temperature 700°C) shows small differences (heating rate 10 K/min): the amount of char is ~6% higher (**25 - 19%**) and the corresponding amount of ash is ~6% lower (**16 – 22%**). The formation of oxides may cause a weight increase of the mineral components during ashing in air and thus compensate a part of the weight loss due to the burning of char.

11.2.9 Chlorine

Compared to wood without bark fast growing biomass contains a higher level of chlorine. The release of chlorinated compounds during pyrolysis may cause severe problems due to corrosion, formation of hazardous compounds or blocking of downstream piping. If possible the chlorine should remain together with other ash components in the pyrolysis char therefore. As figure 24 shows the chlorine is focussed in the char up to a temperature of ~500°C. If the pyrolysis temperature exceeds 500°C the chlorine is released and its concentration in the chars decreases. Especially at temperatures above 500°C a high chlorine content is reported to enhance the alkali metal emission during pyrolysis of biomass [60]. Thus it seems that KCl is liberated from the biomass at higher temperatures. Consequently to avoid any depositions in downstream piping or corrosion effects the operation temperature of a technical pyrolysis plant should be at 500°C maximum.

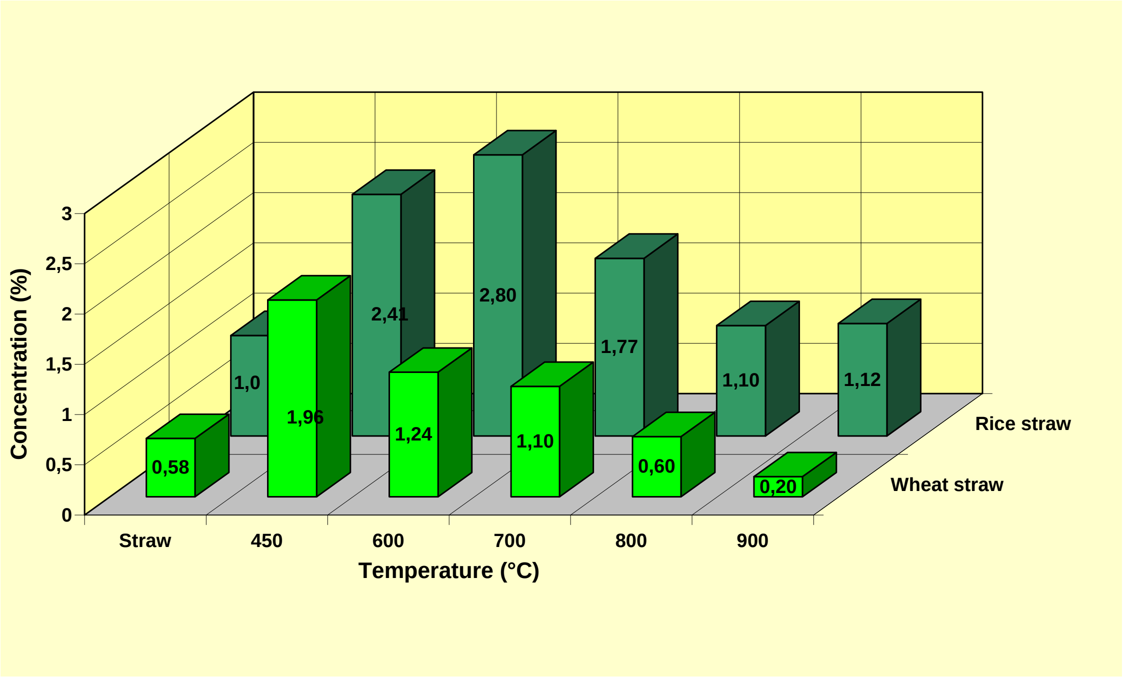


Figure 24: Chlorine content of rice straw and wheat straw and their pyrolysis chars as a function of temperature.

11.2.10 Calorific Value of Pyrolysis Chars

A considerable fraction of the energy of the initial feedstock is found in the liquid and gas products and about 40% in the char. Charcoal from wood has a higher heating value of about 27 MJ/kg but charcoal from rice straw shows only heating values of about 15 - 17 MJ/kg depending on the pyrolysis operation temperature. The reason for this unfavourable result is the initial high ash content of the feedstock. During the pyrolysis the ash is concentrated in the char up to 42 % weight (dry basis). With respect to the planned process it is therefore important to perform the pyrolysis of rice straw under conditions resulting in a high amount of pyrolysis condensate with a high heating value. For a detailed study rice straw char was prepared by pyrolysis under nitrogen at different temperatures. The HHV of the chars were determined by adiabatic combustion under oxygen in a bomb calorimeter. The resulting values were compared with the empirical calculations based on the ultimate analysis by the equations from Dulong, Michel [62], IGT [39] and Ebeling [50]). The results are shown in figure 25 (attachment C, table VII). The results show that the calculation

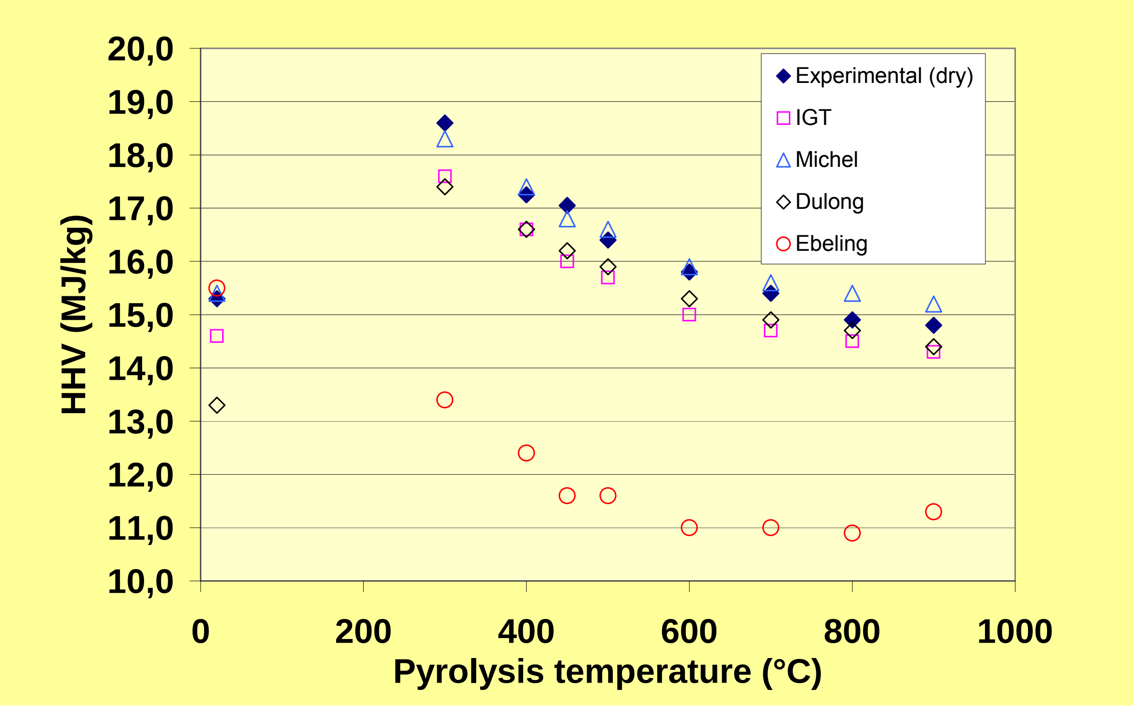


Figure 25: Experimental and calculated HHV of rice straw and rice straw chars prepared at different pyrolysis temperatures.

according to Michel gives the best results with an average deviation of +1% whereas calculations according to Dulong and IGT show differences of - 4%. Especially for the initial biomass greater differences are found using the Dulong formula. The equation given by Ebeling is derived for determinating the HHV especially for biomass. The calculated results for rice straw itself fit the experimental result very well in contrast to the char values which are about 28% lower compared to the experimental data. For the planned operation pyrolysis temperature of 500°C the HHV of the char is expected to be about 16 – 17 MJ/kg.

11.3 SEM Study

11.3.1 General

It is well known from agriculture that the decreased digestion of rice straw cell wall is associated with the presence of silica. In 1976 it was found that the spatial distribution of silica is a factor limiting the digestion of rice hulls [51]. After the removal of the organic matter by ashing at 500°C McManus et al. studied the resulting mineral material of sixteen mature forages with SEM and x-ray analysis [52] showing that the mineralised components is located on the outer surface possibly constituting a masking layer around the digestible organic material. The silica structural network in rice husks and rice straw after acid leaching of the organic part was studied in 1987 by Prasanna and Patel [53]. A mineral layer on the surface of rice straw will also influence the pyrolysis behaviour of rice straw. The issue of the variation of the surface composition of rice straw and chars with pyrolysis temperature is explored in the following section.

11.3.2 Sample Preparation

Several rice straw stem pieces of about 1cm length were pyrolysed for 2 hr at 300, 500 and 900°C under nitrogen. After cooling small longitudinally fractured pieces were mounted on SEM stubs inside and outside up. For energy dispersive X-ray analysis these samples were vacuum-coated with carbon. SEM investigations were performed using a LEO (Oberkochen, Germany) Gemini 982 field emission scanning electron microscope, equipped with a LINK ISIS 300 energy dispersive X-ray (EDX) microanalysis unit (Oxford Corp., UK) An annular diode-type backscattered electron detector (K.E. Develop, UK) was used for EDX spectra acquisition. The X-rays emitted from the sample are recorded to yield data on the elemental composition of a visual field. Finally the pictures were coloured according to the elemental distribution: carbon and oxygen in red, silica yellow/green and sodium blue.

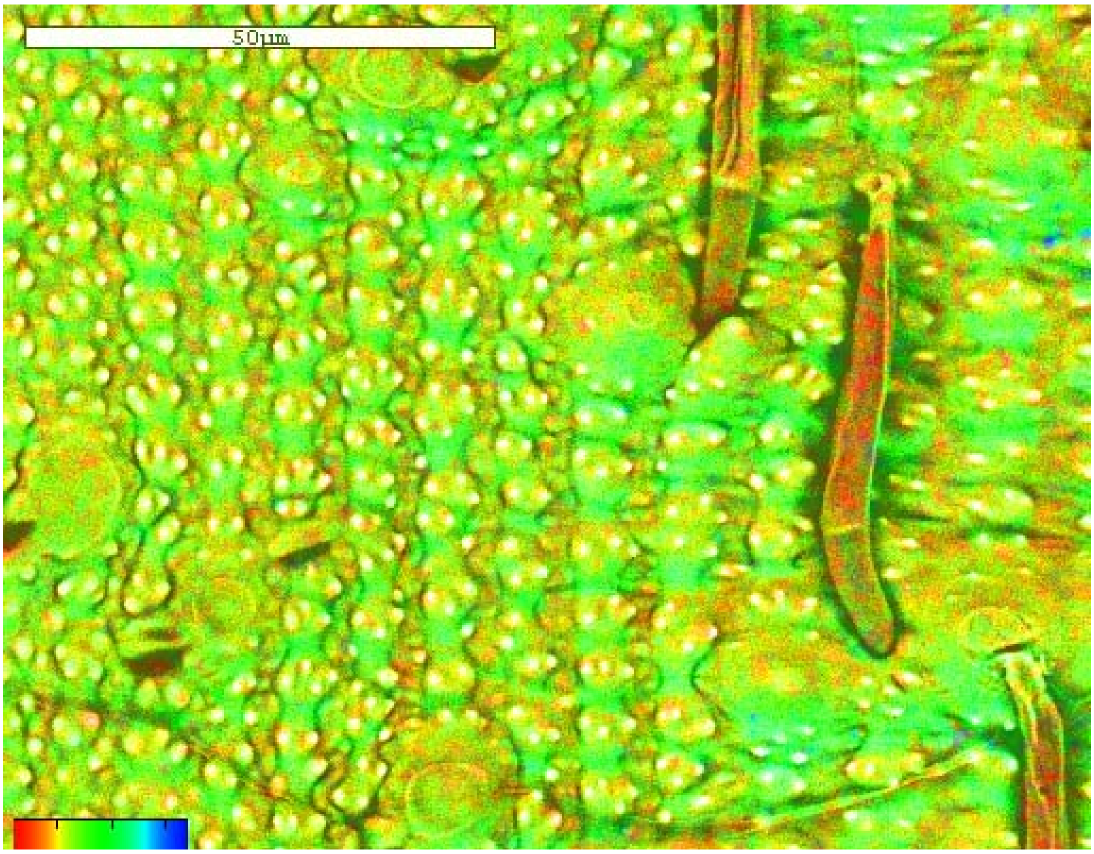


Figure 26: SEM, Rice straw stem outer surface before pyrolysis

The outer and inner surface of a rice straw stem are shown in figure 26 and 27. The green colour of figure 25 indicates a close layer of silica with numerous bumps and silica grains. The energy-dispersive X-ray analysis shows the major elemental components (atom%) to be oxygen (55), Carbon (27) and silicon (16). The inner surface of a single rice stalk, on the other hand, is almost completely flat as shown in figure 26. The main elemental components (atom%) are oxygen (42), carbon (53) and only small amounts of silica (2). Silicon occurs primarily as silica grains on the outer surface of the stems, possibly constituting a masking layer on digestible organic material on the cell wall. In contrast wheat straw shows only a light difference of the elements (atom%) between inside / outside surface: O (43/36), C (55/56) and Si (0,1/4,7).

