

## PRESSURISED ENTRAINED FLOW GASIFIERS FOR BIOMASS

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### ABSTRACT

A new concept for the gasification of dry lignocellulosic biomass has been developed. Special attention was paid to the process compatibility with biomass feedstocks from agriculture, mainly straw, which have a higher ash, potassium and chlorine content and a lower ash softening point than wood.

The first process step is a *fast* pyrolysis at atmospheric pressure, which produces much condensate and only little char and gas. Pyrolysis condensate and pulverised pyrolysis char are then mixed to a slurry, containing up to 90% of the initial biomass energy. In contrast to the loose-packed original biomass the dense slurries are easily pumped and stored in tanks. From a number of regional pyrolysis plants, the slurries can be transported by rail to a large central gasification facility. Thus, the economy of scale can make possible an efficient but more complex gasification and syngas utilisation technology, to produce the most valuable products.

The slurries are pumped into a slagging entrained flow gasifier and are atomised and converted to syngas at high operating temperatures and pressures, above the operating pressure of a downstream synthesis plant. At very high pressures, alternative operation of pressure locks with a low-bulk-density biomass will become too expensive. High gasification temperatures and pressures help to produce a tar-free syngas, simplify downstream gas cleaning steps and obviate intermediate compression before synthesis. To achieve a high process efficiency, the utilisation of chemical energy in synthesis products like methanol must be complemented and combined with a use of the sensible heat for electric power generation.

Various chemical and engineering aspects of the new process concept are being investigated in the laboratory. A test campaign at a pressurised entrained flow gasifier with ca. 5 MW(th) slurry throughput is under preparation. A fast pyrolysis facility designed for continuous operation with several kg/h biomass throughput is under construction. Fast pyrolysis of biomass will be achieved by mixing with an excess of hot sand in a special twin screw reactor.

### INTRODUCTION

Biomass - mainly firewood - has been the major energy source in the past. Today, almost 80% of the world primary energy is supplied by fossil fuels; the share of biomass energy has dropped to about 10%. The world population of 6 billion today, is expected to increase via ca. 9 billion in 2050, to a flat maximum of almost 10 billion in 2100. Despite many technical improvements in energy efficiency, the increasing power consumption per capita in the developing countries will cause at least a doubling of the future energy demand.

The economically recoverable oil, gas and coal reserves will be gradually exhausted in the course of the 21<sup>st</sup> century. Therefore, a safe, sufficient, environmentally compatible and sustainable energy supply for the still quickly growing world population is urgently needed and among the key challenges for a peaceful and human future. Development and worldwide implementation of new sustainable energy systems, based on renewable or almost inexhaustible energy sources, requires much time and money. Only the rich industrialised countries are able to manage this big task in due time during the next several decades.

**Energy potential of biomass:** The world primary energy consumption of 9+ Gtoe in 2000 is expected to double within 50 years. A sustainable share of biomass of about 20% in a future energy mix seems to be achievable without energy plantations and exhaustion. This corresponds to ca. 3.6 Gtoe biomass per year or ca. 12% of the harvestable worldwide upgrowth of ca. 30 Gtoe of land biomass per year (1). A significant fraction of about one quarter of the potential biomass energy is expected to come from residual agricultural biomass, mainly cereal straw (wheat, rice, maize, barley). About half of the straw harvest is not needed and available as energy and carbon resource. These agricultural by-products are automatically cultivated and harvested together with the crops at marginal additional expenses. Biomass energy from special plantations will be twice as expensive.

**Benefits of biomass fuel:** Biomass is a renewable source of energy and carbon and will be still available, when fossil fuels become too expensive or exhausted. Combustion, either directly or via gasification, is CO<sub>2</sub>-neutral, thus mitigating global warming and potentially adverse climate changes.

Biomass is a domestic energy source in most countries and easily storable in contrast to wind energy and direct solar radiation. Biomass combustion and gasification technologies are known and can contribute to an early substitution of fossil fuels. Some technology improvements in view to flexibility, efficiency and environmental compatibility are needed.

**Economic aspects:** In the industrialised countries residual wood from forestry or residual agricultural biomass like cereal straw are usually more expensive (about 1.5 €cent/kWh(th)) than coal; the subsidised German hardcoal is an exception. At present, the biomass fuel costs are about comparable to crude oil on a heating value basis, but biomass is cheaper than the comfortable heating oil plus tax. Biomass *wastes* are available at zero or negative cost. The economic situation will inevitably change on the long term: with the dwindling resources of cheap fossil fuels, the competition will gradually disappear. In many developing countries with unemployment and low wages, biomass fuels are cheaper than fossil fuels and are frequently the main energy source with a high risk of exhaustion.

Compared to large fossil fired power stations, biomass fired facilities are smaller and less automated. Specific investment and operating costs are therefore higher. If the usual cost degression exponent of 0.7 is assumed, the specific investment costs for a ten times smaller biomass plant are twice as high. The economy problems of scale can be overcome by co-firing of small biofuel fractions into large fossil power plants. This would be without problems for natural wood, but co-firing of herbaceous biomass like straw, the large ash K- and Cl-content may impair the ash use and the flue gas cleaning procedures.

**Policy aspects:** In the Kyoto protocol, the international community has agreed, that a worldwide reduction of CO<sub>2</sub> emissions is desirable to fight global warming. The EU intends to double the contribution of biomass in their energy mix from about 3.5 to 8.5% until 2010 (2). In Germany, the "renewable energy law" (Erneuerbare Energie Gesetz, EEG since 2001) subsidises electric power production from biomass with 8.5 - 10 €cent per kWh (electric).

