GASIFICATION OF BIOMASS IN A CIRCULATING FLUIDIZED BED WITH SPECIAL RESPECT TO TAR REDUCTION

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ABSTRACT: Circulating Fluidized Bed Gasification (CFBG) combined with Block Heat and Power Plant (BHPP) can lead to economically attractive solutions for the utilization of biomass for energy (electricity and heat) production. However, tar content in the produced gas should be kept below a limit value in the range of 50-100 mg/Nm^3 for internal combustion engine applications. The development of a reliable, efficient and economically feasible gas cleaning system for biomass gasification is one of the major tasks of the R&D work being carried out at Fraunhofer UMSICHT sponsored by the German Federal Minister for Nutrition, Agriculture, and Forests (FKZ 94 NR 140F and 98 NR 075).
Two main different strategies for tar yield reduction based on the hot gas catalytic conversion of tar have been investigated: the use of in-bed additives in the CFB and the use of a secondary catalytic tar cracker/reformer after the gasifier. Different bed materials in the gasifier as well as solids/catalysts (including monolithic Ni-catalysts) in the secondary reactor have been tested. All the experimental work has been carried out at pilot scale (0,5 MW).
The combination of the in-bed use of solids with catalytic activity in the CFB-gasifer and a catalytic reformer after the gasifier using Ni-monolith catalysts seems to be a promising solution for the tar problem in CFB biomass gasification and clearly improves the efficiency of the global process (see also poster V8.80).

1 INTRODUCTION

In the field of energy recovery from biomass, technologies are needed which enable efficient conversion at profitable costs. Biomass gasification in circulating fluidized bed combined with internal combustion engines for electricity and heat production (figure 1) is a reliable and efficient technology which can be an attractive alternative to combustion processes [1, 2].
The air blown biomass gasification process generates a gas mixture with a heating value between 3 and 6 MJ/Nm^3 depending on the operation conditions. Unfortunately, a small fraction of the fuel is converted into tar, a complex mixture of condensable hydrocarbons, mainly naphthalene and other polycyclic aromatic hydrocarbons (PAHs). Since tars will impact downstream process equipment causing fouling and corrosion, the tar content in the produced gas must be kept below a limit value in the range of 50-100 mg/Nm^3 for internal combustion engine applications [3]. Tars and the necessary technology for tar elimination has caused a delay in commercialising this type of processes.
The development of a reliable, efficient and economically feasible gas cleaning system for biomass gasification is one of the major tasks of the R&D work being carried out at Fraunhofer UMSICHT. The most suitable strategy for elimination of the tar components of the gas is considered to be hot gas catalytic conversion [4, 5]. The use of in-bed dolomite in the gasifier reduce the tar yield and increase the efficiency of the gasification process [6, 7]. Also steam reforming Ni-based catalysts have demonstrated their usefulness in biomass gasification gas upgrading [4, 5, 8, 9, 10]. Two main different strategies for tar yield reduction based on the hot gas catalytic conversion of tar have been investigated: the use of in-bed additives in the CFB and the use of a secondary catalytic tar cracker/reformer after the gasifier. Different bed materials in the gasifier as well as solids/catalysts (including monolithic Ni-catalysts) in the secondary reactor have been tested. All the experimental work has been carried out at pilot scale (0,5 MW).
The pilot plant used for process development is given schematically by figure 1. The biomass is gasified in the first stage in an air-blown atmospheric circulating fluidized bed (CFB). In the secondary gas cleaning stage, the raw gas is upgraded (tar compounds are catalytically converted). After cooling and dedusting the produced fuel gas is sent to a block heat and power plant (BHPP) with internal combustion engine for heat and power production.

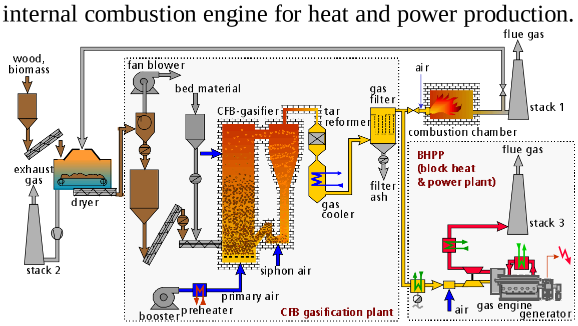

Figure 1: Scheme of the pilot plant at Fraunhofer UMSICHT (0,5 MW): CFB Biomass Gasifier (including catalytic hot gas cleaning) combined with Block Heat and Power Plant.