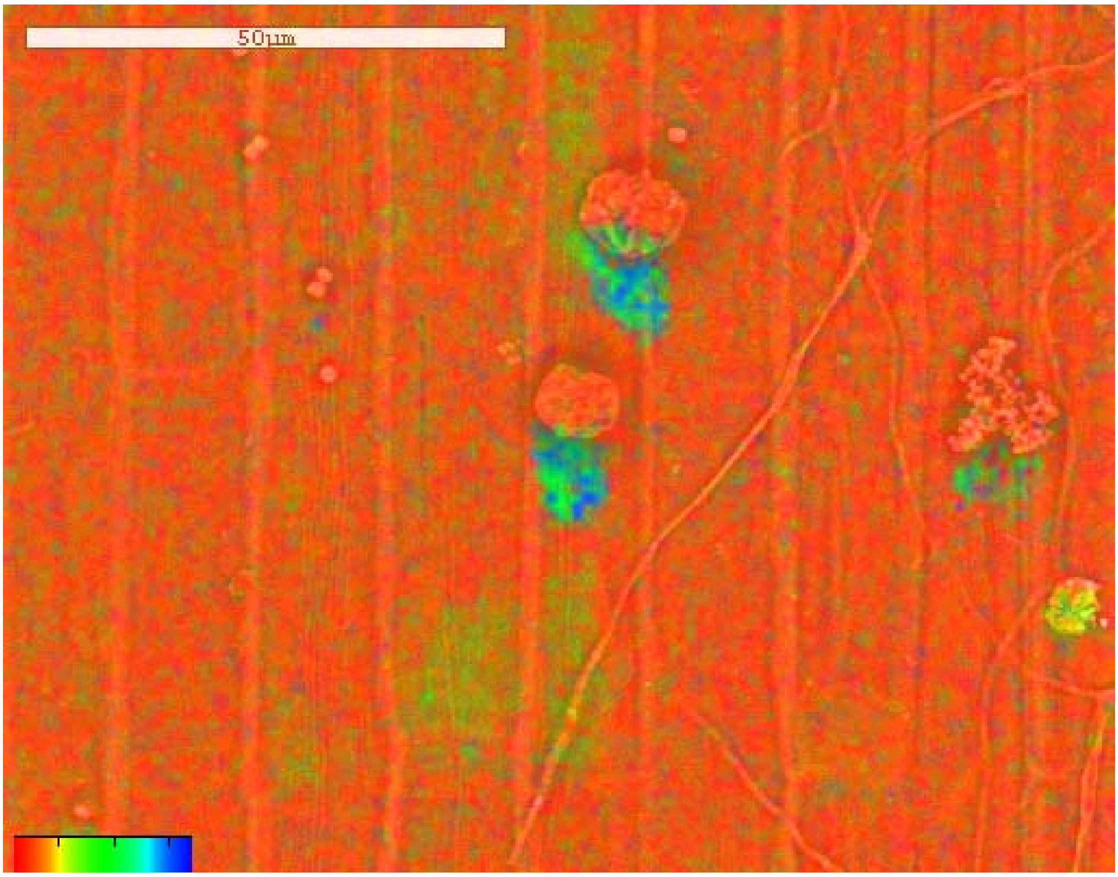


Figure 27: SEM, Rice straw stem inner surface before pyrolysis

11.3.3 Results and discussion

In order to study the effects of thermal decomposition single rice straw stems were pyrolysed at 300, 500 and 900°C and analysed. The corresponding SEM pictures are listed in appendix B, figures I - VI. For a detailed study of the elemental contribution at the surface the amount of carbon, oxygen and silicon was measured over the whole area (figure 28). The mineral composition of the outer surface does not change significantly during the pyrolysis at different temperatures. On the inside however carbon becomes more and more dominant and the oxygen amount decreases due to a loss of oxygenated compounds during the pyrolysis process. The decomposition of rice straw takes place mainly only at the inside of the walls. In general on both sides no pore formation or crumbling was observed at this magnification. This fact becomes visible if the char is burned leaving the mineral structure as a residue. On the outside the bumps and silica grains are still visible without any significant change. In contrast after burning the carbon the inside now shows a very rough structure full of holes (see appendix B figures VII and VIII). The permeability is of great importance in pyrolysis. During heating, the pyrolysis gases and liquids are generated within the particle and must pass through the porous structure to the surface. Low permeability may significantly affect the product distribution by increasing the residence time of the primary pyrolysis products in the hot zone,thereby increasing the probability to enter into secondary reactions which may result in a higher yield of char and permanent gases. The behaviour of the mineral components was also apparent from this studies. Generally for all biomass potassium is atomically dispersed in the fuel in ionic or organometallic form. Potassium is probably released with the decomposition of organic species. As the fuel contains chlorine, potassium appears as the salt, KCl. Already at 300°C the deposition of small KCl crystals starts at the inner surface. At 500°C this effect becomes more evident and is shown in figure 28. Finally at 900°C no KCl crystals depositions were

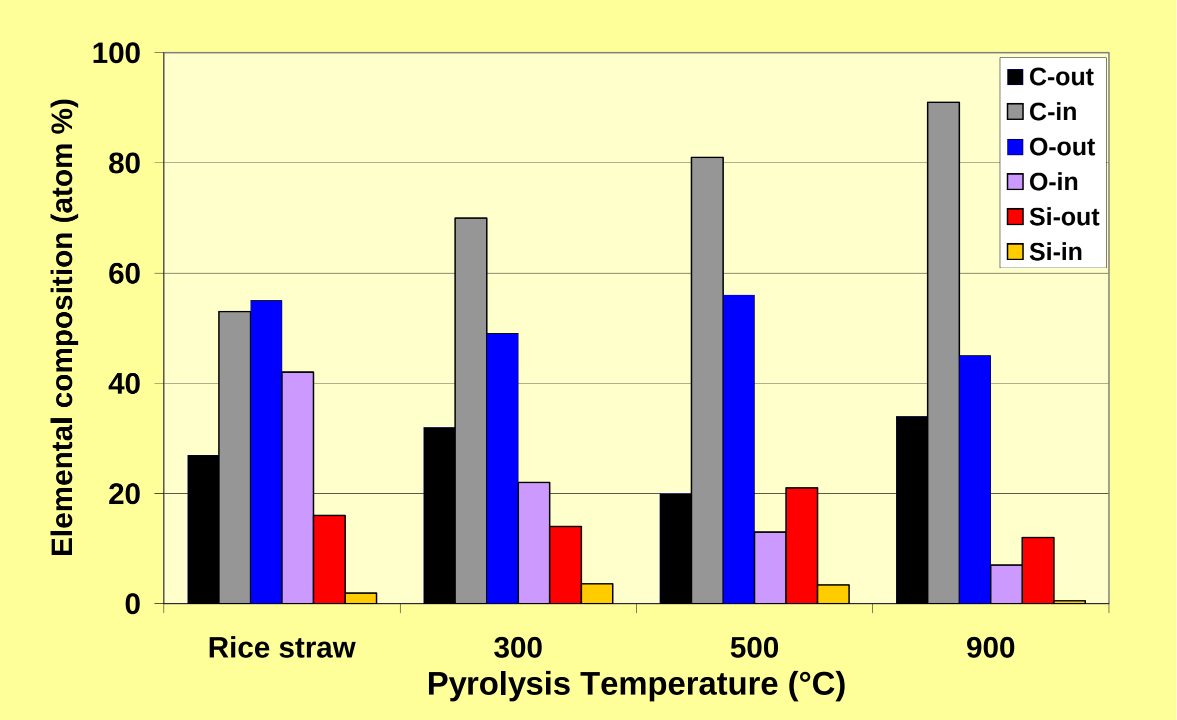


Figure 28: Elemental contribution to the inner and outer surface of single rice straw stems, before and after pyrolysis at 300, 500 and 900°C.

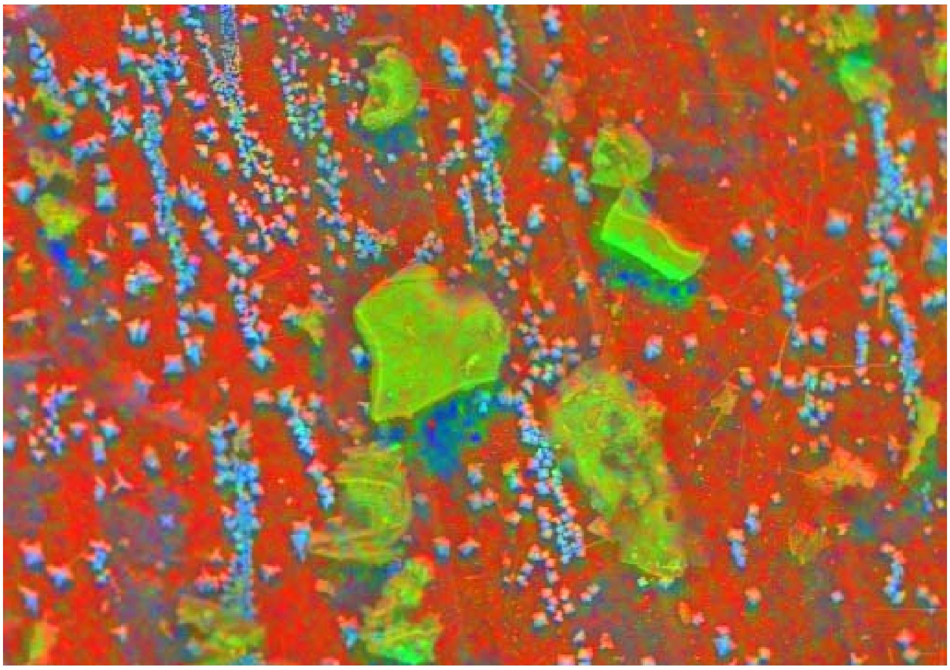


Figure 29: Inner surface of a single rice straw stem after pyrolysis at 500°C; small crystals of KCl (blue) and larger silica particles (green) on the surface of the char.

found any more confirming the results of the chlorine analysis, which shows that chlorine sublimates away.
As a consequence for a technical process before pyrolysis the rice straw feed has to be copped very carefully in order to brake up short stem pieces and to split them up. Operation temperatures above 500°C are problematic. Chlorine seems to be an important factor in the deposition of alkali species on the downstream piping heat transfer surfaces. The risk is high that KCl is deposited on the surface for example by small particle transport. In the following impaction of silicates and other species within a suitable size range increases the layer of deposits on the surface of the piping system.