## PROPERTIES OF BIOMASS FUELS

Lignocellulose, e.g. wood or straw is the most abundant biomass, with cellulose fibres as the main constituent plus hemicellulose and lignin. Aside from the various shapes and bulk densities, a crude biomass classification can be based on increasing contents of intrinsic ash and heteroatoms N, S, P:

- **Wood** without bark is a relatively clean fuel with usually  $\leq 1\%$  ash.
- **Herbaceous biomass**, mainly straw, hay and strawlike biofuels from agriculture have a higher content of ash and heteroatoms, especially potassium and chlorine. These inorganic elements are needed as catalysts for the faster metabolism. The same rule of thumb applies to the even faster growing aquatic and marine biomass species and also for animals, which contain still higher ash and heteroatom contents than the plants. Cultivation of all fast growing species requires much expensive fertiliser or inorganic nutrients and is not well suited for bioenergy production.
- The combustible **organic** fraction in solid municipal or special **wastes** originates mainly from biomass, e.g. paper, cardboard or kitchen refuse; waste plastics are a minor part. A clean combustible fraction is sometimes recovered as a special refuse derived fuel (RDF) before the remainder receives an expensive treatment in a waste incineration facility, primarily for destruction of toxic materials and volume reduction; the large remaining ash fraction amounts to ca. 30%.

The technical complexity and expenses increase with increasing amounts of ash and heteroatoms. Combustion of clean wood is commercial practice. Combustion of cereal straw in amounts worth mentioning (1Mt/y) is practised only in Denmark. The largest contribution to herbaceous biomass combustion is sugar cane bagasse in Brazil; soluble inorganic constituents e.g. alkali and chlorine, are leached with the sugar liquor. All fast growing land biomass contains about an order of magnitude more ash and heteroatoms than wood. Straw and hay contain 5 - 10% ash, typical K- and Cl-contents are in the range of 1 and 0.5% respectively. A high K-content can reduce the ash softening point to below the combustion or gasification temperature. A sticky ash causes reactor slagging and fluid bed agglomeration. Desublimation of volatile potassium compounds involves severe corrosion and plugging risks in downstream gas ducts. Chlorine is released as HCl and causes corrosion, catalyst poisoning and promotes the formation of toxic polychlorinated "dioxins" and "furans" at unsuitable combustion conditions. The technology especially for the gasification of "dirty" herbaceous biofuels is not well developed. But the large arisings of agricultural residues corresponding to about 5% of the world primary energy consumption, justify even the development of a special gasifier.

## ANALYSIS OF AVAILABLE GASIFICATION TECHNOLOGY

Our analysis of gasification technology for solid biofuels (3,4) has been focussed on their suitability for straw. Straw is used here as a synonym for all herbaceous biomass with thin walls, which dries easily.

The following analysis confines to fundamental characteristics of the three well known and commercially available gasifier types: fixed bed, fluidised bed and entrained flow gasifiers. Pressurised versions up to several MPa are available for all types. The gasification rate increases with about the square root of the operating pressure. Most gasifiers operate in the autothermal mode with air or oxygen in the feedgas stream for heat generation via partial fuel combustion directly in the gasification reactor. The good heat transfer in fluidised bed gasifiers allows also allothermal operation, either with heaters installed directly in the bed or by circulation of the hot sand between an endothermic gasification reactor and a separate exothermal combustion reactor. This combined operation of twin fluid beds allows a separation of combustion gases in combination with continuous operation.

**Fixed bed gasifiers**, either updraft or downdraft, require mechanically stable fuel pieces of one or few cm size, to guarantee an unblocked passage of gas through the bed. Straw, hay or paper must be pelleted or briquetted: This is an expensive procedure, but if it is performed directly with a harvester, it could simplify all transport and storage operations later on. But some slagging risk will remain at the typical gasification temperatures of  $\approx 800^{\circ}\text{C}$ . An advantage, especially of updraft (counter-current) gasifiers, is the high cold gas efficiency connected with the low syngas exit temperature. But this advantage is obtained at the expense of a high tar content in the syngas. Efficient tar removal requires considerable technical efforts downstream. To summarise: Fixed bed gasifiers are well suited for stable wood pieces. There are many companies who offer various types of small or medium size fixed bed gasifiers for wood. Gasifiers specially designed for straw are not found in the market.

**Fluidised bed gasifiers** are operated either in the bubbling or the circulating mode, usually with quartz sand as bed material and fuel particles of few mm up to 1 or few cm size. For biomass feedstocks at least  $750^{\circ}\text{C}$  is required, to achieve a reasonably high gasification rate. The bed temperature must be kept below the ash softening temperature, since a sticky ash would glue together the bed particles and this agglomeration causes a breakdown of fluidisation. Fluidised sand beds are suited for woods, which have a high ash melting point, usually  $> 1000^{\circ}\text{C}$ . The ash melting points of cereal straw however can drop to even below  $700^{\circ}\text{C}$ .

On the other hand, a hot fluid bed allows a fast heat-up of large-surface biofuels, like hay or straw chops, to a definite temperature. The advantage of high heat transfer coefficients can also be used for fast pyrolysis. Contrary to gasification, the ash is not liberated during pyrolysis, but contained in the remaining char particles. At temperatures below  $600^{\circ}\text{C}$ , gasification reactions with  $\text{CO}_2$  or water vapours liberated during pyrolysis are rather slow.

