

Paper II

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A parametric modelling study for pressurised steam/O₂-blown fluidised-bed gasification of wood with catalytic reforming

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ABSTRACT

A model for pressurised steam/O₂-blown fluidised-bed gasification of biomass with catalytic reforming of hydrocarbons and tars was developed using Aspen Plus simulation software. Seven main blocks were used to model the fluidised-bed gasifier and two for the catalytic reformer. Modelling blocks were complemented with FORTRAN subroutines to simulate the observed non-equilibrium behaviour of the process. The model was fitted with experimental data derived from a 0.5 MW scale test rig operated with crushed wood pellets and forest residues and was shown to be capable of predicting product gas composition from gasification of clean wood. A parametric analysis indicated that a significant improvement in the syngas efficiency could be achieved by rising the filtration temperature and reformer conversions. Other improvement possibilities include fuel drying and lower reforming temperature.

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1. Introduction

1.1. Biomass gasification

Increasing energy prices, depleting fossil resources and growing awareness about human-induced environmental issues have provoked major interest towards renewable sources of energy. Gasification of biomass enables the advanced utilisation of these resources and has significant commercial and environmental potential in the production of green chemicals, synthetic fuels and electricity.

Gasification is a thermochemical conversion process that turns carbonaceous feedstocks into a gas mixture rich in carbon monoxide and hydrogen, called product gas or synthesis gas. Other major compounds include carbon dioxide, nitrogen, water, methane and a rich spectrum of

hydrocarbons. A general objective of gasification is to maximise the yields of gaseous products and minimise the amounts of condensable hydrocarbons and unreacted char. The exact composition of product gas depends on the type of process feeds, their feed ratios, process parameters and the type of gasification reactor used.

In contrast to coal gasification, where char gasification reactions determine the overall yield, in biomass gasification the devolatilisation stage and secondary reactions of primary pyrolysis products play the major role [1].

1.2. Steam/O₂-blown fluidised-bed gasification

The main factors that influence the heating value of product gas are the selection of the heat transportation method and oxygen-carrier medium. Low heating value gas is produced

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with autothermal reactors using air as the oxidising agent, whereas medium heating value gas can be generated with indirectly heated reactors or by using oxygen instead of air in an autothermal reactor.

According to Ref. [2] synthesis gas produced by oxygen gasification and reforming is suitable for all known end uses, whereas synthesis gas produced by air gasification is best suited for power applications and for syntheses that exclude recycling loops, namely hydrogen production with pressure swing adsorption (PSA) separation and once-through Fischer-Tropsch synthesis. Once-through processes also exist for methanol (CH_3OH) and synthetic natural gas (SNG), but they can not be considered promising when using air as an oxidant.

1.3. Modelling of fluidised-bed gasification of biomass

The objective of process modelling is to construct a mathematical description of a process that can be used to predict reactor temperature and outlet concentrations from inlet flows and operating conditions. A model that fits well to the experimental data can help to reveal major trends in a multi-variable system and be a great comfort when an engineer is faced with scaling-up a reactor to produce the full-scale design [3]. A suitable model also permits more efficient control of the reactor and offers a safe way to simulate reactor behaviour in continuous and transient conditions [4].

Numerous mathematical models for fluidised-bed gasification of biomass have been developed and reported in the literature. Many of the models are based on theories about fluidisation hydrodynamics, coupled with kinetic schemes for the heterogeneous and homogeneous processes occurring inside the gasifier [5]. These can include such fuel-related phenomena as drying, volatilisation, partial combustion with O_2 , char gasification with H_2O and CO_2 as well as secondary reactions of condensable hydrocarbons. Taking all these phenomena into account requires the utilisation of numerous empirical correlations and hypotheses about chemical and physical phenomena occurring in different phases (bubble and emulsion) of the fluidised-bed, adding to the mathematical complexity of the model [6]. A large number of these dynamic parameters are also unknown and very difficult to measure, which makes product gas composition estimates often exceedingly difficult for kinetic models [7].

Another group of gasification models is based on the idea of chemical equilibrium. In this approach, the complex kinetics can be disregarded by assuming that gasification reactions occur fast enough for them to reach equilibrium at the reactor outlet. However, equilibrium models fail to predict some of the most important characteristics of fluidised-bed gasification. These include kinetically and hydrodynamically controlled phenomena such as unconverted solid carbon and the formation of gaseous hydrocarbons [6,8,9]. To eliminate these problems, equilibrium models are usually adjusted using empirical parameters or correlations to match measured data from the gasification reactors.

Despite their limitations, equilibrium models have been widely published in the literature. A number of simulation models have been proposed for gasification of coal, while the work done for gasification of biomass has been more limited [5,9]. Especially models for steam/ O_2 -blown fluidised-bed

gasification of biomass with reforming of tars are not abundant among scientific literature. However, very similar features pertain to both air and steam/ O_2 -blown fluidised-bed gasification of biomass and reviewing the recent development in the field of air gasification modelling can thus be considered justified.

It has been recently suggested in Ref. [10] that a gasifier could be modelled by dividing it into separate blocks, which enable the modelling of drying, pyrolysis, partial oxidation and gasification reactions. The final composition of the syngas is formed in a Gibbs reactor under restricted conditions and additional block is used to separate solids entrained in the gas. The validation of this model was performed for three test runs and the results were reported to be in good agreement with experimental data, with the exception of overpredicted methane. Any heavier hydrocarbons were not considered in the model.