2 EXPERIMENTAL

The pilot plant is designed for a fuel consumption of 80-100 kg/h dry weight, which corresponds to a heat capacity of 400-500 kW (figure 1). The technical and operational data of the CFB-gasifier is shown in table 1. The CFB reactor is constructed with heat resistant stainless steel that allows operation temperatures up to 1000°C. The produced raw gas at the gasifier exit is let through a catalytic reforming stage and then cooled down indirectly with air in a pipe heat exchanger. Remaining particulate content is removed by conventional filter technology, i.e. cyclone and bag filter at temperatures below 150°C. The produced gas can be burned in a combustion chamber with a natural gas incinerator or fed to a Block Heat and Power Plant with internal combustion gas engine which is the desirable use of the gas in future commercial plants. The separate housing of the test rig includes a 10 m^3 hopper for biomass fuel. The hopper can be fed pneumatically from a continuously operating dryer which also enables the use of biomass with high moisture content.

Table 1: Technical and operational data of the CFB gasifier.

gasifier height		8 m
gasifier diameter		0,31 m
gasification temperature		850 - 950 °C
wood fuel consumption		60-125 kg/h
typical air ratio		0,25 -0,45
superficial gas velocity	(inlet)	1,3-1,9 m/s
	(exit)	2,4-4,0 m/s

Two different catalytic reactors for hot gas upgrading have been used in the experimental tests:

A *'small-scale' catalytic reactor* which is located in a slip-stream was used in the preliminary tests. Only around 1% of the raw gas coming out from the gasifier passes the monolith in this case (0,4 - 3,8 Nm^3/h). It is externally electrically heated and the temperature is measured at the inlet and exit of the monolith and also at the inlet and exit of the reactor. The reactor has a total height of about 1,5 m and a circular cross-section with an internal diameter of 8 cm.

Data gained in the tests with the 'small-scale' catalytic reactor were used to develop, construct and install a *'full-scale' catalytic reactor* for upgrading of the gasification gas using Ni-monolith catalysts. This reactor has a square external section of 1 x 1 m and a height of about 4,5 m. All the gas coming out from the gasifier is upgraded in this reactor (170 - 260 Nm^3/h). The temperature is measured in different points at the inlet and at the exit of each layer of catalyst.

In order to obtain the maximum amount of data, the pilot plant is equipped with a multitude of measuring instruments for pressure, temperature, gas flows, and also on-line gas analysis for CO, H_2, CO_2, H_2O and O_2. All process controls as well as all on-line measurements and data recording are made by a computer based control system.

Wood chips with a average particle size of 5-10 mm and maximum particle size of 15 mm have been used in the experiments as feedstock. Its proximate and ultimate analysis are given in table 2.

Table 2: Characterisation of the wood fuel used.

Proximate analysis [Mass-%]	moisture (raw)	(range: 7-29) 9.5
	volatile (dry)	77.2
	ash (dry)	0.7
Ultimate analysis (daf) [Mass-%]	C	49.2
	H	5.9
	O	44.8
	S + N	0.1
LHV (daf) [kJ/kg]		16 600

Tar measurements are made by off-line sampling with gas absorption in cold traps with ice, using acetone as solvent, followed by GC-MS analysis. The values gained by this method are in very good agreement with results from other methods such as impinger cold trapping with DCM-solvent or semi-online by FID-analyzer. Since there is no standard definition of tar [2], in this paper, tar is considered as naphthalene and PAH compounds heavier than naphthalene, i.e. compounds which are expected to cause problems to the engine operation.

3 RESULTS

Aiming at an improved operation of the gasifier, the experiences optimizing the operation of the CFB-gasifier, using silica sand as bed material, conclude that they seem to be not enough for a significant decrease of tar production below the level required for IC-engine operation. Therefore, the use of solids with catalytic activity for tar destruction seems to be useful. Following this conclusion two different strategies have been investigated: use of minerals with catalytic activity for tar destruction as bed material in the CFB and the use of a secondary tar cracker after the CFB gasifier testing different solids and catalysts.

In-bed use of solids with catalytic activity.

Silica sand, dolomite and other minerals with catalytic activity for heavy tar elimination have been used as bed materials in the CFB biomass gasifier. The use of some of these minerals generates a gas with a significantly lower tar content (figure 2). Usual tar load at the exit of other CFB-gasifiers is about 10 g/Nm^3 [3] and the levels shown in figure 2 are comparatively very low thus.

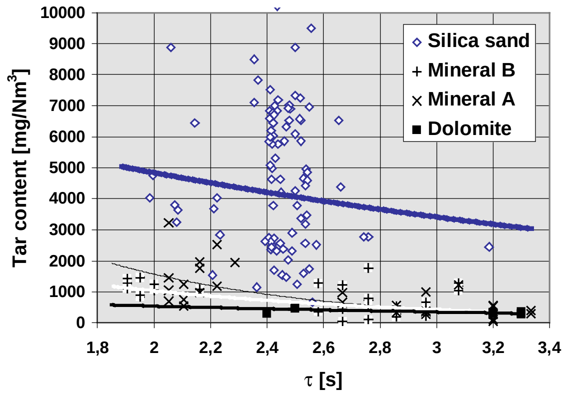

Figure 2: Tar content in the gas at the exit of the CFB biomass gasifier vs. residence time for different bed materials (T=880-930°C; 10-20 wt% biomass moisture content).