In **entrained flow gasifiers** a pulverised solid fuel is mixed with a steam/oxygen stream and converted in a turbulent dust flame at high temperatures above  $1200^{\circ}\text{C}$  in a very short time of few seconds. At the high temperature, an almost tar-free syngas and a leach-resistant molten slag are produced. This is achieved at the expense of a higher percentage of energy converted into sensible heat, whose transformation into electric power is less efficient than for the chemical energy in the syngas.

To produce a biomass powder suitable for entrained flow gasification from feedstocks with long cellulose fibres, is a big and expensive technical effort. Additional expenses are connected with gasification at high pressure: The low bulk density of a fibrous biomass powder requires large voluminous pressure locks and much inert gas for periodic pressurisation and depressurisation. This complex technology is only applied at moderate pressures in combination with powders of higher bulk density.

**Conclusion:** None of the common gasifier types are directly suited for agricultural biomass feedstocks, either because of the low ash softening temperature or expensive preparation steps like pelleting or grinding. A desirable tar-free syngas can be produced only at higher temperatures in entrained flow gasifiers.

## SELECTED PROCESS CONCEPT

The concept for generation and utilisation of syngas is shown in fig. 1 and explained in the following. It is comparable with a biomass IGCC plant combined with synfuel or chemicals production prior to electric power generation. The individual steps in the multistep process are not independent from each other; all mutual interactions in the process train have been taken into consideration. Biomass conversion into the most valuable products promises the most economic biomass use: synfuels, chemicals, hydrogen, electric power or – in general – any special combination of these products.

A tar-free syngas can be produced in pressurised entrained flow gasifiers. Complex downstream facilities for an efficient syngas use are justified only in large units with the economic benefit of scale. The two energy forms in the syngas, chemical energy and sensible heat, require the combination of at least two different processes. If a production of synfuel is intended, co-production of electric power is an almost automatic consequence and being practised for example in the SVZ-facilities at "Black Pump", Germany (5). Unconverted rest gas from the methanol synthesis plant is used for efficient electricity generation in a downstream combined cycle system. Efficient syngas cleaning steps are required to protect the highly selective but sensitive Cu-catalyst for CH<sub>3</sub>OH synthesis; the purity of the rest gas is thus automatically suited for a downstream gas turbine.

Methanol is the most versatile synthesis product: (1) It can be used directly as a CHO-fuel, (2) it can be converted to CH-fuels in the MTG-process or (3) converted to olefins and aromats in the MTO and MTA-processes, to produce organic base chemicals for the chemical industry. (4) Methanol is a compact storage medium for H<sub>2</sub>:  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$ ; . Low pressure CH<sub>3</sub>OH-synthesis requires about 250°C and at least about 50 bar. Gasification slightly above this pressure obviates an expensive syngas compression step downstream. High pressures in general can considerably simplify the expensive syngas cleaning steps prior to synthesis.

Solid fuels are usually introduced into a pressurised gasifier through an alternating pressurised and depressurised lock. The periodic procedure is suited for high bulk density fuels and moderate pressures. At low bulk densities and higher pressures > 50 bar, e.g. for straw chops with ~ 50 kg/m<sup>3</sup>, the amount of lock gas can exceed the fuel weight. Investment and operating costs of the locks may become more expensive than gasification.

Liquids or slurries can easily be pumped into highly pressurised gasifiers. Such processes are used with coal(75%)/water(25%) slurries in entrained flow gasifier types developed by Texaco-Ruhrchemie/Ruhrkohle or Destec Energy Inc.. Various waste slurries are being successfully gasified in a special 130 MW(th) entrained flow gasifier at SVZ, Germany since more than 15 years (5, 12).

Dry lignocellulosic biomass is represented by the simplified formula C<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>, which is formally equivalent with a 50/50% mixture of carbon and water. This is already more water than in the coal/water slurries. Gasification of a pumpable biomass/water slurry is therefore undesirable in view to gasification efficiency. But if a relatively dry biomass can be converted to a pumpable liquor, a similar feed procedure can be feasible. Fast or flash pyrolysis of solid biomass is a special pyrolysis mode, developed to produce a high yield of liquid biofuel in a single step at atmospheric pressure. By rapid heating to 500°C in an inert atmosphere and rapid condensation of the vapours in one or few seconds, more than half of the biomass can be obtained as a liquid pyrolysis oil at the expense of a low char and gas yield (6). In this mode, the pyrolysis gas contains ≤ 10% of the biomass energy and will be consumed on-site for pyrolysis. The brittle char will be milled to a fine powder and suspended in the liquid pyrolysis oil. To a crude first approximation, the maximum char content in the char/pyrolysis oil slurry corresponds to the char bulk density. The specific heating value of the slurry is only slightly higher than the original biomass. The energy content in the slurry amounts up to 90% of the biomass energy and can be transported by rail to a large central gasification facility, as shown in fig. 2. The size of a regional pyrolysis facility in rural Europe is compatible with a maximum radius of about 25 km (ca. 2000 km<sup>2</sup>) for delivery of agricultural residues like straw by the farmers. An annual throughput of 90000 t of air-dried straw then corresponds to about half of the cereal straw harvest. Circa 20 - 30 of such pyrolysis plants can supply a large and more economic central gasifier with efficient but more sophisticated syngas cleaning and utilisation facilities downstream.