The approach of Ref. [11] was to divide the gasifier into four distinctive parts, namely decomposition of the feed, volatile reactions, char gasification and gas solid separation. In addition, the effects of hydrodynamic parameters and reaction kinetics pertaining to biomass gasification in fluidised-beds were simulated with FORTRAN codes. This slightly more complex approach did not seem to result in much improved predictions, probably due to the absence of higher hydrocarbons and tars in the model.

In several modelling studies, the formation of higher hydrocarbons and tars is often completely neglected. This exclusion is usually defended by pointing out to the very low concentrations of tars in the product gas, suggesting that even if tars are a factor to consider in the plant operation, they do not play an important role in the modelling of biomass gasification.

This assumption seems to be in contrast with the experiences accumulated during our modelling work. It is true that the volume concentrations of tar and higher hydrocarbons are very low in comparison with the main gas components like H_2 , CO , CO_2 , H_2O and even CH_4 , but this should not lead to a conclusion that the modelling of tars is purposeless. The tar components generally have very high molar masses in comparison to the main gas components, which greatly increases their importance. It seems that without the inclusion of tar and hydrocarbon formation in a biomass gasification model, an accurate prediction of product gas composition is not likely to succeed.

1.4. Experimental work

In this work, an equilibrium model for pressurised steam/ O_2 -blown fluidised-bed gasification of biomass with catalytic reforming is developed using Aspen Plus simulation software. The model is fitted with experimental data from gasification tests using crushed wood pellets and forest residues. The tests were conducted with a 0.5 MW scale process development unit (PDU) in a project titled "Development of Ultra-Clean Gas Technologies for Biomass Gasification". The project was aimed for the development of innovative biomass gasification and gas cleaning technologies for the production of ultra-clean synthesis gas. It was carried out from 2004 to 2007 and co-ordinated by the Technical Research Centre of Finland

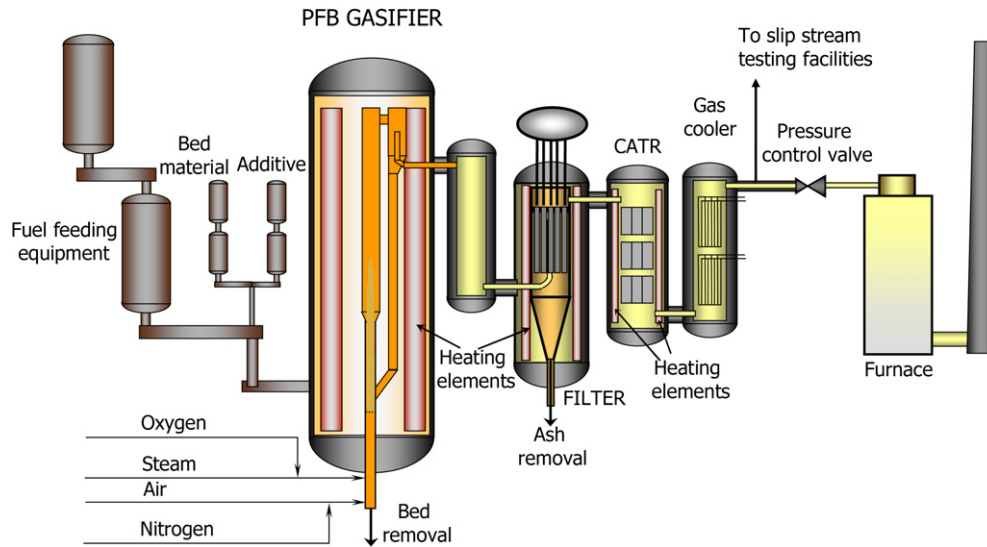


Fig. 1 – The pressurised fluidised-bed gasification test rig.

(VTT). The results of these gasification experiments are published and summarised in Ref. [2]. A brief description of the process and the gasification experiments are also given in the following paragraphs.

1.5. Description of the experimental equipment and arrangement

A 0.5 MW test rig, located at VTT, was taken into operation at the end of 2006. The heart of the gasification test rig is a fluidised-bed reactor, mounted inside of an electrically heated oven to compensate heat losses. The oven is thermally insulated and placed inside of a pressure vessel that contains a gasifier, a cyclone separator and a return leg. The vessel is approximately 11 m high with a diameter of 1.6 m.

The product gas flows from the gasifier's outlet to another pressure vessel that reserves space for a pre-reformer and contains a gas cooler and a hot-gas filter. The actual reformer is situated downstream from the filtration unit and is constructed in a way that allows modifications in the inner vessel for the study of different kinds of catalysts. After the reformer, product gas is cooled, depressurised and eventually destroyed in a small boiler.

It is possible to separate small sidestreams from the process for various additional research purposes. The test rig is also equipped with a wide variety of process measurements, all collected to a data logger and processed by a microcomputer. An illustration of the test rig is presented in Fig. 1.

2. Materials and methods

2.1. Description of the gasification experiments

The data that was used to fit the model parameters consists of 5 individual operating variable sets, each referring to a specific array of process conditions. During the set point periods, feed rates of fuel, oxygen and steam were kept as constant as

possible. Measurement lengths lasted several hours for each set point, while process data was recorded at few minutes intervals. Discharged cyclone and filter fines as well as bottom ashes were collected, weighed and sampled at the set points. Carbon conversion η_C was calculated based on these measurements according to the following equation:

$$\eta_C = 1 - \frac{C_{\text{ash}}}{C_{\text{fuel}}}, \quad (1)$$

where C_{ash} represents elemental carbon in the ash and C_{fuel} elemental carbon in the fuel.