12 Fast pyrolysis – Technical studies

For the detailed study of the fast pyrolysis of rice straw (9% moisture, 18% ash) the material was pyrolysed in three technical facilities:

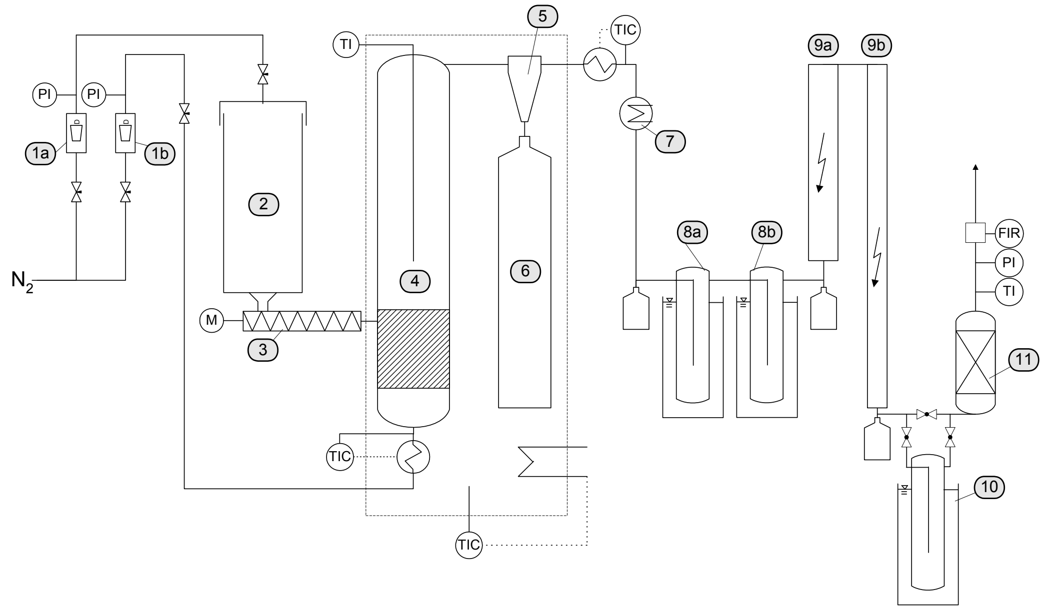
- bench scale pyrolysis (0,3 kg/h) with a fluidised bed reactor (FZK),
- process demonstration unit (PDU) at the Lurgi Lentjes company (twin screw reactor ~0,3 kg/h);
- process demonstration unit (PDU) at the FZK (twin screw reactor, 10kg/h)

12.1 Fluidised bed reactor - Bench scale

For screening purposes, a bench scale reactor with a stationary fluidised bed and a maximum throughput of ca. 0.3 kg/h was operated with rice straw. The data from the fluidised bed reactor are useful for a quick first orientation with an unknown material. The investigations are focused on the yields of char, condensate and pyrolysis gas after the pyrolysis process at p = 1 bar and T = 500°C. Condensate and char yields and respectively the condensate-to-char ratios are of interest for the preparation of slurries or pastes suitable for the gasification in an entrained flow gasifier.

12.1.1 Experimental

The bed of the cylindrical reactor (Ø = 40 mm) consists of 400-630 µm SiO_2 particles, fluidised by 0.6 m^3/h (STP) hot nitrogen. Fluidised beds are characterized by a good temperature distribution and improved heat and mass transfer properties. Biomass particles with a size of < 2 mm are heated quickly within seconds to the final temperature (heating rates >100 K/s) and disintegrate to char, gases, tar and water vapours. The generated vapours and gases are immediately diluted by the fluidising N_2-gas and transported out of the reactor. Entrained char particles are separated from the gas flow by means of a hot cyclone. Finally, the gas is cooled down in multiple stages along with the stepwise condensation of tar, oil and reaction water formed in the process. The process flow sheet and the general view are given in figures 30 and 31. Typical operation conditions for lignocellulosic feedstock are summarised in table XXIII.



1a,b: suspended body flow meters, **2**: storage tank, **3**: screw feeder, **4**: fluidised bed reactor, **5**: hot cyclone **6**: char container, **7**: heat exchanger, **8a,b**: cold traps, **9a,b**: electro filters, **10**: cryo trap (optional), **11**: glass wool vessel

Figure 30: Process flowsheet of the bench scale fluidised bed reactor.

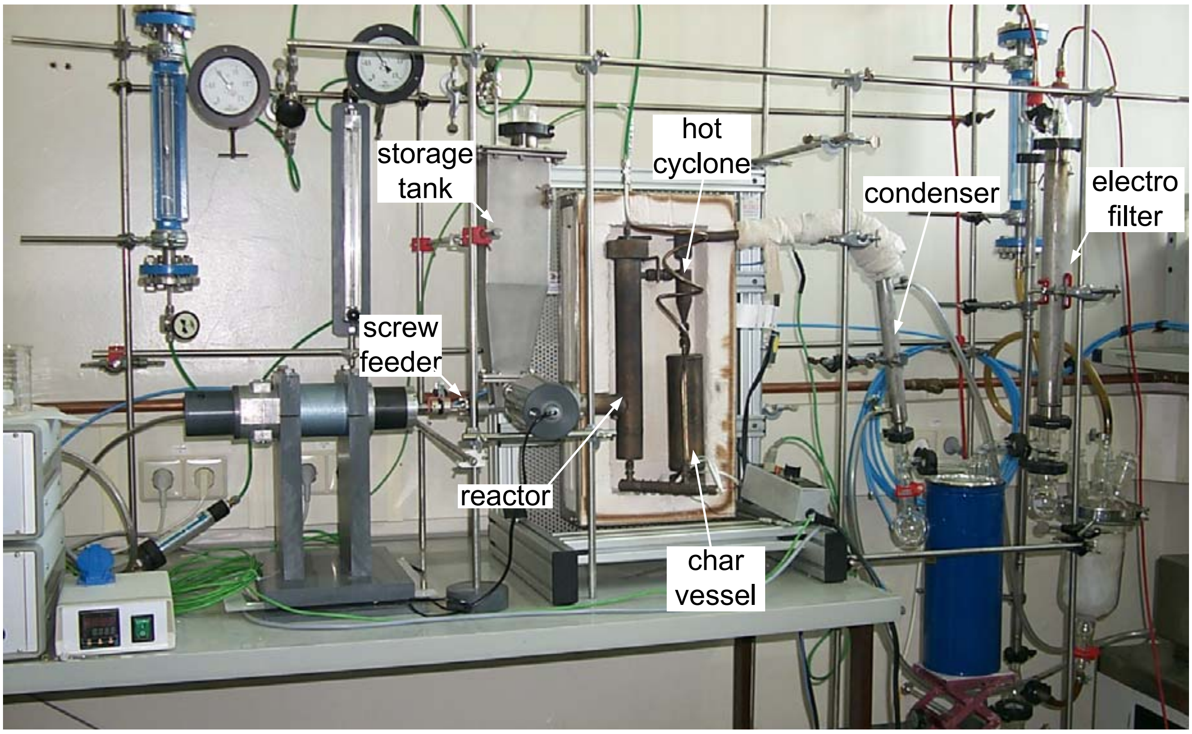


Figure 31: General view of the bench scale fluidised bed facility. Fluidised bed reactor, hot cyclone and char vessel are installed in an electrically heated oven.

Table XXIII: Composition and operating conditions

Reactor temperature	475-525°C
N_2-flow for fluidization	0,6 m^3/h (0°C, 1.013 bar)
N_2-flow for inertisation	50 l/h (0°C, 1.013 bar)
Throughput	240 g/h
Amount of biomass per experiment	60 g / 120 g
Particle size of biomass	< 2 mm
Amount of quartz sand	90 g
Particle size of quartz sand	400 – 630 µm
Electrofilter 1 (operating voltage)	8-10 kV
Electrofilter 2 (operating voltage)	4 kV
Average gas residence time in the reactor	1-2 s
Minimum fluidisation velocity (20°C)	0,183 m/s
Minimum fluidisation velocity (500°C)	0,101 m/s

12.1.2 Results

Three experiments were conducted under the same operating conditions. As seen in table XXIV below, the mass balance could be closed to almost 90 %. It is frequently observed in fast pyrolysis experiments that the sum of the identified product mass is up to 10% below input. There were many hints that low molecular volatile oxygenates escaping from condensates or leaving unanalysed with the pyrolysis gas were the most likely explanation. With the large N_2 flow rate in our experiments most of these species were expected to escape diluted and unanalysed with the gas, thus contributing to the observed deficit.

TableXXIV: Product mass yields (%) of rice straw pyrolysis in a fluidised bed reactor, three Experiments (8% humidity, 17% ash on dry basis).

	as delivered				**dry**				**daf**			
product				**mean**				**mean**				**mean**
condensates	48,4	47,4	45,4	**47**	44,5	43,2	41,2	**43**	54,3	52,9	50,3	**53**
gas	12,3	13,6	12,4	**13**	13,3	14,7	13,3	**14**	16,2	17,9	16,2	**17**
volatiles	60,7	61,0	57,8	**60**	57,8	57,9	54,4	**57**	70,5	70,8	66,5	**69**
char (+asch)	30,8	32,1	33,1	**32**	33,2	34,6	35,7	**34**	18,4	20,1	21,5	**20**
total	91,5	93,1	90,9	**92**	90,9	92,5	90,1	**91**	88,9	90,9	88,0	**89**
deficit	8,5	6,9	9,1	**8**	9,1	7,5	9,9	**9**	11,1	9,1	12,0	**11**
condensates/solids ratio				1,47				1,25				2,63
amount of solids in slurry (%)				40,5				44,5				27,6

The yield of char for bamboo, rice and wheat straw is always about 20% (daf) which is quite low compared to literature data and to fast pyrolysis experiments conducted in other fast pyrolysis reactors (char ≈ 25%). A potential explanation is that the char is not milled to powder like in a LR-mixer reactor and kept separately in the collection vessel at 500°C during the whole experimental time.

12.2 Twin srew reactor - Pyrolysis unit (PDU) at the Lurgi Lentjes company

Two experimental campaigns were performed at the fast pyrolysis unit at Lurgi Lentjes. Central part is a LR (Lurgi-Ruhrgas)-mixer reactor with a pneumatic sand loop. The LR reactor has been developed in the fifties and has been applied for various processes on a technical scale. That technical experience helps to accelerate the scale up of the biomass pyrolysis reactor to a commercial scale.

12.2.1 Experimental

Within two days (each about 8h of operation) 2,2 and 3,4 kg of rice straw were used for pyrolysis. The dimensions of the feeding section and the pyrolysis reactor of the PDU limit the particle size. In a technical plant the particle size will be larger. The effects of the irregular shapes of the particulate biomass can cause problems of clogging by bridging, rat-holing or unloading variations in the storage vessels under gravity flow. The pre-treatment for the PDU takes place in two steps): first the straw is chopped to a size of 1-2 cm. Straw chopping is being investigated in a commercial 15 kW (el.) chaff-cutter with a maximum throughput of 0.5 t/h of air-dry (~15% water) straw. Long chops are recycled with the help of a sieve classifier (size 3 x 30mm). Further size reduction is achieved in a hammer mill (15 kW el.) as the stem nodes that contribute about 5 % of weight must be smashed to ensure a fast heat up during pyrolysis. Small amounts of fine dust particles were separated and not used for pyrolysis. The suitable short chops are stored with a loose bulk density of ~60 kg/m^3 in big bags (~0,5m^3) for further treatment. Finally they were transported to the PDU with a small forklift and a crane.

The condensable volatiles were collected in a two step condensation operating at 100-130°C and 2 – 5°C respectively. The formed char was separated by a cyclone. Small amounts (5-10%) of char were assumed to remain together with the sand in the heat carrier loop. The main operating conditions are summarised in table XXV.

Table XXV: Operating conditions (PDU - Lurgi)

Reactor temperature	503°C (outlet)
N_2-flow for sand loop	1 -10 m^3/h (0°C, 1.013 bar)
Throughput of biomass	2 – 3 kg/h
Amount of biomass per experiment	14 – 21 kg
Particle size of biomass	< 2 mm
Amount of quartz sand	90 g
Particle size of quartz sand	0,4 – 1,2 mm
Electrofilter	1 filter after each condensation
Average gas residence time in the reactor	1-2 s

12.2.2 Results

12.2.2.1 Product yields

In the first experiment (no.I) the gas residence time was about 2,0 s. In the second experiment (no. II) it was reduced to 1,3 s. The results , shown in table XXVI, illustrate that with decreasing retention time the amount of condensables increases and the amount of permanent gases decreases as the cracking of the vapours is reduced.

TableXXVI: Product mass yields (%) of rice straw pyrolysis in a LR-mixer reactor, two Experiments (I and II) (8% humidity, 17% ash on dry basis).

	HHV	as delivered		dry		daf	
	(MJ/kg)	I	II	I	II	I	II
water condensate	**4,9**	**26,6**	**29,2**	**20,2**	**23,1**	**24,4**	**27,8**
organic condensate	**25,5**	**19,4**	**18,7**	**21,1**	**20,3**	**25,4**	**24,5**
sum condensates		**46,0**	**47,9**	**41,3**	**43,4**	**49,8**	**52,3**
gas	**6,7**	**19,1**	**16,2**	**20,7**	**17,6**	**25,0**	**21,2**
volatiles		**65,1**	**64,1**	**62,0**	**61,0**	**74,8**	**73,5**
char	**15,1**	**34,9**	**35,9**	**38,0**	**39,0**	**25,2**	**26,5**
total		**100,0**	**100,0**	**100,0**	**100,0**	**100,0**	**100,0**
condensates/char ratio		**1,3**	**1,3**	**1,1**	**1,1**	**2,0**	**2,0**
amount of char in slurry (%)		**43,1**	**42,8**	**47,9**	**47,3**	**33,6**	**33,6**
higher heating value (MJ/kg)		**14,2**	**14,1**	**15,3**	**15,0**	**15,3**	**14,9**

Tab. XXVII Pyrolysis gas composition

CO2	**53,7**
CO	**34,5**
H	**2,5**
CH4	**5,7**
C2H6	**1,0**
C2H4	**1,0**
CxHy	**1,6**

12.2.2.2 Pyrolysis Gas

As expected from the Proximate analysis ~60% of volatiles are produced (dry basis) consisting of ~40% char plus minerals and ~20% of gas. The composition of the pyrolysis gases remaining after condensation of the vapours has been determined quantitatively by gas chromatography (Table.XXVII). About 90% of pyrolysis gas is formed as a mixture of the main components carbon dioxide, carbon monoxide and small amounts of hydrogen, methane and lower hydrocarbons. Its higher heating value is about 6,7MJ/kg. In a technical plant pyrolysis gas will be used as fuel for heating the pyrolysis unit.