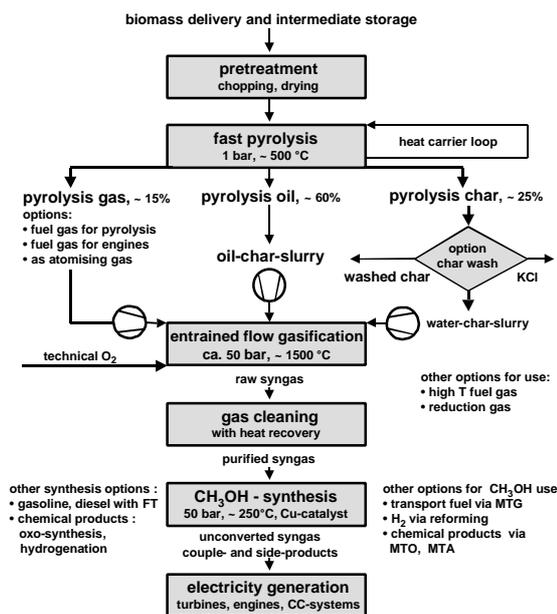


Fig. 1: Total concept for biomass gasification and syngas utilisation

## FAST PYROLYSIS OF BIOMASS

**Principles:** The aim of fast or flash pyrolysis is the production of much liquid pyrolysis oil and little char and gas (7,8). Typical yields from lignocellulose (daf) like wood or straw are 60 - 80% pyrolysis liquor and < 20% gas or char, depending on the feedstock and the operating conditions. High liquid yields are attained at special pyrolysis conditions: Rapid heating to the decomposition temperature and rapid condensation of the sensitive vapours. The heat-up time and especially the vapour residence time should not exceed one or few seconds, to prevent the secondary decomposition of large organic vapour molecules. Rapid heating is frequently obtained by mixing with an excess of hot sand in a fluidised bed. The optimum temperature window is a narrow range at about 500°C. At lower temperatures, the pyrolysis rates become too low and above, secondary vapour decomposition becomes too fast. Lignocellulosic biomass and the chars have a poor thermal conductivity and diffusivity. Thus only small, thin or fibrous particles are heated fast enough. A very crude estimate is the time required to heat the centre of a particle to the decomposition temperature. The characteristic length  $L$  (= volume/surface) of a biomass particle should be less than 0.5 mm. Water evaporation retards the heating at high moisture contents. Predrying the feed to a few % moisture content increases the liquid yield and the reactor throughput.

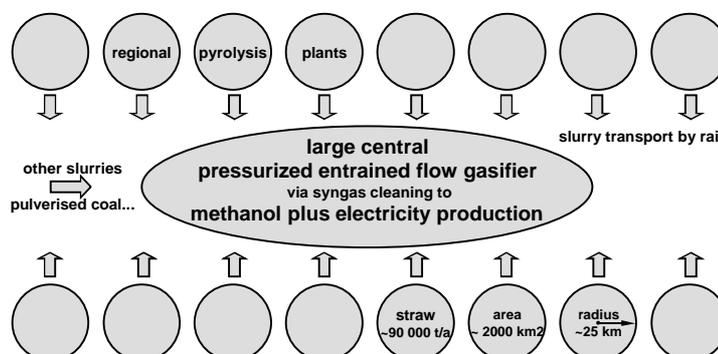


Fig. 2: Pyrolysis/gasification concept for syngas production from biomass

High liquid yields are attained at special pyrolysis conditions: Rapid heating to the decomposition temperature and rapid condensation of the sensitive vapours. The heat-up time and especially the vapour residence time should not exceed one or few seconds, to prevent the secondary decomposition of large organic vapour molecules. Rapid heating is frequently obtained by mixing with an excess of hot sand in a fluidised bed. The optimum temperature window is a narrow range at about 500°C. At lower temperatures, the pyrolysis rates become too low and above, secondary vapour decomposition becomes too fast. Lignocellulosic biomass and the chars have a poor thermal conductivity and diffusivity. Thus only small, thin or fibrous particles are heated fast enough. A very crude estimate is the time required to heat the centre of a particle to the decomposition temperature. The characteristic length  $L$  (= volume/surface) of a biomass particle should be less than 0.5 mm. Water evaporation retards the heating at high moisture contents. Predrying the feed to a few % moisture content increases the liquid yield and the reactor throughput.

**Enthalpy of pyrolysis:** The pyrolysis reactions of lignocellulose -simplified formula  $C_3(H_2O)_2$ - can be either exothermic or endothermic, depending on the reaction products, for example:



Biomass gasification reactions with CO<sub>2</sub> or water vapour are always endothermic:  $C_3(H_2O)_2 + H_2O \rightarrow 3CO + 3H_2$  ; ?H + 274 kJ/mol. From charcoal production it is known, that an exothermic pyrolysis contribution begins somewhat above 200°C and has a maximum at about 270°C (9). The self-sustained reaction causes a fast spontaneous temperature rise to 400°C or more and a release of much condensable organic vapours. Thus, even in a slow pyrolysis process, there is a fast section and the condensate composition is not much different from fast pyrolysis.

**Condensation of pyrolysis oil:** Prior to condensation, the small char particles entrained in the hot pyrolysis gas and vapour stream are usually retained with a cyclone. Since a slurry is prepared later, the char removal need not be very efficient. Even fine quartz sand particles from attrition in the pyrolyser bed can be tolerated; they contribute to the molten slag in the downstream gasifier. Direct use of pyrolysis oil as a liquid fuel for internal combustion engines or turbines, requires much more technical effort to obtain the desired purity. Expensive upgrading processes are being developed: catalytic hydrogenation and O<sub>2</sub>-removal as H<sub>2</sub>O using zeolite catalysts. Such expensive efforts are not needed for char/oil- slurry preparations for gasification.