After a test run, material balances for individual set points were calculated based on the average values of the data. Hydrogen and carbon balances were used to calculate water vapour content and raw gas flow rate, as they are difficult to measure with the same accuracy as the other parameters.

A summary of the key operational parameters at different set points is shown in Table 1. Set points 1, 2, 3 and 5 were run with crushed wood pellets while forest residues were used at set point 4. Ultimate and proximate analyses of the feedstocks are presented in Table 2. The wood pellets were made from dry sawmill residues originating from pine wood (*Pinus sylvestris*). The forest residues (i.e. logging residues) were from eastern Finland from Norway spruce (*Picea abies*) dominated forests. Forest residues were branches and tops of trees from final cutting area. The residues were collected in summer 2006, dried in a storage dryer to circa 10% moisture using warm air at 30 °C and crushed to below 10 mm screen. Then the feedstock was packed in 1 m³ air tight super bags.

Wood pellets were crushed to make particle size closer to that of realistic wood fuels. Crushed peat pellets were also used as fuel during some of the experiments. This data, however, is not included in this work. Sand and limestone were fed into the gasifier along with the feedstock in order to maintain a stable bed.

The composition of the product gas was measured before the filter and after the reformer with continuous gas analysers and gas chromatographs. Product gas compositions related to

Table 1 – Process parameters related to set point conditions.

Set point	1	2	3	4	5
Feedstock	Wood chips	Wood chips	Wood chips	Forest residues	Wood chips
Fuel moisture, wt%	6.9	6.9	6.9	10.4	7.4
Pressure, MPa	0.25	0.25	0.25	0.25	0.25
Oxygen to fuel ratio, kg kg ⁻¹	0.31	0.37	0.42	0.37	0.46
Steam to fuel ratio, kg kg ⁻¹	0.50	0.54	0.54	0.54	0.75
Gasifier freeboard temp, °C	823	838	886	830	868
Reformer outlet temp, °C	856	864	867	866	870
Carbon conversion, %	98.86	99.39	99.80	98.72	97.13

For the oxygen to fuel ratio and steam to fuel ratio the fuel is considered as dry and ash free.

each set point are presented in Table 3. The high amounts of nitrogen in the gas can be explained by nitrogen purges that were used in the fuel feeding system and measurement leads to seal off leakages and to keep the equipment operational. However, the effect of these nitrogen purges to product gas composition can be ignored and removed computationally if wanted, as the dilution effect of the purges is much smaller in commercial-scale gasifiers than in a PDU-scale test rig.

2.2. Utilisation of experimental data in the model

The limitations of equilibrium models, as discussed in Section 1.3, were dealt with by fitting selected parameters to experimental data. The intention was to first construct a simple and generic model for gasification of biomass that could then be fitted to match a more specific gasifier and fuel type, using easily measurable empirical correlations.

For this reason the incorporation of such parameters as feedstock particle size and reactor geometry were decided to be ignored, although their effects are indirectly embedded in

the empiric correlations. Also, the inclusion of these parameters into the model's generic framework would have required much more complex model, still not necessarily able to generate more accurate predictions.

2.3. Model description

The core blocks of the model are the equilibrium blocks 5 and 9 (RGibbs), where major parts of feeds are converted to equilibrium products, based on the minimisation of Gibbs-free energy. Almost all the other blocks of the model are used to simulate phenomena that are observed not to comply with the rules of chemical equilibrium. The division of the model to separate blocks could have been conducted in many ways.

Table 2 – Proximate and ultimate analyses of the feedstock. For the calculation of the higher heating value (HHV) see Section 2.5.2.

Set point	1,2,3	4	5
Fuel type	Wood chips	Forest residues	Wood chips
Proximate analysis, wt% d.b.:			
Fixed carbon	16.5	20.6	16.7
Volatile matter	83.3	76.8	82.9
Ash	0.2	2.6	0.4
Ultimate analysis, wt% d.b.:			
C	50.7	51.3	51.1
H	6.2	6.1	6.1
N	0.1	0.5	0.1
Cl	0	0	0
S	0.01	0.05	0.01
O	42.8	39.5	42.3
Ash	0.2	2.6	0.4
Moisture content, wt-%	6.9	10.4	7.4
HHV	20.58	20.96	20.64

wt% d.b. = weight percent dry basis.

Table 3 – Product gas compositions after the gasifier (Raw Gas) and after the reformer (Clean Gas) at the set points.