12.2.2.3 Energy Balance

For the energy balance the higher heating values (HHV) for all products of these experiments have been determined carefully. As shown in table XXIII the HHV for the aqueous condensate is very low (~5 MJ/kg) and the HHV of the organic condensate is about 26 MJ/kg. On the average the condensate has a HHV of 12 MJ/kg. After mixing with the char the higher heating value of the slurries calculated from the components is about 14 -15 MJ/kg - high enough for gasification. Under these pilot plant conditions the slurry contains about 80% of the biomass energy (Table .XXVIII). In a large plant the energy yield will be higher. About 10% of the initial energy input are not found within the pyrolysis products. This might be the contribution to the heat of reaction.

TableXXVIII: Energy content of different products in relation to rice straw

	HHV	**I (as delivered)**		**II (as delivered)**	
	MJ/kg	**MJ/kg feed**	**%**	**MJ/kg feed**	**%**
aqueous condensate	**4,9**	**1,3**	**9,2**	**1,4**	**10,1**
organic condensate	**25,5**	**4,9**	**35,1**	**4,8**	**33,8**
sum condensates		**6,3**	**44,3**	**6,2**	**44,0**
gas	**6,7**	**1,3**	**9,1**	**1,1**	**7,7**
volatiles		**7,5**	**53,4**	**7,3**	**51,7**
char+ash	**15,1**	**5,3**	**37,4**	**5,4**	**38,4**
total		**12,8**	**90,8**	**12,7**	**90,1**
Difference to rice straw 1)	**14,1**	**-1,3**	**9,2**	**-1,4**	**9,9**
Energy in the slurry		**12**	**82**	**12**	**82**

1) 9% moisture 2)

The resulting slurries have a higher energy density then the initial biomass. As shown in figure 32 the volumetric density of a slurry based on rice straw is about 10 times higher. The relatively high ash content of the rice straw is retained in the char and in the slurry respectively. Therefore the energy density of a slurry based on rice straw is lower than a slurry based on products from wood or wheat straw pyrolysis. In both cases the energy efficiency for the conversion of straw to BTL synfuel is about 45%. The produced slurry of 2,3 Mt/a and can be used to produce about 350 Mt of Fischer Tropsch diesel per year. This corresponds to about 7% of the diesel consumption in Egypt in 2001 [72] .

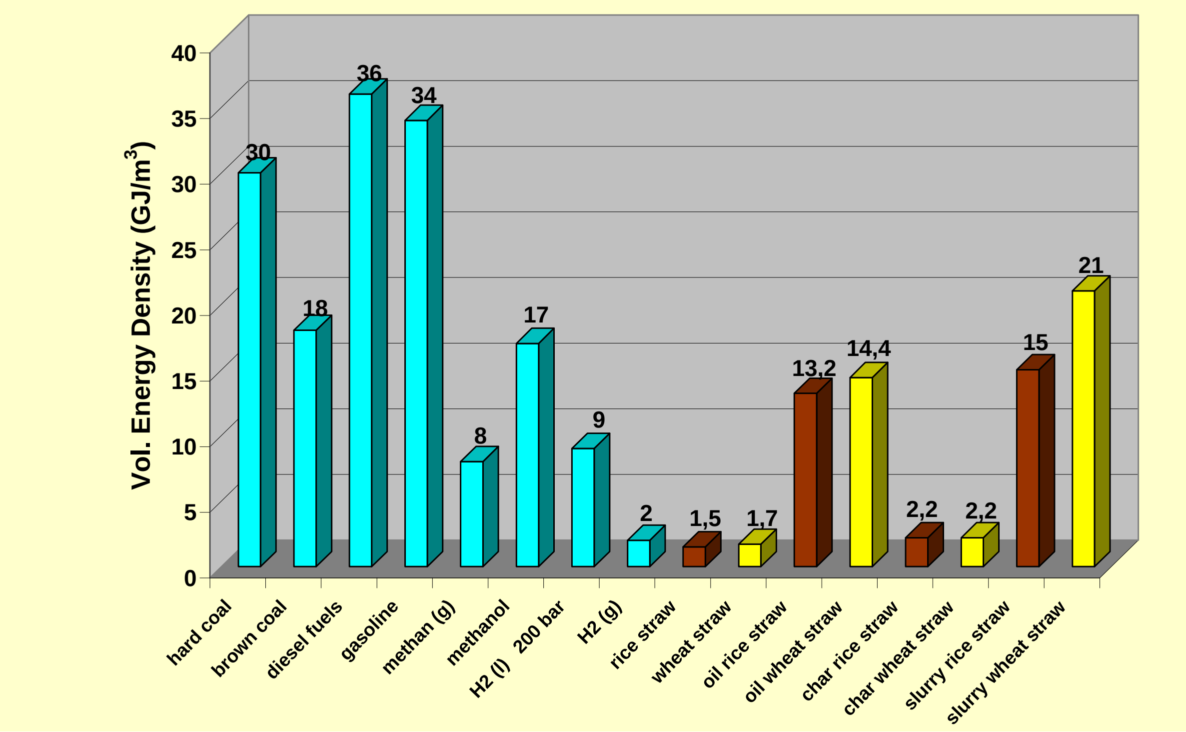


Figure 32: Volumetric energy density of different fuels and pyrolysis products

12.3 Twin screw reactor - process demonstration unit (PDU) at the FZK

12.3.1 Experimental

The simplified process flow sheet is shown in figure 33 and has been described elsewhere [75]. The **p**rocess **d**evelopment **u**nit (PDU) for FP at Forschungszentrum Karlsruhe, has been designed for a maximum throughput of 10 kg/h dry small particles of ligno-cellulose plus at least 100 kg/h ~ 1 mm quartz sand, SiC or steel sheres as heat carrier. The plant is subdivided into two main sections: a 500°C hot heat carrier loop section in the front end and a product recovery section with condensers in the tail end. A bucket elevator is used to lift the heat carrier material for recycle by gravity through a heater. The main operation conditions are shown in table XXIX.

Table XXIX: Operating conditions (PDU - FZK)

Reactor temperature	~ 500°C
N_2-flow for inertisation	1 m^3/h (0°C, 1.013 bar)
Throughput	6 – 7 kg/h
Amount of biomass per experiment	25 – 38 kg
Particle size of biomass	< 20 mm
Amount of steel sheres	45 kg
Particle size of quartz sand	1,5 mm
Electrofilter	Not available, option
Average gas residence time in the reactor	~1 s

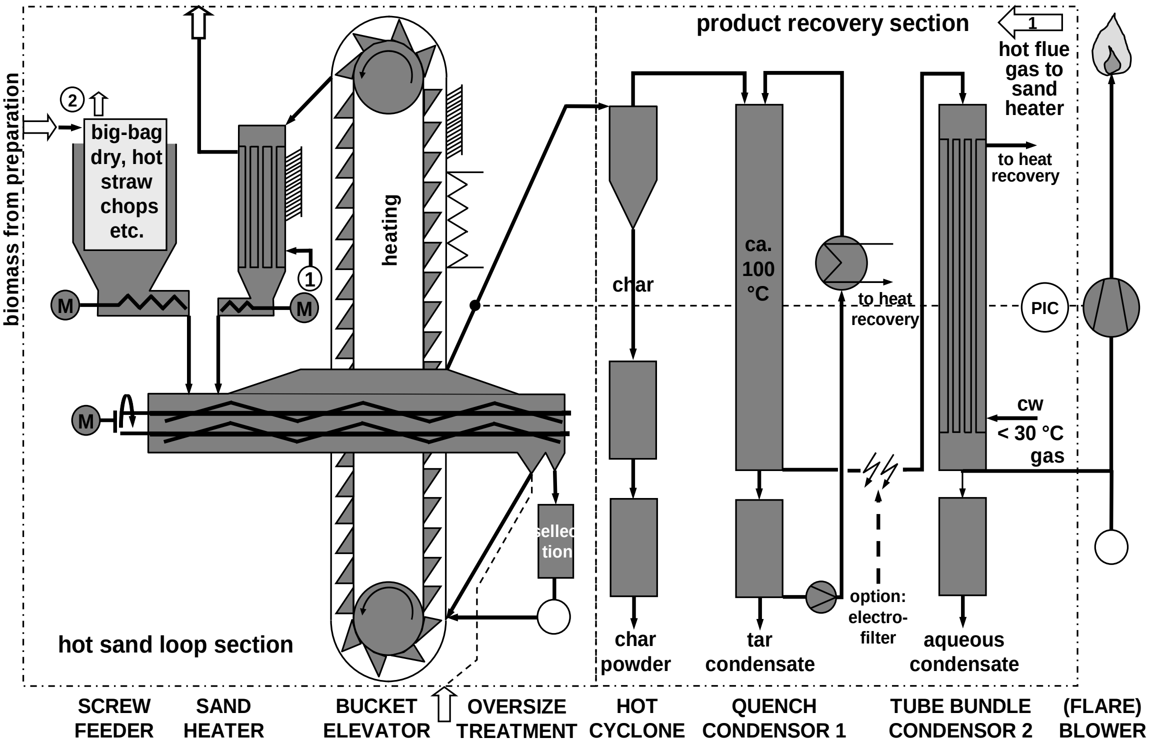


Figure 33: Simplified process scheme of the Karlsruhe process development unit (PDU) for fast pyrolysis (FP) of dry ligno-cellulosic materials.

The pyrolysis char leaves the LR-mixer reactor in form of a fine powder together with the vapours and the gas via the same exit. Most of the char can be removed with a hot cyclone directly downstream from the reactor at the same temperature of about 500°C. During handling of the char, a significant small-size dust fraction < 10 µm is easily suspended in the air and can partly penetrate simple safety filters on mouth and nose of the operating personnel. Careful or remote char handling helps, but some wetting with tar or aqueous condensate will be a more efficient protection measure against dust formation and self-ignition. The fine FP char powders are pyrophoric and can be deactivated by controlled air access. The auto-ignition risk can also be reduced or eliminated by preparing slurries or pastes for a safer storage and transport.

12.3.2 Results

The percentage yields of the FP products char, tar and aqueous condensate and gas for different feedstock's are summarised in table XXIV. All feed materials have been relatively dry with water contents between 6 to 9 %wt.. The size of the straw chops has been an average length of ca. 1 cm, few mm widths and a wall thickness of ~ 0.3 mm with a large scatter. Pyrolysis conditions have been a throughput of 3 to 5 kg/h with 6 to 10 times more hot sand leaving the FP reactor at 500°C. A trend observed with increasing ash content, is an increase of the char and gas yield and a corresponding decrease of the desired condensate yields, especially for the tar condensate. This probably indicates catalytic tar decomposition at the ash surface.

The ash remains contained within the char particles. The tar condensate was obtained above the water dew point at about 100°C; the aqueous condensate has been recovered downstream in a second condensation step at about 0°C.

Amount and composition of the pyrolysis gases remaining after condensation have been determined by gas chromatography using an internal standard. Main components are CO_2 and CO. The mass yields of the pyrolysis products of rice straw feedstock are summarised in table XXX.