Organic and water vapours are usually condensed simultaneously by quench condensation in a packed scrubber or jet scrubber, operated at temperatures below 100°C with the circulating and cooled pyrolysis condensate. A fine condensate mist usually escapes with the pyrolysis gas and must be recovered downstream in an electrostatic precipitator.

### PROPERTIES OF FAST PYROLYSIS PRODUCTS:

**Pyrolysis oil:** The term pyrolysis *oil*, pyrolytic *oil* or *bio-oil* refers only to the viscosity of usually 20 - 100 mPas comparable with edible oil, but is misleading in view to properties and composition. The

same product is termed raw tar in charcoal production. Essential properties and composition data are summarised in table 1.

**Table 1: Properties and composition of pyrolysis oil from lignocellulose**

Synonyms: pyroligneous oil, bio-oil, biocrude oil, raw tar, wood tar. The values are averages and depend on the lignocellulose feedstock and the pyrolysis and condensation conditions.

**Properties:** Density : ~ 1200 kg/m<sup>3</sup> pour point: ~ -20°C pH 2 – 3 (corrosive)  
 Viscosity: 20 - 100 mPas flash point: ~ 60 - 100°C

Dark brown; acrid smoky odour; irritates eyes and skin; harmful by inhalation

<b>Composition:</b>	percentage:	major constituents:
water	15 - 30	reaction water ~15% plus feed moisture
pyrolytic lignin	20 - 25	complex precipitate after water addition
organic acids	5 - 10	acetic acid ("wood vinegar")
aldehydes and hydroxyaldehydes	5 - 20	hydroxyacetaldehyde (about half)
ketones and hydroxyketones	0 - 10	acetone, hydroxyacetone
phenolics	20 - 30	substituted guajacols, vanillin etc.
methanol	~ 3	"wood spirit"

Pyrolysis oils are complex mixtures of over 400 CHO-compounds. These mixtures are obtained by quench condensation, form a homogenous solution and are not miscible with hydrocarbons but with water. The usual water content is 15 - 30%, the lower percentage corresponds to the reaction water formed during pyrolysis. Addition of an excess of water precipitates 20 - 25% of so-called pyrolytic lignin. After distillation almost half of the liquor remains as a solid residue. The high liquid density of ~ 1200 kg/m<sup>3</sup> is favourable for transport and storage.

The overall CHO-composition and the heating value of a pyrolysis oil does not differ much from the original feed, LHV 15 - 20 MJ/kg. Liquors with a high water content can be unstable in view to separation of a water phase and solid precipitates. The slow viscosity increase at room temperature accelerates at higher temperature and is an indication of the liquor instability in principle. Nonetheless, pyrolysis oils have been stored over years.

**Char:** Pyrolysis chars are rather brittle and are easily milled to a fine powder, suitable for suspension in pyrolysis oil, water or any organic solvent. Different from coal, the porosity of the char particles is high,  $e > 0,6$ ; lower heating values are in the 24 - 30 MJ/kg range. Chars still contain the whole ash, which is required for slag formation in the gasifier. The bulk density of the char powders is in the range of 200 - 500 kg/m<sup>3</sup>, depending on the feedstock and the pyrolysis conditions; the true char density is ca. 1400kg/m<sup>3</sup>.

**Gas:** Pyrolysis gas from fast pyrolysis is obtained downstream from the char/sand cyclone and the quench condenser. Major constituents are CO<sub>2</sub> and CO, a little CH<sub>4</sub> and higher hydrocarbons and negligible H<sub>2</sub>. The specific heating value per kg is low, about half that of the biomass.

**Char-slurries:** High char content in the slurries is desirable, since the pyrolysis oil yields from the same feedstock are frequently limited. Different from coal, the porosity of a pyrolysis char is much higher. The porous particles first soak a large volume of pyrolysis liquid until a surplus fills the interstitial space as a lubricant. As a crude first estimate it can be assumed, that the bulk density of a char powder can be maintained as a pumpable slurry, which can be atomised in the gasifier.

## REACTOR TYPES FOR FAST PYROLYSIS

**State of the art:** A number of different reactor types has been developed and investigated for fast biomass pyrolysis within the last 20 years. The various types are summarised in table 2:

**Technology analysis:** Most development work for fast pyrolysis of biomass is being focussed on reactor types using a solid heat carrier, which ensures a fast heat transfer. In a bubbling or circulating fluid bed the residence time spectrum of solids is similar to a continuously stirred tank reactor (CSTR) and about exponential. This results in larger reactor volumes compared with co-current flow and low axial mixing.

A fluidising gas is cooled down in the quench condenser together with the organic vapours. Only poor heat recovery can be realised during quench condensation and the additional gas stream causes additional heat loss. The fluidising gas can be saved by mechanical fluidisation.