Wet gas composition, vol-%					
Set point	1	2	3	4	5
Raw gas					
CO	0.13	0.12	0.12	0.11	0.09
CO ₂	0.19	0.20	0.20	0.20	0.18
H ₂	0.15	0.14	0.14	0.15	0.13
N ₂	0.10	0.09	0.10	0.10	0.13
CH ₄	0.05	0.05	0.05	0.05	0.04
C ₂ H ₂	0.0004	0.0004	0.0004	0.0004	0.0003
C ₂ H ₄	0.0146	0.0130	0.0131	0.0140	0.0094
C ₂ H ₆	0.0033	0.0024	0.0025	0.0031	0.0018
C ₃ -C ₅	0.0003	0.0002	0.0002	0.0003	0.0001
NH ₃	0	0.0004	0	0	0.0004
H ₂ O	0.36	0.38	0.37	0.37	0.42
Total	1.00	1.00	1.00	1.00	1.00
Clean gas					
CO	0.11	0.09	0.09	0.10	0.08
CO ₂	0.16	0.17	0.16	0.17	0.14
H ₂	0.18	0.16	0.16	0.17	0.15
N ₂	0.09	0.11	0.13	0.09	0.12
CH ₄	0.01	0.01	0.01	0.01	0.01
C ₂ H ₂	0.00003	0.00002	0	0.00004	0
C ₂ H ₄	0.0010	0.0007	0.0005	0.0008	0.0006
C ₂ H ₆	0.00017	0.00010	0.00005	0.00012	0.00005
C ₃ -C ₅	0	0	0	0	0
NH ₃	0.0003	0.0003	0	0	0.0002
H ₂ O	0.45	0.47	0.45	0.46	0.50
Total	1.00	1.00	1.00	1.00	1.00

However, it was considered rational to handle most of the non-equilibrium phenomena in separate blocks, rather than treating them all at once in a single equilibrium block with various restrictions.

The schematic structure of the model is illustrated in Fig. 2. The simulation begins with the decomposition of the biomass to elemental gases, carbon and ash, based on the ultimate analysis of the feedstock. In the next two blocks the approach to equilibrium sulphur removal and carbon conversion are modelled by extracting fixed amounts of sulphur and elemental carbon to a bypass and to an outlet stream, respectively. The formation of tars is simulated next and they are handled as inerts in the following block, where other parts of the feeds are converted to equilibrium products. This is followed by mixing of streams and a separation of the feedstock ash to an outlet stream. The outlet stream of block 7 is the end product of the gasifier, and is labelled as 'Raw gas'.

The Raw gas is then cooled down to simulate the filtration of the gas, followed by a reformer modelling block. For the purposes of the sensitivity study, an additional block 10 was added to adjust the H₂/CO ratio of the gas to a desired value. More detailed descriptions of the model blocks are given in the following paragraphs.

2.3.1. Biomass decomposition

A yield reactor (R_{yield}) is used to simulate the decomposition of the feed. In the first block, biomass is converted to hydrogen,

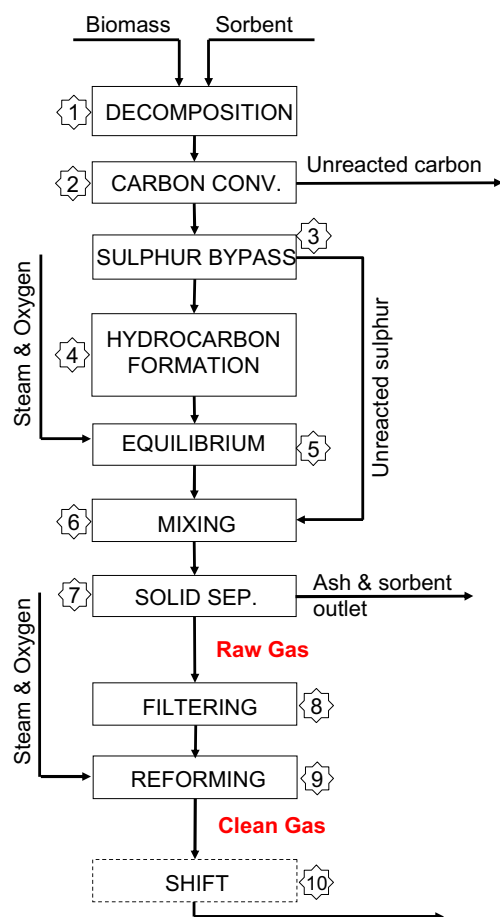


Fig. 2 – A schematic illustration of the model.

oxygen, nitrogen, carbon, sulphur and ash based on the ultimate analysis of the feedstock.

2.3.2. Carbon conversion

According to equilibrium calculations, feedstock's carbon should convert completely to products under typical gasification conditions in a fluidised-bed. However, a significant amount of carbon is usually found from the reactor's ash streams. Carbon conversion has thus a major effect to the gasifier's efficiency and high conversion levels are therefore desired.

Carbon conversion is adjusted in the model to match with experimental data by conveying part of the feed carbon to an outlet stream. The calculation is based on the observed correlation between carbon conversion and gasification temperature (see Table 4) and nested in block 2 (Sep) as a FORTRAN subroutine.

2.4. Sulphur capture with calcium-based sorbents in reducing conditions

In gasification processes the removal of sulphur is usually carried out in two steps. The bulk of the sulphur can be removed by feeding calcium-based sorbents in the gasifier at temperatures from 700 °C to 1100 °C. Additional step is however needed later in the process to remove sulphur completely, since in gasification conditions the calcium-based capture is thermodynamically limited.

According to [12] the principal sulphur capture reactions in the reducing (gasification) atmosphere are:

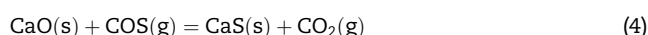
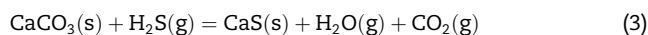
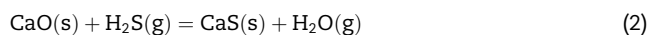


Table 4 – Conversion correlations used to model the non-equilibrium phenomena.