TableXXX: Product mass yields (%) of rice straw pyrolysis in a LR-mixer reactor, at the PDU at FZK, three Experiments (8% humidity, 17% ash on dry basis).

	as delivered				dry				daf			
product				mean				mean				mean
condensates	42,3	41,7	43,2	**42**	36,8	35,6	37,2	**37**	45,3	43,8	45,8	**45**
gas	11,9	11,8	12,2	**12**	13,2	13,0	13,5	**13**	16,2	16,1	16,6	**16**
volatiles	54,2	53,5	55,4	**54**	50,0	48,6	50,7	**50**	61,5	59,9	62,4	**61**
char (+ash)	34,3	35,5	35,5	**35**	38,0	39,2	39,2	**39**	23,6	25,1	25,2	**25**
total	88,5	89,0	90,9	**89**	88,0	87,8	89,9	**89**	85,1	85,0	87,6	**86**
deficit	11,5	11,0	9,1	**11**	12,0	12,2	10,1	**12**	14,9	15,0	12,4	**14**
condensates/solids ratio				**1,2**				**0,94**				**1,83**
amount of solids in slurry (%)				**45,5**				**51,5**				**35,3**

13 Discussion

13.1 Slow pyrolysis

On a moisture and ash free basis (maf) the amounts of volatiles and char formed during fast pyrolysis are identical to those obtained as mean value from thermal analysis at different heating rates (25% V, 75% FC). The more detailed study by extrapolation from low heating rates expects about 78% volatiles and 22% of char (maf) (see figure 17). The possibility that condensables vapours are cracked on the surface of the char forming an additional amount of char and permanent gases could not be confirmed in this case. The results indicate that the yield of volatiles is similar too. Calculated on 100% product yield (daf) in the fluidised bed reactor 80% of volatiles and 20% of char were formed. As a consequence slow pyrolysis in a thermo balance can be used under special conditions to estimate the yield of pyrolysis char produced in a fast pyrolysis reactor.

13.2 Material Balance

A typical fast pyrolysis (FP) mass distribution for dry bark-free wood is: gas ~15 %, char ~15 %, condensates ~70%. Typical FP-mass distributions for cereal straw are: a) wheat straw (8% ash) gas 15 %, char 30%, condensate usually ca. 50%, b) rice straw (18% ash) gas ~20 %, char ~40 %, condensates ~40%.

For the empirical biomass $C_6H_9O_4$ (without ash and moisture) the condensate/char ratio is 2.0 (1). Under these conditions all the char can be suspended in the own condensates.

1) 100 Biomass (daf) → 25 gas + 50 condensate + 25 char

The high ash content (18%) in rice straw is retained in the char and increases the amount of solid product (2):

2) 100 Biomass → 21 gas + 41 condensate + 38 char
(18% ash)

Finally the amount of moisture (8%) contributes to the amount of condensates (3):

3) 100 Biomass → 19 gas + 45 condensate + 36 char
(18% ash, 8%moisture)

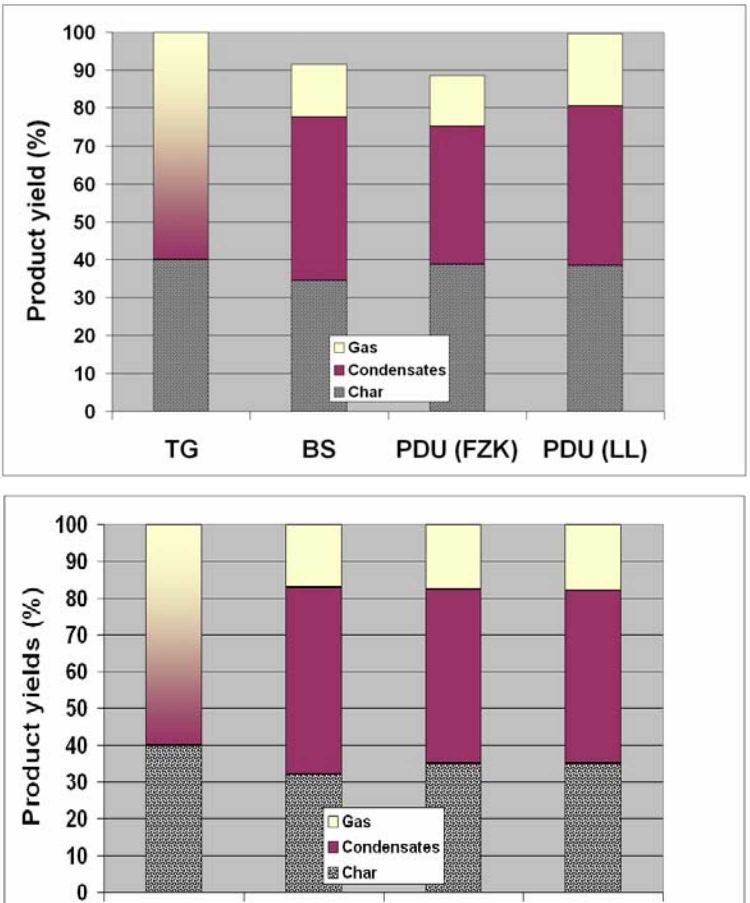


Figure 34: Product yields of rice straw pyrolysis (18% ash, 8% humidity), Thermal Analysis (TG), **B**ench **s**cale (LS), Process demonstration unit (PDU) at FZK and **L**urgi- **L**entjes.

The experimental pyrolysis results of rice straw (18% ash, 8% humidity) in different facilities are summarised in figure 34 (top). The char mass yield is relatively high because of the ash content of the biomass feedstock. Assuming that the mass balance deficit is caused by equal gas and condensates gaps the yields were corrected and illustrated in figure 34 too (bottom). Because of the slow heating rate the highest char yield of 40% (average) was found in the thermal analysis experiments. In the bench scale reactor about 32% of char and 51% of condensates were formed. Fast pyrolysis tests in different PDUs showed identical results. The yields were found to be about 35% of char and 47% of condensates. Because of intermediate reactions of the fine char powder with the pyrolysis vapours in the hot reaction zone a higher amount of char and less condensates were formed in this case. These experimental product yields are identical to the expected theoretical yields.

13.3 Product yields ratio

As a rule of thumb a bio-oil/char mass ratio of ≥ 2 is suitable to prepare a pumpable slurry. In practice there is a larger range from about 1.5 to 3 (40 – 25 %wt solids), depending on bio-oil and char properties like viscosity, particle size spectrum, porosity etc.. Higher solid loadings which result in stiff pastes or even pourable char crumbs may be preferred for a safer storage and transport; the final gasifier feed slurry is then prepared in a single place at the gasifier site by mixing with a hot pyrolysis liquid.

The bio-oil/char mass ratio after FP of lignocellulose depends on the ash and water content. For wood or other types of biomass with little ash mass ratios of 3 – 4 and an excess of bio-oil is obtained. For cereal straw with 5 – 10 %wt ash, the mass ratios are about 2 and at the limit. For rice straw with ~ 20 %wt. ash the risk is high that there will be a deficit of bio-oil. In case of need the excess of oil can be supplied e.g. from wood or other sources. An alternative is to use surplus char for other purposes. To mix some straw char into the wood derived slurries is also desirable to reduce the slag melting point in the gasifier.

There is no standard slurry required for the gasification step, a wide spectrum of different slurry types can be used and contributes to the feed flexibility. The possible gasifier feed diversification guarantees a corresponding biomass feedstock diversification.

13.4 Slurry production

The potential slurry composition for the product distribution at different testing facilities are shown in table XXXI. For rice straw containing 8% of water and 18% of ash the condensate to solid ratio decreases to 1.2 resulting in a slurry with about 46% of char. If the biomass is dried before use the amount of char in the slurry goes up to 50%. In all cases the condensate volume is close to the limits to suspend the pyrolysis char. Even only small differences in the product distribution result in significant differences of the corresponding slurry: for the bench scale pyrolysis the amount of char is about 41% whereas for the FZK –PDU it will go up to 46%. As a consequence the design of the plant and its operation conditions have to be chosen very carefully. At any case the preparation of such slurries will only be possible with a

TableXXXI: Slurry composition for different product yields:
Solid/liquid ratio (R), solid content (%wt)

	as delivered		dry		daf	
	R	solids (%wt)	R	solids (%wt)	R	solids (%wt)
Bench Scale	**1,5**	**41**	**1,25**	**45**	**2,6**	**28**
Lurgi-Lentjes	**1,3**	**43**	**1,1**	**48**	**2**	**34**
FZK	**1,2**	**46**	**0,9**	**52**	**1,8**	**35**

special equipment like a colloid mixer as it is studied at the Forschungszentrum Karlsruhe [74].

The dense and stable slurries can easily be stored and pumped and the transport to a larger central plant for further use now is much more economic. Conventional and slow pyrolysis generates too much char and do not allow a complete suspension in only own condensates anymore.

13.5 BTL production

For the total available amount of rice straw in Egypt (~2,8 Mt/year) about 28 fast pyrolysis units each with a capacity of 100.000t/a are necessary. Square bales with ~ 100 kg/m^3 bulk density are the preferred feedstock for compact transport and storage. In the regions of the Nile delta the unused half of the straw harvest amounts to ~ 120 - 250 t per year and $km^{2.}$ For a capacity for a regional pyrolysis plant of 100.000 t/a a maximum delivery radius of 15 km comprises about 700 km^2 resulting in a throughput of 12 to 15 t/h of airdry rice straw. In-time straw delivery to an intermediate storage facility at the pyrolysis plant must be fixed by contracts with the local farmers, as is known from Danish district heating plants. The straw should be as dry as possible (<15% moisture) when delivered at the plant gate.

Figure 35 shows the expected mass flow for the BTL process based on rice straw as feedstock. The whole process from biomass to synthetic fuels, chemicals or energy is a sequence of several processing steps like pyrolysis, gasification, gas cleaning, gas conditioning and synthesis. The overall efficiency for the total process chain results as a product of the efficiency of the individual process steps. From table XXI it can be seen that from 1t of rice straw (18% ash, 8% moisture) about 0,8 t of slurry can be prepared (condensates + char). The results indicate that under standard conditions (15% moisture) 8t of rice straw are necessary to produce 1t of BTL synfuel. Along the process chain additionally about 1,2 t of slag are produced at the gasification step. The slag can be used as fertilizer or building material. Because of the special ash

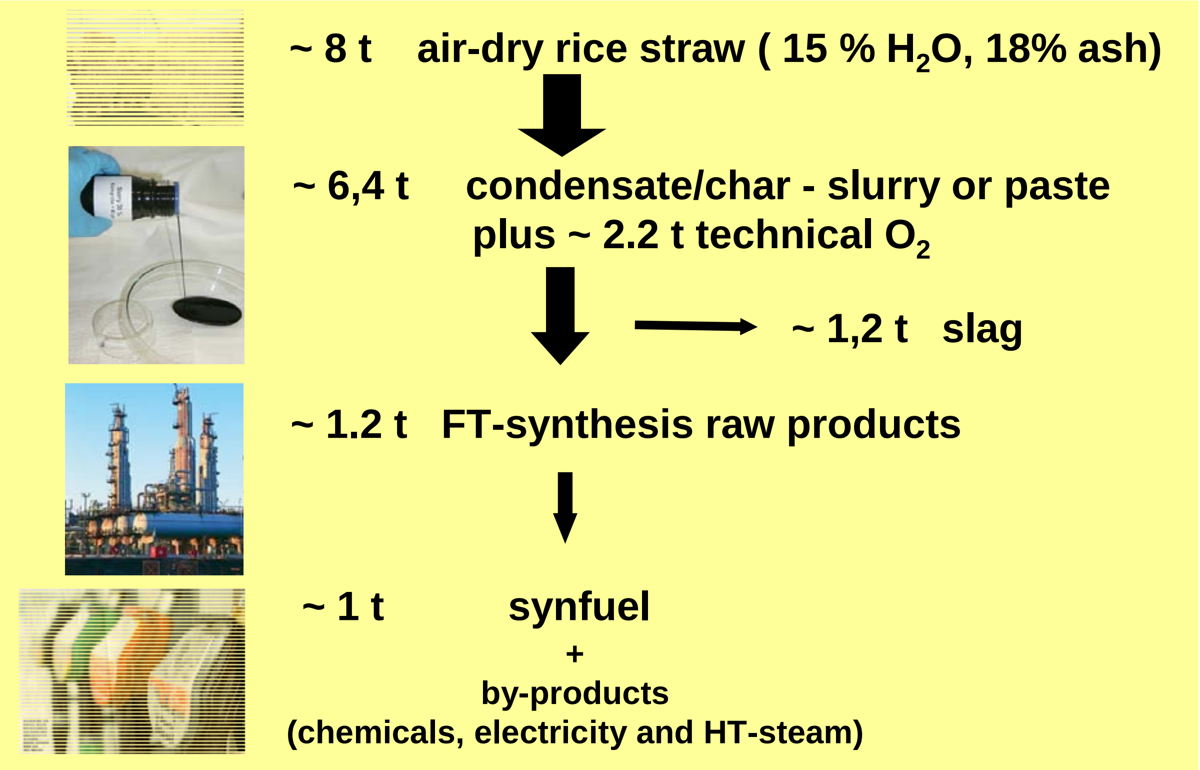


Figure 35: Mass flow in the BTL process based on rice straw

content the specific mass throughput is higher when compared to wheat straw (15% moisture, 8% ash) where only 7t of straw are necessary.
Assuming that about 20% of the rice straw is used for other purposes about 2.8 Mt were left on the fields for burning in 2004. The amount of slurry will be about 2,2 Mt/a and could have been used to produce about 350000 t of Fischer Tropsch diesel per year. This corresponds to about 7% of the diesel consumption in Egypt in 2001 [72].