The heating value of the produced gas, the gas yield and the thermal efficiency of the gasifier is shown in figure 3. The use of bed materials with catalytic activity for tar destruction increases the heating value of the gas since the energy content of tars is high (for Naphthalene 5,2 MJ/mol). Therefore the higher the tar content reduction is, the higher is this increase in the energy content of the gas. Also the gas yield increases as a result of the increased tar and carbon conversions when these materials are used. A similar increase of the heating value and gas yield by in-bed use of dolomite has been previously reported [6, 7]. Therefore, as consequence of the increase of the heating value of the gas and gas yield, the thermal efficiency of the process is also improved (figure 3).

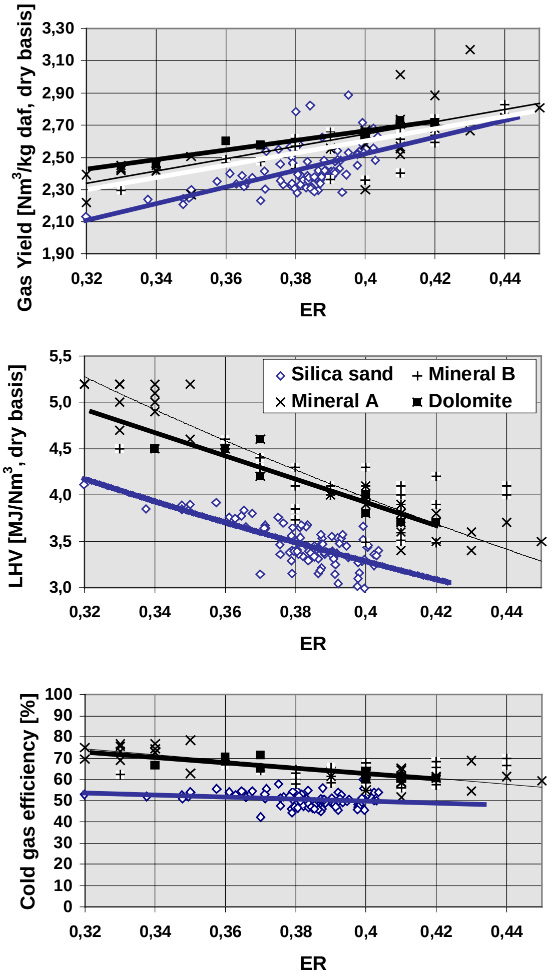

Figure 3: Gas yield, heating value of the gas and thermal efficiency at the exit of the CFB gasifier vs. the equivalence ratio (ER) for different bed materials. (T=880-930°C; 10-20 wt % biomass moisture content).

Although the use of these materials in CFB reduces the tar content and increases the efficiency of the process, residual tar contents are higher than the target value of 50-100 mg/Nm^3, and therefore the produced gas is not clean enough to be used in a gas engine. The use of a secondary hot gas cleaning catalytic reactor is necessary.

Tar conversion in a secondary 'slip-flow' reactor.

Different materials/catalysts have been tested for tar conversion in a downstream catalytic reactor located in a slip-flow from the main gas stream at the gasifier exit.

In gasification gas, the main gas reactants are in large excess to tar compounds. So the changes in the content of the main gas components are small compared to changes in tar compounds contents in tar conversion reactions. Therefore the kinetic equation for the conversion of tars can be simplified to [5, 8, 11, 12]:

$$(-r_{tar}) = k_{app}\, C_{tar}^{\,n}$$

The decomposition rate of tar can be assumed to be first order [5, 13]. If plug flow reaction model is considered and gas expansion, radial and axial diffusion are neglected, the apparent kinetic constant can be calculated using the integrated form according to the equation:

$$k_{app} = -\ln(1-X_{tar}) / \tau$$

where X_{tar} is the tar conversion and τ is the gas residence time (catalyst bed volume divided by gas rate). These so calculated apparent first order kinetic constants (k_{app}), could be used as an index of the catalytic activity of each solid/catalyst tested for comparison purposes [11].

The kinetic constant for naphthalene conversion for each solid calculated in this way are shown in figure 4. The steam-reforming Ni-catalyst G117, the Dologran dolomite and the Ni-monolithic catalysts show the highest activity for tar destruction of all the materials tested. The high activity of Dologran dolomite is caused by its particle size. This dolomite is provided in form of pellets or conglomerates of smaller particles. Therefore internal diffusions resistance is low and the catalytic activity is quite high [12].