Conversions related to gasification	
Carbon	0.0155 * G + 86.068 %
CH ₄	-0.003 * G + 7.074 mol kg ⁻¹
C ₂ H ₂	-0.00004 * G + 0.06454 mol kg ⁻¹
C ₂ H ₄	-0.002 * G + 2.987 mol kg ⁻¹
C ₂ H ₆	-0.001 * G + 1.196 mol kg ⁻¹
C ₃ H ₈	-0.000155 * G + 0.150921 mol kg ⁻¹
C ₆ H ₆	0.27 mol kg ⁻¹
C ₁₀ H ₈	0.3 mol kg ⁻¹
NH ₃	0.04154 mol kg ⁻¹
Conversions related to reforming	
CH ₄	0.2247 * R - 127.36 %
C ₂ H ₂	0.8439 * R - 634.66 %
C ₂ H ₄	0.3818 * R - 237.31 %
C ₂ H ₆	0.2753 * R - 143.5 %
C ₃ H ₃	100 %
C ₆ H ₆	0.1875 * R - 76.532 %
C ₁₀ H ₃	94.6 %
NH ₃	1.0679 * R - 899.25 %

G = Gasifier freeboard temperature [°C].

R = Reformer outlet temperature [°C].

It can be observed, that the gaseous products (H_2O and CO_2) of sulphur capture in gasification conditions are also major compounds in the product gas. Thus the overall efficiency of sulphur capture is not controlled by pressure and temperature alone (as is the case with combustion), but also by the product gas composition [12].

The approach to equilibrium sulphur removal is modelled first in block 3 and the actual equilibrium removal in block 5. Fig. 3 illustrates the experimental correlation between approach to equilibrium sulphur removal and Ca/S molar ratio. The data is based on a pressurised fluidised-bed gasification tests with Finnish peat and German brown coal published in Ref. [12]. It can be observed that sulphur capture is strongly affected by the Ca/S ratio in the reactor. The higher the ratio, the better the approach to equilibrium sulphur removal has been obtained. This observed correlation can be represented with the following equation:

$$A_{\text{eq}} = 0.213R + 0.029, \quad (5)$$

where A_{eq} is the approach to equilibrium and R the molar ratio of Ca/S. In the block 3 (Sep) a $1 - A_{\text{eq}}$ share of the fuel sulphur is conveyed to a bypass stream, representing the amount of sulphur that does not take part to the equilibrium sulphur removal.

The sulphur removal feature of the model does not rise into a relevant role in this work, as the concentration levels of sulphur in the gas are already below the equilibrium concentrations that limit the removal potential. This is due to the very low levels of sulphur in the fuels (see Table 2). However, this feature becomes important when modelling fuels with higher amounts of sulphur, such as peat.

2.4.1. Hydrocarbon, tar and NH_3 formation

According to [13], hydrocarbons formed in a fluidised-bed gasification of biomass are mainly a product of secondary reactions of condensable hydrocarbons (usually referred to tars), formed in the primary pyrolysis stage. These secondary reactions can take place both homogeneously in the gas phase and heterogeneously on the surfaces of char, gasifier bed material, fuel particles and on reactor walls.

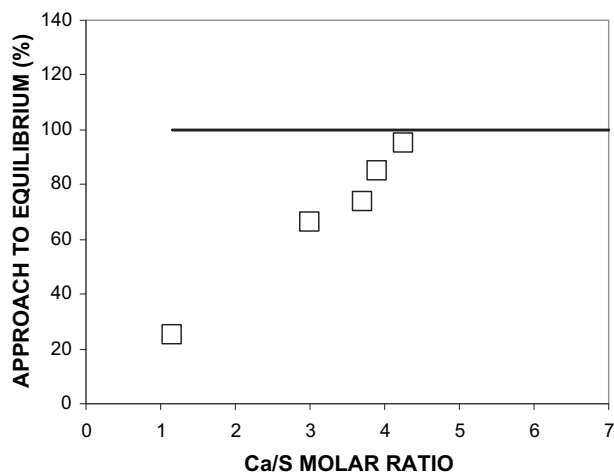


Fig. 3 – Approach to equilibrium sulphur removal as a function of Ca/S molar ratio [12].

The formation of tars and nitrogen species are under-predicted by equilibrium models. The model was thus adjusted to better match with these observations by calculating the correct conversions to tars and hydrocarbons in block 4 (RStoic) from the experimental data. The hydrocarbons were modelled as CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8 , and C_6H_6 , the nitrogen species as NH_3 and tars as C_{10}H_8 . The formation equations for these compounds were formed as a function of the gasifier's freeboard temperature, as it is known to have a strong correlation with the total tar concentration in fluidised-bed gasification of biomass [14–16]. The equations are presented in Table 4 and used to calculate the molar extent of each compound that is formed from the feed in block 4.

2.4.2. Equilibrium phenomena

In block 5, a Gibbs reactor (RGibbs) is used to mix the feed with oxygen and steam and to convert these into equilibrium products. The hydrocarbons, tars and NH_3 are handled as inerts to prevent their decomposition.

2.4.3. Mixing

In block 6, a stream mixer is used to connect the bypass stream with products from the equilibrium block.