14 Outlook

The study of the rice straw pyrolysis must be performed in Egypt too. Some basic equipment is already available: a) fast pyrolysis in a screw reactor (Helwan university, Kairo, figure 33), b) fluidised bed pyrolysis reactor (Atomic Energy Authority,Hot Lab in Inshas) or c) Gasification system for pelletised agricultural residues (New and Renewable Energy Authority (NREA) in Cairo). In addition several other types of biomass feedstock should be studied to enlarge the potential use of the technique in Egypt. Typical biomass residues in Eypt are cotton stalks, sugar beet, sugar cane and others. A mor detailed summary is given in attachment C in table XV. In cooperation with the neighbouring universities and the German University in Cairo (GUC) the technology can be optimised and adapted to the local conditions. Step by step the technology can be introduced in Egypt within the next years where the technological and scientific support and the training of the staff should be supported by the German side. Training programmes in basic engineering and gasification technology are needed. Although university educated engineers are expected to be capable in the basic aspects they often lack practical experience, especially where financial resources are extremely limited. Seminars and symposiums are excellent for drawing attention to problems. In addition continuous workshop-type training is needed for all operating personal.

Figure 36: General view of the bench scale facility at the Helwan university, Cairo; screw reactor, electrically heated.

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16. Appendix

Appendix A

Table. I Ultimate Analysis of Rice Straw (dry)

Reference	C	H	N	S	O	Cl
[36]	34,0	5,0	1,1	0,1	34,7	
[33]	39,6	4,6	0,7	0,1	36,4	0,3
[35]	34,8	4,6	0,7	0,1		
[10]	41,0	5,0	0,7	0,1	38,0	0,4
[39]	39,2	5,1	0,6	0,1	35,8	
[42]	41,8	4,6	0,7	0,1		0,3
[37]	34,6	4,4	0,6	0,1		0,3
[37]	35,2	4,6	0,7	0,1		0,5
[37]	38,9	4,7	0,8	0,1		0,5
[37]	39,2	4,8	0,9	0,1		0,6
[37]	41,8	5,1	1,1	0,2		0,6
[37]	48,2	5,6	1,4	0,2		
[38]	48,1	5,9	1,7	0,1	43,6	
[40]	40,9	5,2	0,8	0,2	37,6	
[40]	41,5	5,1	0,4	0,1	36,7	
[40]	37,7	4,9	0,3	0,1	36,8	
[43]	38,2	5,3	0,3			
This work	37,8	5,0	0,4	0,2	37,7	1,9
Minimum	34,0	4,4	0,3	0,1	34,7	0,3
Maximum	48,2	5,9	1,7	0,2	43,6	1,9
Mean	39,6	5,0	0,8	0,1	37,5	0,6
Stand.Dev.	4,0	0,4	0,3	0,0	3,5	0,1

Table. II Proximate Analysis and HHV of Rice Straw;
A,V and FC on dry basis.

Reference	M	A	V	FC	Calorific value MJ/kg
[36]	10	15,2	69,1	5,7	15,18
[33]	8,5	18,3			15,09
[34]	9	18,1			14,03
[35]	7,9	20,5	79,5		
[39]		19,2			
[42]		13,4	69,3	17,3	16,28
[37]		15,9			14,76
[37]		17,2			15,03
[37]		17,8			15,1
[37]		19,1			15,22
[37]		19,2			15,95
[37]		19,8			16,3
[38]		19,1			15,95
[40]	15	12,9	58,4	13,7	13,65
[40]	11,6	13,9	59,5	15	14,78
[40]	9,9	19,6	56,2	14,3	12,9
[43]		15,5	68,4	16,2	
This work	10	20	60	20	15,3
Minimum	7,9	12,9	56,2	5,7	12,9
Maximum	15	20,5	79,5	20	16,3
Mean	10,2	17,5	65,1	14,6	15,0
Stand.Dev.	2,2	2,4	7,9	4,5	0,9

Table. III Lignin, Cellulose and Hemicellulose
found in rice straw

Reference	Cellulose	Hemicellulose	Lignin
[34]	28		13
[45]	32	36	12
[10]	33	28	10
[46]	32	24	13
[18]	39	24	14
Minimum	28	24	10
Maximum	39	36	14
Mean	33	28	12
Stand.Dev.	4	6	1

Table. IV Results from thermal analysis (dynamic) of rice straw

Heating rate (K/min)	Volatiles dry (%)	Char dry (%)	Ash dry (%)	Volatiles daf (%)	Char daf (%)
50	62,31	17,69	20,06	77,95	22,13
35	60,74	17,61	22,76	78,64	22,80
20	60,72	18,39	20,77	76,65	23,21
10	60,24	18,55	21,48	76,72	23,62
5	59,68	19,43	21,06	75,63	24,59
2	58,40	21,74	20,18	73,19	27,21
1	59,27	22,08	18,39	72,62	27,06
0,5	59,32	22,83	18,02	72,36	27,85
Mean	60,09	19,79	20,34	75,47	24,81
Stdev.	1,20	2,11	1,56	2,45	2,25

Appendix B

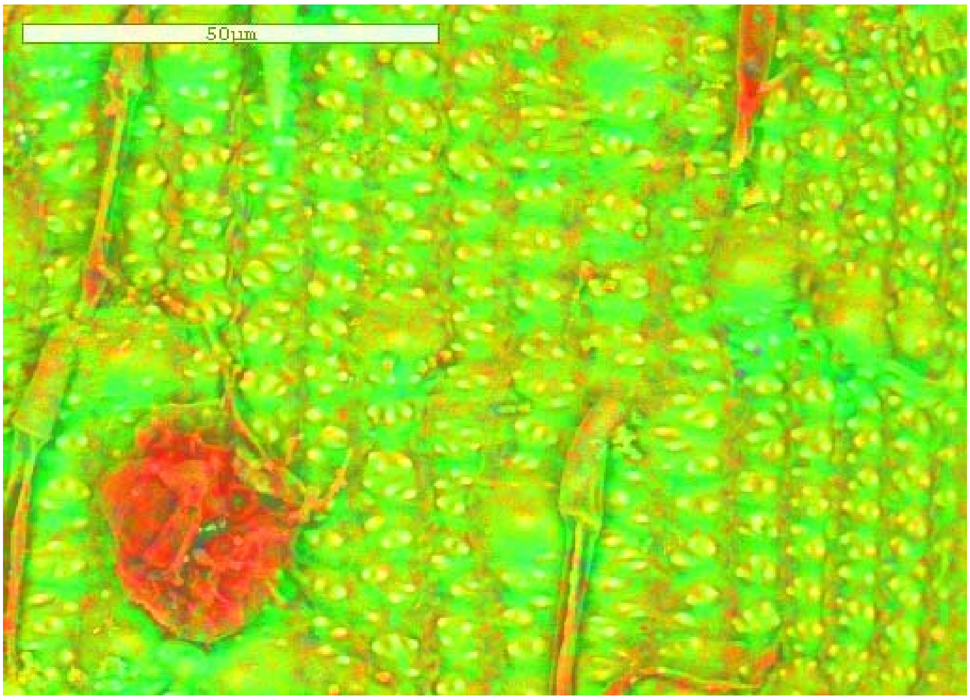

Fig. I SEM, Rice straw stem outer surface after pyrolysis at 300°C.

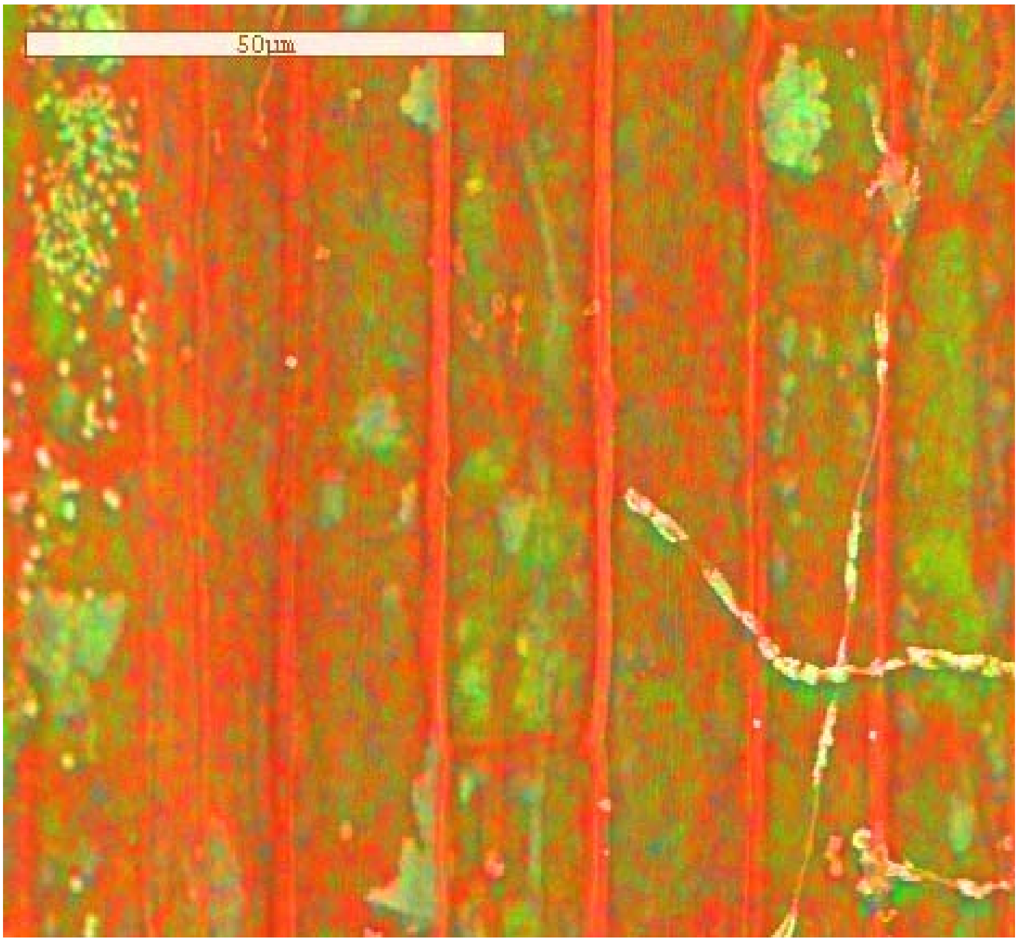

Fig. II SEM, Rice straw stem inner surface after pyrolysis at 300°C

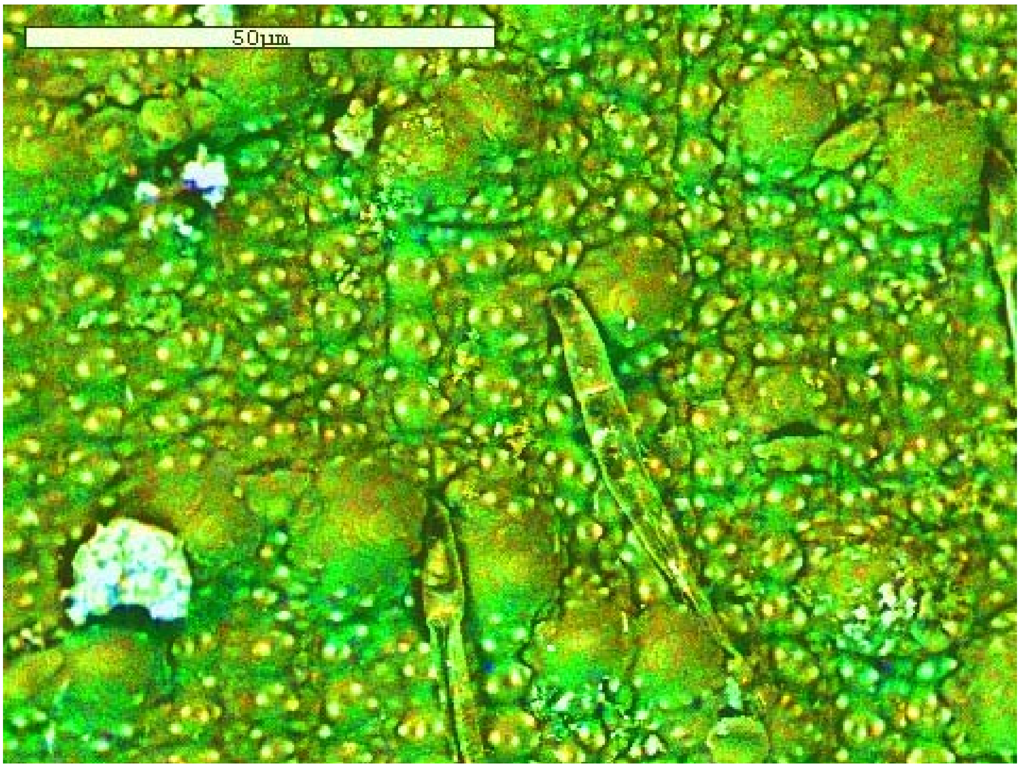

Fig. III SEM, Rice straw stem outer surface after pyrolysis at 500°C.