**Table 2: Reactor types for fast pyrolysis of biomass**

Principle	Reactor type	Developer
<b>operation with solid heat carrier (e.g. sand):</b>		
heat carrier bed fluidised with gas	bubbling fluid bed	Dynamotive (CA), Wellmann (UK), Uni Waterloo (CA), RTI (CA)
	circulating fluid bed (twin bed version)	Ensyn (CA), CRES (GR), VTT (FI)
heat carrier bed fluidised mechanically	rotating cone (10)	BTG (NL), Uni Shenyang (China)
	twin screw (11)	FZK (Germany), (Lurgi)
<b>operation without heat carrier:</b>		
vacuum pyrolysis	heated wall	Pyrovac (CA), Uni Laval (CA)
ablative pyrolysis	vortex reactor	NREL (USA)
	rotating disc, blade, cylinder	Aston University (UK)

BTG Biotechnology Group, Enschede (NL); CRES Center for Renewable Energy Sources (GR); NREL National Renewable Energy Laboratory, Golden (USA); RTI Resource Transform Int. Ltd., Ontario (CA); VTT Technical Research Centre, Espoo (FI)

In both the rotating cone (10) and the twin screw reactor (11), the co-current flow of heat carrier and biomass results in a shorter char residence time and a smaller reactor volume. Crosscurrent removal of the pyrolysis vapours from a thin fluid sand layer as shown in fig. 3, results in a short vapour contact time with the bed sand.

**Twin screw reactor for fast pyrolysis:**

The twin screw reactor has been applied for almost 50 years for the fast pyrolysis of various oil products in large technical facilities (11). The principal scale-up problems are already solved and further development can concentrate on various biomass feedstocks, suitable preparation procedures and optimum pyrolysis and condensation conditions. Short straw chops or wood sawdust are potential feed shapes. The simplified drawing in fig. 4 shows the two co-rotating screws for fast plug-like co-current transport of solids along the axis combined with efficient radial mixing to improve heat transfer. Automatic self-cleaning of the two screws with intertwining flights ensures reliable operation.

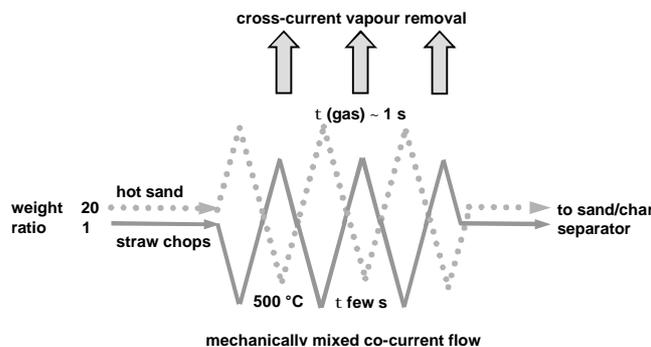


Fig. 3: Desirable characteristics for fast pyrolysis with a heat carrier

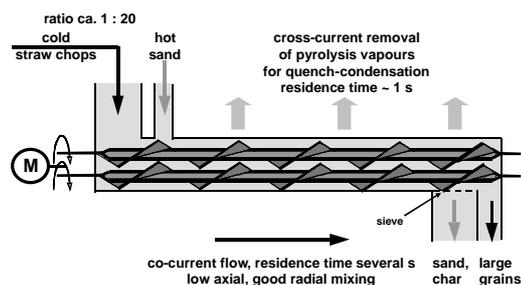


Fig. 4: Twin screw reactor for fast pyrolysis

**ENTRAINED FLOW GASIFICATION**

Large pressurised entrained flow gasifiers fired with pulverised coal or petcoke are being operated in several IGCC-demonstration plants. Practically all gasifier types are also compatible with a slurry feed and higher ash contents. Gasification temperatures and pressures are high, usually above 1200°C and 20 bar. Advantages are a tar-free syngas and a leach-resistant molten slag. The higher sensible heat fraction in the syngas is less desirable. Its transformation into electricity is less efficient than for the chemical energy. The efficiency of a coal fired power station and a combined cycle plant fired with natural gas of 40+ and 60-% respectively, gives an idea of the different efficiency.

At higher temperatures  $> 1000^{\circ}\text{C}$ , part of the heat in the hot syngas can be converted into more valuable chemical energy. This was first applied in the Destec Energy Inc. entrained flow gasifier. Char powder is dispersed in the hot raw syngas and gasified in endothermic reactions with  $\text{CO}_2$  or  $\text{H}_2\text{O}$ ; tar production during char gasification is negligible. Unreacted char must be recovered and recycled. The efforts for chemical quenching or chemical cooling will be weighed against a somewhat lower gasification temperature possible at higher gasification pressure.

The Texaco gasifier developed together with Ruhrkohle/Ruhrchemie, Oberhausen, Germany, has been particularly designed for a coal/water slurry. Because of the high operating temperatures  $> 1200^{\circ}\text{C}$ , a molten slag and a tar-free syngas with little  $\text{CH}_4$  is obtained. We have chosen the gasifier type developed 20 years ago by Deutsches Brennstoff Institut (DBI), Freiberg, now Babcock Borsig Power, BBP. A 130 MW gasifier of this type is being operated successfully in the SVZ-facilities, Black Pump, Germany since  $> 15$  years, with various feeds including slurries and a special lignite with high NaCl contamination. Straw with a high KCl-content poses similar problems. The particular characteristic of this gasifier depicted in fig. 5, is a thin cooling screen inside a cooler steel shell designed for high pressure. The viscosity of the molten slag layer draining down on the inner screen wall can be adjusted with the gasification temperature ( $\text{O}_2$ -flow), the screen cooling with pressurised water and also by suitable inorganic additives in the feed, which modify the slag composition. The gasifier is expected to be particularly flexible towards large variations of composition and amount of ash in herbaceous biomass.