2.4.4. Separation of solids

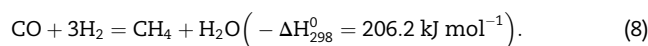
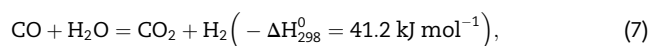
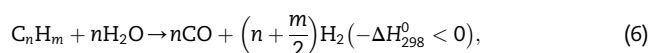
As the last step of the gasifier model, ash removal is simulated in block 7 (Sep) by directing the feedstock ash to an outlet stream. The product stream of block 7 is the model's estimation of the product gas composition coming out of the fluidised-bed gasifier at given conditions and is labelled as 'Raw gas'.

2.4.5. Filtration

Before product gas can be fed into the reformer, its dust load has to be lowered to an allowable level. Barrier filters are normally used for this as the purity requirements can not be met with cyclone separators alone. The filtration step is modelled with a cooler block that lowers the temperature of the raw gas to a level acceptable for the barrier filters to operate without problems. There is no need to simulate any actual dust removal as the formation of fly ash is not modelled in the gasification part.

2.5. Catalytic reforming of hydrocarbons

According to [17] the stoichiometry of a steam reforming system can be described with three individual reactions: the steam reforming reaction (6), the water gas shift reaction (7) and the methanation reaction (8), represented by the following equations:



Although reaction (6) is endothermic, the overall heat of the reactions can be positive, zero or negative, depending on the

process conditions. For most processes that involve the production of synthesis gas, low methane content is desired at the reformer outlet. Achieving this requires the use of high steam to carbon ratios and high catalyst exit temperatures, leading to an endothermic overall reaction [17].

To drive this endothermic overall reaction, enough heat has to be supplied into the reformer. This can be achieved by using either tubular or autothermal reformer design [18]. In a tubular reformer the catalysts are loaded into a number of tubes and placed inside of a furnace, whereas in an autothermal reformer the reaction heat is generated by internal combustion with oxygen. The latter design is usually considered more suitable for gasification processes where partial oxidation is already used in the gasifier.

In the model, a Gibbs reactor (RGibbs) is used to convert streams of Raw gas, steam and oxygen to equilibrium products. However, according to experimental data, complete conversion is not achieved for any of the hydrocarbons in the reformer. Especially the conversion levels of methane and ammonia fall well below 100% at every set point.

To match this observation, the conversions have to be adjusted. This is done by estimating the appropriate conversion levels from experimental correlations, defined as a function of the reformer outlet temperature. These correlations, presented in Table 4, are used to calculate the fraction of each compound that doesn't react in the reformer, i.e. is handled as inert in the block.

The product stream of this block is the final product of the simulation and is labelled as 'Clean gas'.

2.5.1. Shift

Depending on the synthesis application, different values for the H₂/CO ratio are required. In typical reforming temperatures, the shift reaction is thermodynamically limited and can thus be used to adjust the H₂/CO ratio of the product gas to a desired value. This is normally performed in a separate shift conversion step over an appropriate shift catalysts.

For the purposes of the sensitivity study, a shift conversion step was added to the model to adjust the product gas H₂/CO ratio to 2. This is done in the block 10 (Rstoic) by setting the fractional conversion of the shift reaction to a level leading to the desired ratio.

2.5.2. Model settings

SOLIDS and RK-SOAVE were used as base and property methods in Aspen Plus. The selection was based on the instructions of Aspen Plus User Guide and VTT's in-house experiences about gasification modelling.

All components were considered as products in Aspen Plus and the fuel was described by its ultimate and proximate analyses. For enthalpy balance calculations, the higher heating value of the fuel was calculated from ultimate analysis according to the following equation proposed by Channiwala and Parikh [19]:

$$\text{HHV} = 0.3491 \text{C} + 1.1783 \text{H} + 0.1005 \text{S} - 0.1034 \text{O} - 0.0151 \text{N} - 0.0211 \text{Ash}. \quad (9)$$

All the heat streams related to the calculation blocks are connected together and summed up (these are not shown in

Fig. 2 for the sake of readability). This sum is interpreted as the heat losses from the system to the surroundings.

When gasifier and reformer temperature were fixed as an input, the energy balance was used to calculate heat losses and when heat losses were assumed, energy balance was used to predict the gasification and reforming temperatures. Inlet temperatures for steam, air and nitrogen were set to 200 °C and for biomass and limestone to 20 °C.

3. Results and discussion

3.1. Validation

Usable and publicly available experimental data about steam/O₂-blown gasification of biomass is not easy to find. This lack of independent data makes the proper validation of the model complicated.

However, previous validation experiences with a similar type of model for fluidised-bed air gasification of biomass [20] seem to suggest that if the model results agree reasonably well with the data that was used to fit some of the model parameters, the results can be expected to hold also for other fuels with similar type of reactivity.

Keeping in mind the restrictions caused by the lack of independent validation data, the values of biomass feed, equivalence ratio, steam to fuel ratio, outlet temperature of the gasifier and process pressure were set to correspond with the values of Table 1, and the model estimations were compared with the experimental data at every set point. The results are illustrated in Fig. 4 with lines demonstrating +10% and -10% deviations between measured and estimated values. Judging from the results, a fairly good agreement between experimental data and the model predictions has been achieved for the main gas components. The average relative error for the concentrations of H₂, CO, CO₂, and H₂O was 12%, while the magnitude of experimental error in the data is expected to be around 5%.