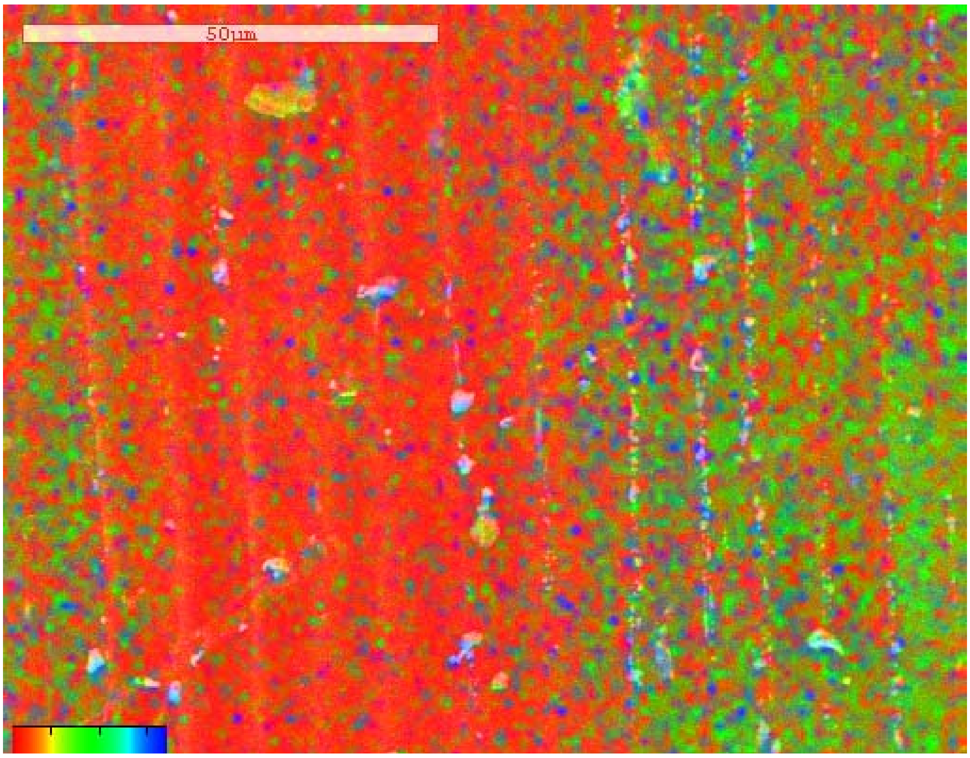

Fig. IV SEM, Rice straw stem inner surface after pyrolysis at 500°C

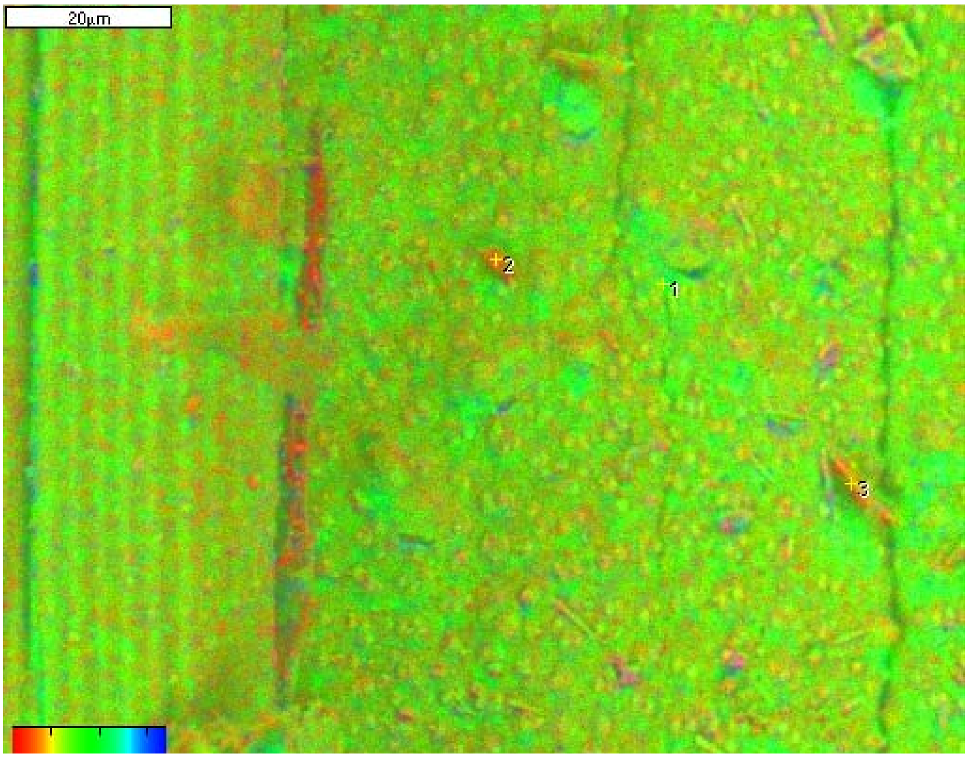

Fig. V SEM, Rice straw stem outer surface after pyrolysis at 900°C

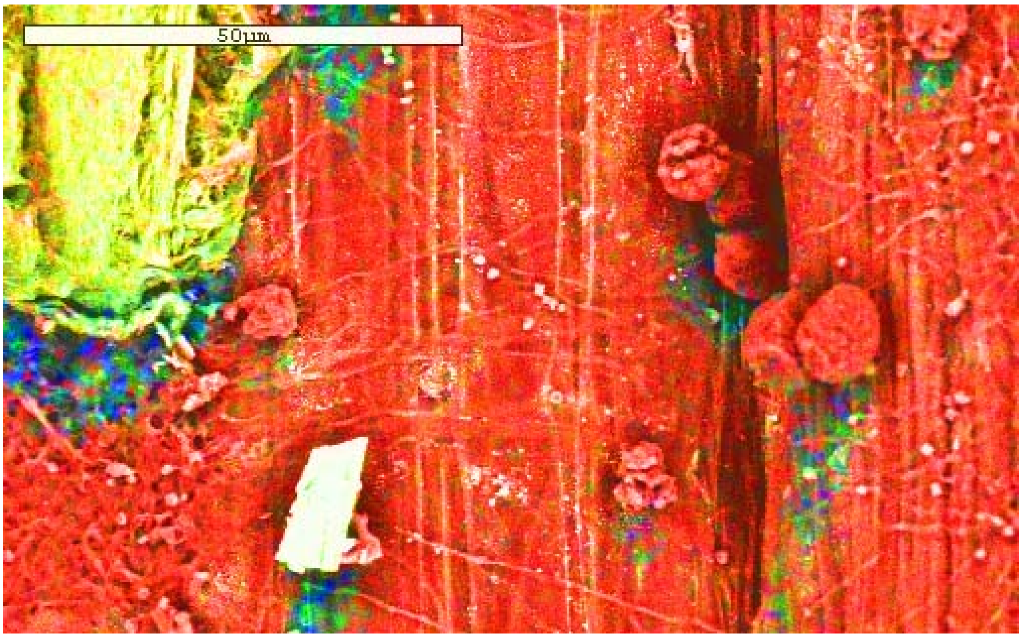

Fig. VI SEM, Rice straw stem inner surface after pyrolysis at 900°C

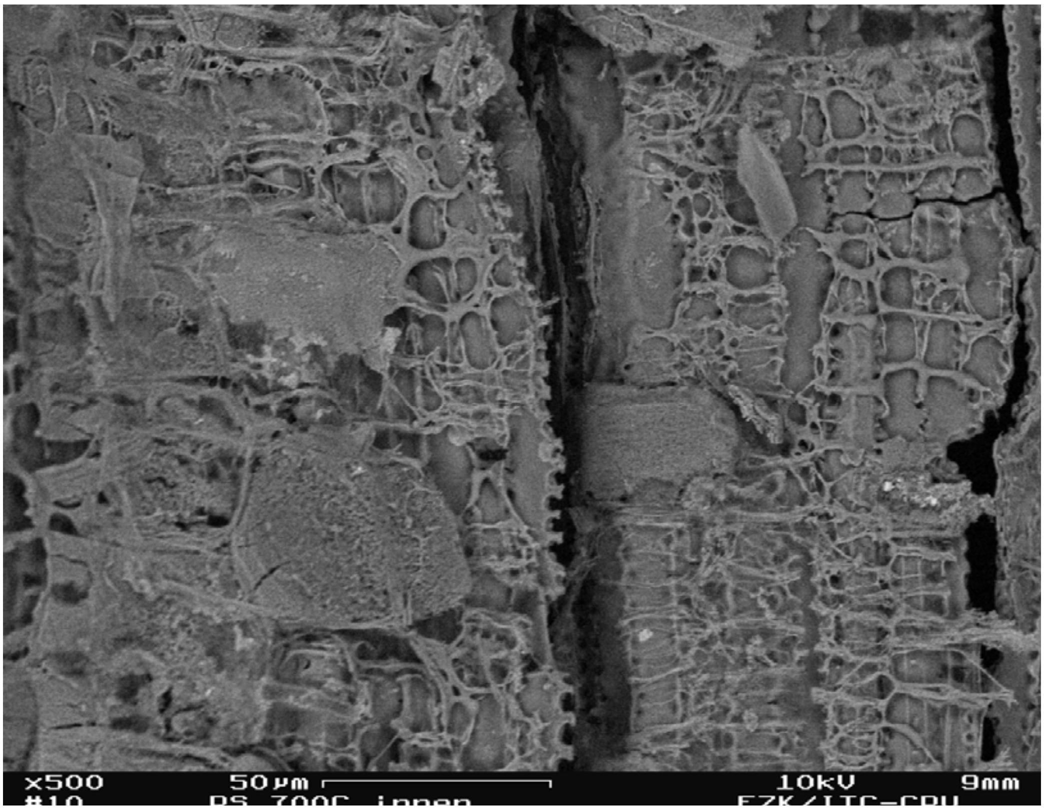

Figure VIII SEM, Rice straw char inner surface after ashing at 700°C

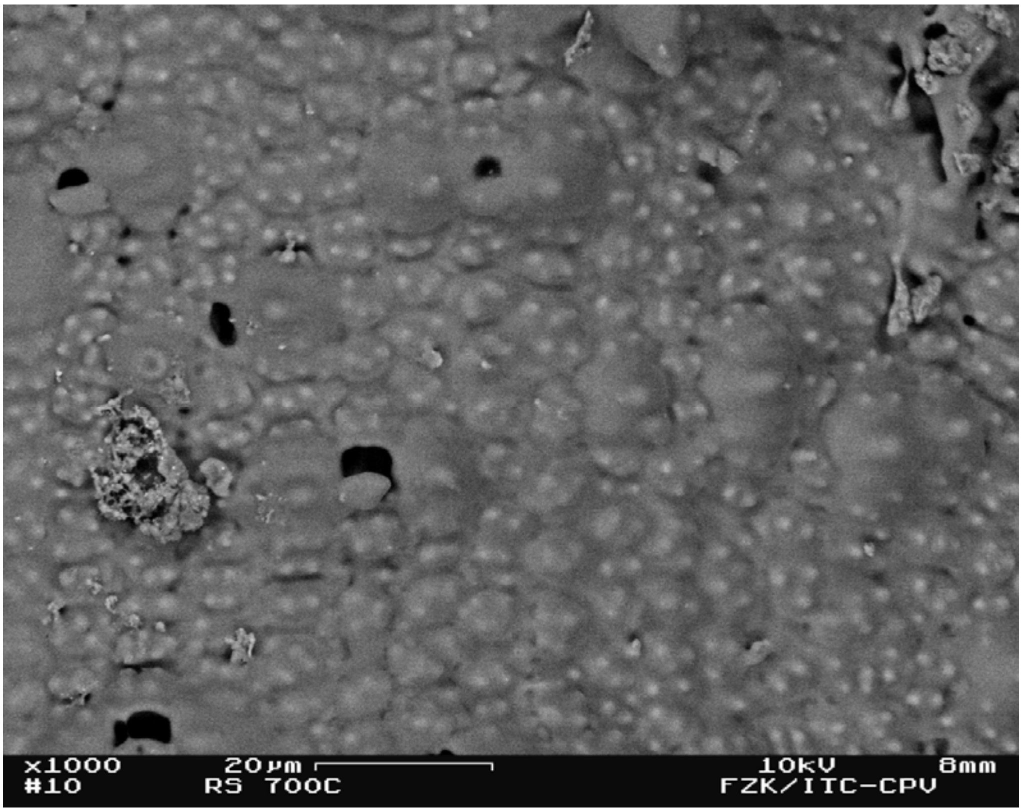

Figure VII SEM, Rice straw char outer surface after ashing at 700°C

Appendix C

Table V Volatiles and char yield of rice straw, cellulose, lignin and hemicellulose for different heating rates dry and on moisture and ash free basis.