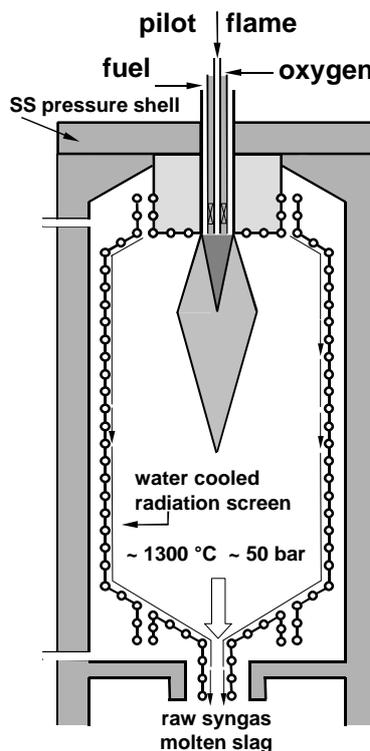


Fig. 5: Entrained flow gasifier for high pressure (with internal water cooled radiation screen, BBP-company, Freiberg, Germany)

## PREPARATORY INVESTIGATIONS

Many aspects of the new process concept are not satisfactorily covered in the literature and are being investigated experimentally. The main emphasis is put on cereal straw as a feedstock.

**Chaff-cutter:** Straw cutting is being investigated in a commercial 15 kW(el.) chaff-cutter with a maximum throughput of 1 te/h of air-dry straw. Long chops are recycled with the help of a sieve classifier; the suitable short chops are stored with the bulk density of  $50 - 100 \text{ kg/m}^3$  in bigbags for further treatment. The life time of the knives presents problems.

**Pyrolysis kinetics:** An expensive size reduction to below the wall thickness of cereal straw  $< 0.5 \text{ mm}$  is neither desirable nor necessary for pyrolysis in a fluid bed of hot sand. Single-walled chop sections of one or a few  $\text{cm}^2$  size are equivalent to flat plates with a characteristic length  $L = \text{volume/surface-ratio}$  of  $< 0.25 \text{ mm}$ . The thin chops are completely covered with about the same volume of hot sand (bulk density  $1500 \text{ kg/m}^3$ , size  $0.4 \text{ mm}$ , sand/straw-ratio  $\sim 20$ ) and are rapidly heated until a center plane temperature of almost  $300^{\circ}\text{C}$  is obtained. At this temperature, the internal reaction heat evolved by exothermic pyrolysis reactions additionally contributes to a fast temperature rise towards the desired final temperature of about  $500^{\circ}\text{C}$  and is accompanied by a fast release of pyrolysis vapours and gases with little delay.

Single walled cold and dry straw chops with  $10 - 100 \text{ mg}$  weight have been plunged from a lock into a vessel with known volume onto a moving sand bed at the bottom. The release rate of the vapours and gases has been followed by the pressure rise; typical examples are shown in fig. 6. At  $500^{\circ}\text{C}$ , the volume of pyrolysis vapours plus gases amounts to about  $0.5 \text{ m}^3$  (STP) per kg.

The measured release rates are within experimental error in accordance with the theory of unsteady-state heating of solid particles, using the Fourier-number  $\text{Fo} = \alpha \cdot t/L^2$  with  $\alpha = k/(d \cdot C)$  and the Biot-number  $\text{Bi} = h \cdot L/k$  and the following material properties: thermal conductivity  $k = 0.1 - 0.3 \text{ J/s} \cdot \text{m} \cdot \text{K}$  (across and with fibres); specific heat  $C \sim 1800 \text{ J/kg} \cdot \text{K}$ ;  $\rho \sim 1000 \text{ kg/m}^3$ ; heat transfer coefficient  $h$  ca.

100 - 200 J/m<sup>2</sup> • K • s; wall thickness 0.5 mm equivalent with L = 0.25 • 10<sup>-3</sup> m. From single-walled chops, the vapours are released within about a second, what is expected, if the surface resistance is assumed to dominate the heat transfer, at least until about 300°C centerplane temperature is reached and fast exothermic pyrolysis starts.

The compact stem node sections of straw are cylindrical, have a size of several mm and contribute ca. 5 - 10% to the total straw weight. Compared to a 0.5 mm thick straw wall with L = 0.25 mm, the characteristic length of a node section with a diameter = length = 5 mm is about 3 times larger. The corresponding heat up time increases with L<sup>2</sup> (t = Fo • L<sup>2</sup>/α) and is almost an order of magnitude longer. Because of the larger size, the Biot-number is Bi > 0.1 and both surface film and internal resistance to heat flow are important. The slower pyrolysis rate is evident in fig. 6. Squeezing of stem nodes is therefore an essential preparation step to eliminate the bottle neck for fast pyrolysis.