As enough information about reformer feedstreams is not included in Ref. [2], the validation was possible to be performed only for the gasification part of the model.

3.1.1. Range of validity

A semi-empirical model can be considered fully valid only within the range of the data that was used to fit the model parameters (Table 1). The gasifier type should also be considered when estimating the suitability of the model for process simulation purposes. It is emphasised that only gasifiers sharing a similar type of geometry with the PDU-gasifier (as described in Section 1.5) should be simulated with this model.

In addition to temperature, the gasifier's carbon conversion is also closely related with the gasification rate of the biomass, i.e. the reactivity of the fuel. As the carbon conversion predictor of this model depends only on the gasification temperature, and does not consider any fuel parameters, it is presumable that its prediction capability is restricted to fuels that share similar reactivity with the feedstocks used to fit the predictor itself.

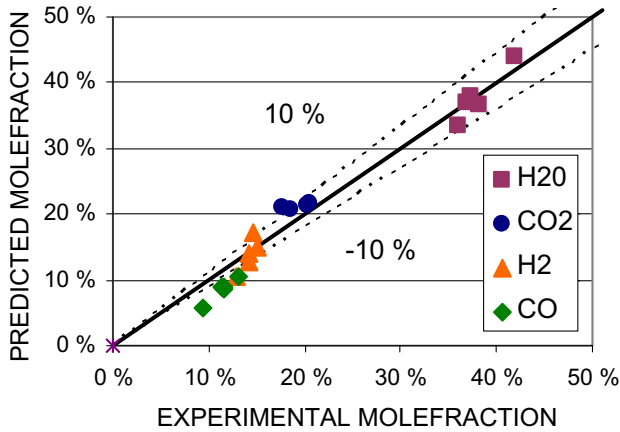


Fig. 4 – Comparison of measured values with values predicted by the model for the main product gas components in wet gas at the gasifier outlet.

3.2. Parametric study

The effects of main process parameters to the gasifier–reformer system are studied in this section. Three different cases were created for these purposes. The cases were:

1. Process development unit (PDU),
2. Industrial base case (IBC), and
3. Target concept (Target).

The PDU case corresponds with the VTT’s process development unit, introduced in Section 1.5, and is characterized by large heat losses and steam/oxygen ratios as well as relatively moderate operating pressure.

The IBC is based on the PDU, but features significantly smaller heat losses, elevated operating pressure and smaller steam/oxygen ratios, thus reflecting the effects of an upscale to about 300 MW_{fuel} size.

The Target concept is in turn based on the IBC, but features elevated filtration temperature and higher conversion levels in the reforming unit.

Shift conversion block was used to adjust the H₂/CO ratio of the gas to 2 for all of the cases. As a final step, the product gas was compressed to 30 bar with three compressors

Table 5 – Main process parameters related to the different cases.

	PDU	IBC	TARGET
Heat losses, %	7	1	1
Gasification pressure, MPa	0.25	1	1
Filtration temperature, °C	538	538	830
Steam/oxygen ratios, kg kg ⁻¹	1.5	1	1
CH ₄ and NH ₃ conversions, %	*	*	80
Other hydrocarbon conversions, %	*	*	100
Final pressure, MPa	3	3	3
H ₂ /C ₀ ratio after shift	2	2	2
Fuel moisture, wt%	10.4	10.4	10.4

* According to equations of Table 4.

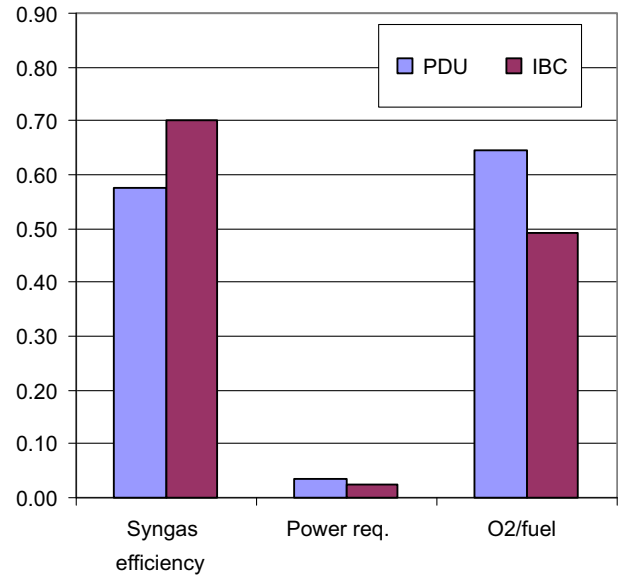


Fig. 5 – Comparison of PDU and IBC, where syngas efficiency and power requirement are given in percentages and O₂/fuel ratio in kg kg⁻¹.

incorporating intercoolers and an isentropic efficiency of 80%. Pressure losses were set to 200 mbar for the gasifier, filter and reformer and to 1 bar for oxygen and steam inlets. The main features are listed in Table 5. Set point 4 of Table 1 was chosen as the base for setting rest of the operating parameters. The performance of each case was calculated and the results are discussed in the following paragraphs.