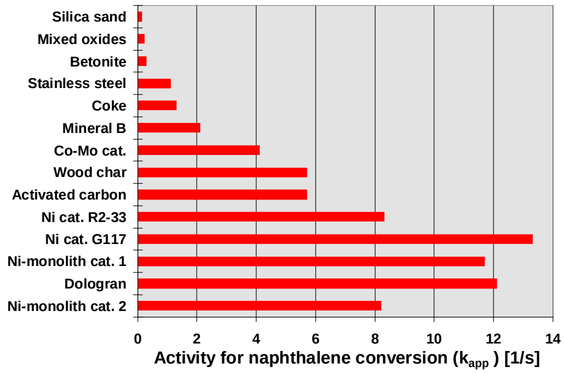

Figure 4: Activity for naphthalene conversion using different solids / catalysts in the secondary fixed bed reactor (located in a slip-flow; T=880-900°C).

Tar removal using the monolithic Ni-catalyst.

Ni-based catalysts have shown a high activity for tar conversion (figure 4). In order to be able to cope with the high dust content in the gas at the exit of the CFB, these catalyst should be used in shape of monoliths [5]. Almost total tar conversion could be achieved with these catalysts for residence times (inside the monolith channels) higher than 0,3 - 0,4 seconds (depending on the catalyst) at 900°C (figure 5).

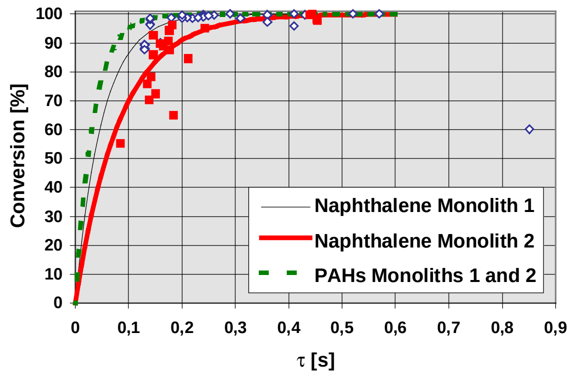

Figure 5: Tar conversion vs. residence time in the catalytic reactor using Ni-monolith catalysts (PAHs = compounds heavier than naphthalene; T=880-920°C).

As a result of the reactions on the catalyst some changes could be observed in the gas composition which are shown in figure 6. The hydrogen and carbon monoxide contents increase while the methane, steam and carbon dioxide contents decrease, approaching the equilibrium values, as the residence time increases, mainly due to the steam and dry reforming reactions. This behaviour is in good agreement with previously published results [4, 5, 8, 14, 15]. For the same reason the produced gas rate increases in the reactor, while the heating value of the gas increases due to the reforming of tar compounds [15].

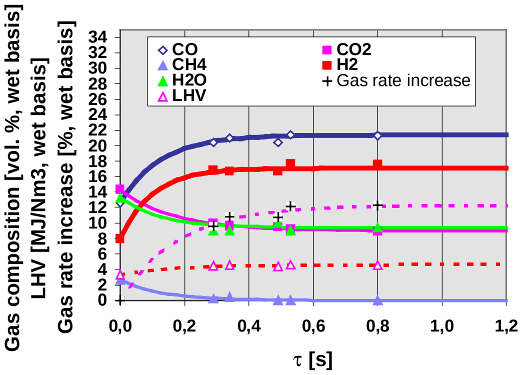

Figure 6: Gas composition, heating value and gas rate increase at the exit of the catalytic reactor vs. residence time (Ni-monolith 1; CFB with sand; ER=0,35-0,36, T=890-910°C, 9-12 wt % biomass moisture).

The apparent activation energies for the conversion of different tar compounds on Ni-monoliths catalysts have been estimated using a first order kinetic model. Temperatures between 790°C and 950°C have been used. Results are shown in table 3. These values are in good agreement with some published results for 'real' tar (coming from CFB gasifiers) reforming on Ni-catalysts [5, 8, 9, 10].

Table 3: Apparent activation energies for the conversion of different tar compounds using Ni-monolith catalysts.

	Methane	Benzene	Toluene	Naphthalene	PAHs
$E_{a,app}$ [kJ/mol]	220	120	110	70	50

PAHs = compounds heavier than naphthalene

CONCLUSIONS

The combination of the in-bed use of solids with catalytic activity in the CFB gasifer and a catalytic reformer after the gasifier using Ni-monolith catalysts seems to be a promising solution for the tar problem in CFB biomass gasification and clearly improves the efficiency of the global process.

In continuous tests runs of more than 150 h no deactivation was observed using monolithic Ni-catalysts. The whole process given by figure 1 was in operation without any problems (see also reference 2).

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