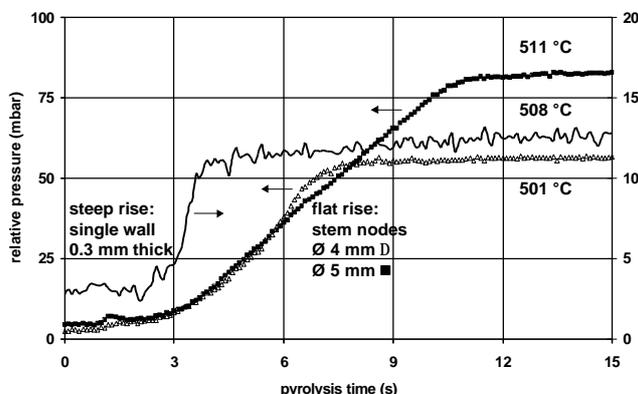


Fig. 6: Pressure rise during pyrolysis of wheat straw chops

A conclusion from these measurements is, that a few seconds residence time (≤ 10 s) in the pyrolysis reactor are sufficient. For a straw throughput of 100 000 te/y (ca. 4 kg/s) this corresponds to a small pyrolysis bed volume of only 0.5 m<sup>3</sup> sand plus chops and char. At operating temperature and pressure ca. 8 m<sup>3</sup>/s of vapours and gas are released. Depending on the bed sand size, the bed surface area should be larger than 4 m<sup>2</sup>, to prevent carryover of bed sand particles at higher superficial velocities. This results in a shallow bed height < 0.2 m. A sufficiently short vapour residence time of ≤ 1 s limits thermal vapour decomposition and is obtained, if the volume of the ducts and the char cyclone upstream from the quench condenser is kept at < 8 m<sup>3</sup>. The atmospheric pyrolysis reactor is a relatively small and not very expensive piece of equipment.

**Continuous fast pyrolysis facility:** A fast pyrolysis facility for continuous operation for a throughput of about 10 kg/h air-dry straw chops, chopped hay, sawdust or other feedstocks is under construction. The schematic is outlined in fig. 7. The pyrolyser volume is too small, to install the required heat exchange surfaces. Therefore the main characteristic is a hot sand loop with a bucket elevator and an external sand heater. The temperature drop of the sand stream in one pass is designed for ≤ 100°C.

**Slurry preparation:** Composition and characteristic properties of various pyrolysis oils and chars from wood and straw are being analysed. Ground pyrolysis chars with different particle sizes are suspended in increasing amounts in pyrolysis oils or water. Rheological and other properties e.g. pneumatic atomisation of the slurries are being investigated. A high char and solids content is desirable but must be compatible with transfer, storage without detergent stabilisation, sedimentation behaviour and atomisation in the gasifier. The viscosity increases steeply above a certain solids content; values above 1 or few Poiseuille (Pas) are not desirable. The viscosity decreases with the char particle size; the maximum size is limited to ca. 0.3 mm, larger sizes can plug the atomiser nozzles. Suitable slurries of 25%+ charcoal powder in raw tar from beechwood pyrolysis have been prepared.

**Test campaign:** The process concept will be verified at a larger scale of several MW(th) in a slagging entrained flow gasifier in the course of this year. The slurries will be prepared with wood pyrolysis products obtained from commercial charcoal production: raw tar LHV ~ 18.5 kJ/kg, density ~ 1.16 kg/m<sup>3</sup>, viscosity at 20°C ~

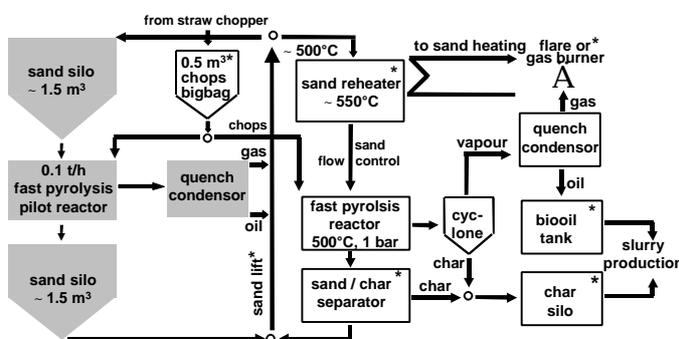


Fig. 7: Fast pyrolysis process development facilities  
 right: 10 kg/h sand loop facility for continuous operation,  
 shares common infrastructure (\*) with  
 left: 100 kg/h pilot pyrolyser for 1h operation

0.1 Pas; charcoal powder bulk density 400 - 200 (straw) kg/m<sup>3</sup>, LHV 25 - 30 kJ/kg, true density ~ 1400 kg/m<sup>3</sup>, grain porosity  $\epsilon = 0.6 - 0.8$ .

## CONCLUSION AND OUTLOOK

The new two-step pyrolysis/gasification process is flexible and suited also for dry herbaceous biomass feedstocks like straw, which have a higher ash, potassium and chlorine content than wood. The biomass is first liquefied by fast pyrolysis at 500°C and atmospheric pressure. The size of the pyrolysis facilities corresponds to the scheduled in-time delivery by the *regional* farmers. A dense slurry is prepared from the condensable pyrolysis oil and the solid char, which contains up to 90% of the original biomass energy. The slurries are easily pumped and compactly stored in tanks and are transported by rail to a large central plant for gasification and efficient syngas use. A slagging entrained flow gasifier operating at high temperature and pressure produces a tar-free syngas, simplifies syngas cleaning and obviates intermediate syngas compression prior to synthesis. This gasifier type can be designed to operate with a number of different gaseous, liquid or slurry fuels and also with pulverised coal. The large flexibility eases market introduction for small biofuel shares.

Though all process steps are known in principle, some need improvements and modification to guarantee an optimum integration into the total process sequence. Key process steps in this direction are development and scale-up of fast pyrolysis technology, slurry preparation and handling and the development of suitable slurry atomisation procedures in the gasifier. All of the theoretical and experimental aspects of biomass gasification are covered by a larger working group at the Karlsruhe research center.

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