Cellulose

Heating rate (K/min)	Volatiles dry (%)	Char dry (%)	Ash dry (%)	Volatiles daf (%)	Char daf (%)
0,5	80,84	15,01	4,15	84,34	15,66
1	80,97	15,82	3,21	83,66	16,34
2	81,64	15,02	3,34	84,46	15,54
5	82,50	14,16	3,34	85,35	14,65
10	84,14	13,38	2,49	86,28	13,72
20	86,15	11,41	2,44	88,31	11,69
35	88,92	9,82	1,26	90,05	9,95
50	89,72	9,19	1,09	90,71	9,29

Lignin

Heating rate (K/min)	Volatiles dry (%)	Char dry (%)	Ash dry (%)	Volatiles daf (%)	Char daf (%)
0,5	54,63	38,49	6,89	58,70	41,30
1	53,60	39,67	6,73	57,46	42,54
2	54,15	40,16	5,69	57,41	42,59
5	55,33	39,01	5,67	58,65	41,35
10	56,03	37,60	6,48	59,88	40,12
20	56,01	35,99	8,00	60,92	39,08
35	58,48	37,06	4,47	61,21	38,79
50	59,86	36,20	3,94	62,32	37,68

Hemicellulose

Heating rate (K/min)	Volatiles dry (%)	Char dry (%)	Ash dry (%)	Volatiles daf (%)	Char daf (%)
0,5	67,50	23,80	8,70	73,93	26,07
1	68,53	22,87	8,60	74,98	25,02
2	68,90	22,40	8,70	75,47	24,53
5	70,39	21,41	8,21	76,68	23,32
10	71,98	20,05	7,97	78,21	21,79
20	73,47	17,84	8,69	80,46	19,54
35	72,77	17,75	9,47	80,39	19,61
50	74,31	17,64	8,05	80,82	19,18

Rice straw

Heating rate (K/min)	Volatiles dry (%)	Koks dry (%)	Ash dry (%)	Volatiles daf (%)	Char daf (%)
50	62,31	17,69	20,06	77,95	22,13
35	60,74	17,61	22,76	78,64	22,80
20	60,72	18,39	20,77	76,65	23,21
10	60,24	18,55	21,48	76,72	23,62
5	59,68	19,43	21,06	75,63	24,59
2	58,40	21,74	20,18	73,19	27,21
1	59,27	22,08	18,39	72,62	27,06
0,5	59,32	22,83	18,02	72,36	27,85

Table VI Mineral composition of rice straw ash found in literature and own study

Reference	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**P_2O_5**
[34]	72,2	0,07	0,22	1,65	1,49	0,42	16,60	1,86
[37]	73,0		0,58	0,72	1,75	0,28	7,85	1,40
[37]	74,7		0,60	1,90	1,80	0,40	11,90	1,41
[37]	75,2		0,85	1,98	2,04	0,85	12,30	1,73
[37]	80,8		0,87	3,01		0,95	13,50	
[38]	73,0		0,60	1,90	1,80	0,40	13,50	1,40
This work	65,7	0,30	0,10	1,70	2,10	3,10	15,00	0,50
Minimum	65,7	0,07	0,10	0,72	1,49	0,28	7,85	0,50
Maximum	80,8	0,30	0,87	3,01	2,10	3,10	16,60	1,86
Mean	73,5	0,19	0,55	1,84	1,83	0,91	12,95	1,38
Stand.Dev.	3,4	0,03	0,26	0,82	0,23	0,30	3,15	0,23

Table VII Experimental and calculated HHV of rice straw and rice straw char (MJ/kg).

T(°C)	experimental	Michel	IGT	Dulong	Ebeling
20	15,3	15,4	14,6	13,3	15,5
300	18,6	18,3	17,6	17,4	13,4
400	17,3	17,4	16,6	16,6	12,4
450	17,1	16,8	16,0	16,2	11,6
500	16,4	16,6	15,7	15,9	11,6
600	15,8	15,9	15,0	15,3	11,0
700	15,4	15,6	14,7	14,9	11,0
800	14,9	15,4	14,5	14,7	10,9
900	14,8	15,2	14,3	14,4	11,3

Table VIII Paddy Production Worldwide

Rice	Metric Ton		
	1995	2000	2003
Albania	0	0	0
Algeria	1,500	300	300
Angola	19,000	16,000	16,000
Argentina	926,200	903,630	717,600
Australia	1,015,830	1,098,000	391,000
Azerbaijan	3,750	22,336	15,651
Bangladesh	26,399,000	37,627,500	38,060,000
Belize	9,628	9,868	13,194
Benin	17,219	49,245	66,000
Bhutan	50,000	50,000	38,000
Bolivia	264,612	310,099	424,454
Brazil	11,226,064	11,089,800	10,198,900
Brunei Darussalam	508	500	400
Bulgaria	4,984	16,784	18,000
Burkina Faso	84,025	103,087	97,103
Burundi	26,819	51,678	63,000
Cambodia	3,447,800	4,026,092	4,300,000
Cameroon	35,300	61,271	78,678
Central African Republic	10,000	23,100	27,400
Chad	78,978	92,624	112,000
Chile	145,899	135,060	140,849
China	187,297,968	189,814,060	166,417,000
Colombia	1,742,547	2,285,718	2,500,000
Comoros	17,000	17,000	17,000
Congo, Dem Republic of	365,818	337,800	314,614
Congo, Republic of	1,101	1,301	1,403
Costa Rica	183,184	296,024	179,987
Cuba	396,100	552,800	715,800
Côte d'Ivoire	764,000	1,231,000	818,000
Dominican Republic	486,741	581,410	609,209
Ecuador	1,290,518	1,246,630	1,235,967
Egypt	4,788,097	6,000,490	5,800,000
El Salvador	51,106	47,204	28,442
Ethiopia	0	0	15,500
Fiji Islands	18,496	13,170	16,000
France	122,400	115,958	105,423
French Guiana	25,276	19,900	24,200
Gabon	800	1,000	1,000
Gambia	18,952	34,100	20,500

Ghana	201,720	248,700	316,000
Greece	211,599	147,468	175,000
Guatemala	30,581	45,223	32,495
Guinea	630,511	739,341	845,000
Guinea-Bissau	133,266	106,081	97,000
Guyana	527,977	449,181	501,500
Haiti	100,000	130,000	105,000
Honduras	34,555	7,262	8,950
Hungary	13,300	11,255	10,000
India	115,440,000	127,464,896	132,013,000
Indonesia	49,744,140	51,898,000	52,078,832
Iran	2,300,901	1,971,462	3,300,000
Italy	1,320,850	1,229,767	1,359,826
Jamaica	158	12	11
Japan	13,435,000	11,863,000	9,740,000
Kazakhstan	184,450	214,300	200,000
Kenya	60,000	52,349	50,000
Korea, DPR	2,016,000	1,690,000	2,284,000
Korea, Republic of	6,387,301	7,196,582	6,068,000
Kyrgyzstan	6,700	18,991	18,342
Laos	1,417,829	2,201,800	2,500,000
Liberia	56,200	183,400	110,000
Macedonia	6,447	18,500	13,042
Madagascar	2,450,000	2,480,470	2,800,000
Malawi	52,077	71,601	86,882
Malaysia	2,127,271	2,140,800	2,145,142
Mali	476,090	742,599	693,203
Mauritania	52,813	76,200	77,409
Mauritius	0	0	0
Mexico	367,030	351,447	191,540
Micronesia, Fed. States of	90	90	90
Morocco	3,470	25,200	8,100
Mozambique	112,982	151,388	200,439
Myanmar	17,956,900	21,323,868	24,640,000
Nepal	3,578,830	4,216,465	4,155,000
Nicaragua	232,456	271,150	290,646
Niger	51,000	60,453	76,500
Nigeria	2,920,000	3,298,000	4,952,000
Pacific Islands Trust Tr.	0	0	0
Pakistan	5,949,750	7,203,900	6,751,000
Panama	176,234	207,429	250,000
Papua New Guinea	650	700	800

Paraguay	136,260	101,049	105,000
Peru	1,141,550	1,892,100	2,139,100
Philippines	10,540,640	12,389,400	14,031,000
Portugal	124,554	142,611	146,000
Puerto Rico	0	0	0
Romania	24,066	3,551	1,500
Russian Federation	461,900	585,750	449,520
Rwanda	2,300	11,654	27,891
Réunion	80	80	80
Saint Vincent/Grenadines	0	0	0
Saudi Arabia	0	0	0
Senegal	155,152	202,293	177,756
Sierra Leone	355,500	199,134	250,000
Solomon Islands	0	4,800	5,000
South Africa	3,000	3,000	3,200
Spain	329,500	827,051	855,000
Sri Lanka	2,809,890	2,859,900	3,071,200
Sudan	1,200	8,000	15,000
Suriname	242,000	163,700	195,000
Swaziland	1,000	170	170
Syria	100	0	0
Tajikistan	24,089	81,978	59,415
Tanzania	622,600	782,300	640,189
Thailand	22,015,500	25,844,000	27,000,000
Timor-Leste	46,696	51,000	65,433
Togo	51,236	62,306	68,100
Trinidad and Tobago	10,193	6,256	2,935
Turkey	200,000	350,000	372,000
Turkmenistan	78,600	27,300	109,500
Uganda	77,000	109,000	120,000
Ukraine	80,000	89,700	84,000
United States of America	7,887,000	8,657,819	9,033,610
Uruguay	806,100	1,209,139	1,250,000
Uzbekistan	327,600	154,800	311,200
Venezuela	756,950	676,775	700,611
Viet Nam	24,963,700	32,529,500	34,518,600
Zambia	12,110	13,936	12,000
Zimbabwe	400	500	600

source: FAOSTAT data, 2004.

Table IX

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Total particulate matter (PM): A collective name for fine solid or liquid particles added to the atmosphere by process at the earth's surface. Particulate matter includes dust, smoke, soot, pollen and soil particles with a diameter less than 100 microns

PM10 - particulate matter less than 10 microns in diameter.

Table X: Agricultural residues in Egypt (2003 – 2004) [13]

No	Kind	Area 1000 Acre (ac)	*waste* Generation Ton/ ac /yr	Total waste Available 1000d.t/yr	For energy uses %	Total waste for energy use 1000d.t/yr	Total Energy 1000 TOE/yr	Month of gathering
1	Cotton-stalks *	535.090	1.80	963.162	90	866.845	**	9 - 10
2	Fruits *	968.822****	1.80	1743.880	80	1395		1 - 2
3	Rice straw *	1507.634	2.18	3286.642	90	2957.9778	**	11
	Rice hulls	…	1.1	1500	90	1350	****	11
4	*Sugar cane	327.215	6.21 1.80	2032.005 5170	85 90	1727.2043 4653	*** **	12 - 1
5	Sugar Beet	131.323	3.04	399.222	40	159.689	****	
6	Maize ©(W/Y)	1658.019	2.30	3813.444	65	2478.7386	****	
	Cobs ©	---------	---	1200	50	600	** / ****	
7	Sorghum	389.767	2.45	954.929			****	
8	Wheat	2506.173	3.5	7643.828	-	-	****	
9	Barley	216.191	2.18	471.296			****	
10	Sugar beet	39.9	0.50	20	50	10	**	
11	Legumes ©	400.1	0.80	320	50	160	****	
12	Vegetables (S/W)	784.467/ 441.723	3.0 3.0	2353.401/ 1325.166	50 50	1176.7005 662.583	** / ****	
13	Date Palm	78.074	11.7	913.466	20	182.69	**	2…3
14	Greenhouses Plant	13.037	13.92	181.475	20	36.295	**	