3.2.1. The influence of heat losses, gasification pressure and steam/oxygen ratios

The influence of heat losses, gasification pressure and steam/oxygen ratios to the performance of a gasification-reformer

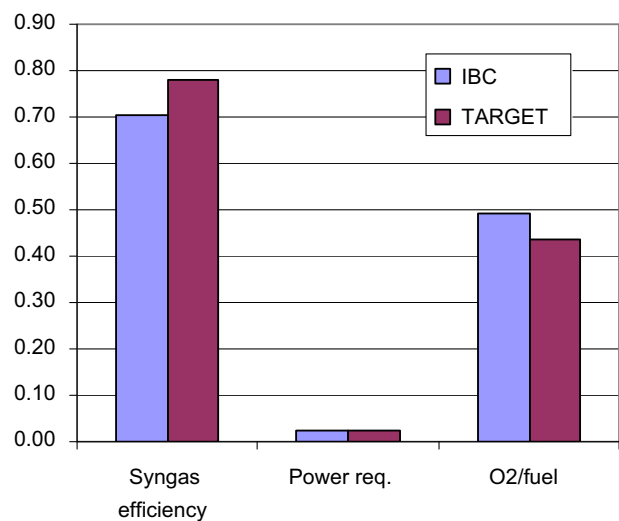


Fig. 6 – Comparison of IBC and Target concept, where syngas efficiency and power requirement are given in percentages and O₂/fuel ratio in kg kg⁻¹.

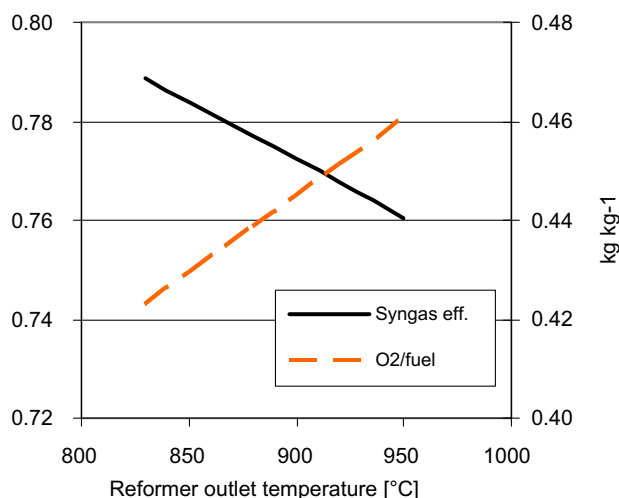


Fig. 7 – The effect of reforming temperature to the syngas efficiency and oxygen consumption.

system are studied first. These effects are of special interest for an engineer facing a task of process scale-up. For a PDU-scale gasifier the heat losses to surroundings are usually around 7–10%, whereas for commercial-scale gasifier these are only around 1%. Usually the gasification temperature is tried to be kept at the same level after the scale-up of reactor size. However, in larger reactors the same temperature can be achieved with smaller amount of oxygen as less heat is lost to the surroundings. This improves the gasifier's cold gas efficiency and also affects the product gas composition. In larger reactors the desired fluidisation properties are achieved with smaller steam/oxygen ratios which also improve the efficiency. The elevated gasification pressure reduces the need of product gas compression to the final synthesis pressure, resulting in a lower overall power consumption requirement.

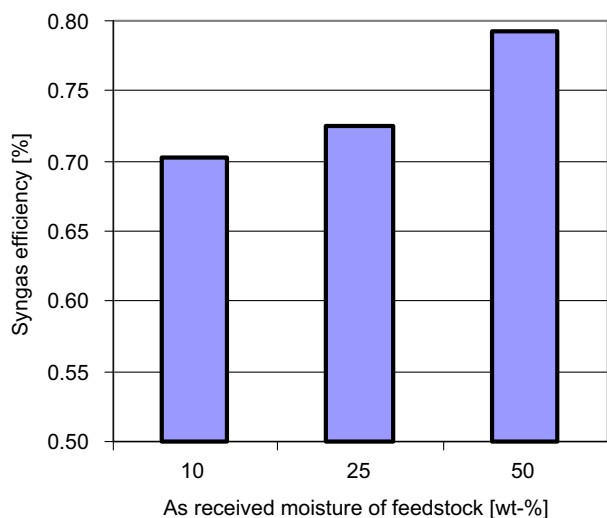


Fig. 8 – The effect of feedstock drying to the syngas efficiency when feedstock is dried to the moisture content of 10% with low level heat streams from the process.

The effects of these parameters are illustrated in Fig. 5, where the PDU case is compared with Industrial base case.

The syngas efficiency η_{syngas} is defined as:

$$\eta_{\text{syngas}} = \frac{\dot{m}_{\text{sg}} \times Q_{\text{sg}}}{\dot{m}_{\text{f}} \times Q_{\text{f}}}, \quad (10)$$

where \dot{m}_{sg} denotes the combined mass flow of H₂ and CO in the product gas, Q_{sg} the combined heating value of H₂ and CO, \dot{m}_{f} the fuel input flow and Q_{f} the heating value of the fuel on LHV basis.

The O₂/fuel ratio is reported in kilograms (kg kg⁻¹) where the fuel is considered dry and ash free. The power requirement η_{power} is defined as:

$$\eta_{\text{power}} = \frac{\text{Internal power consumption}}{\dot{m}_{\text{f}} \times Q_{\text{f}}} \quad (11)$$

where internal power consumption includes the compression of oxygen and steam (water) to gasification pressure and the compression of product gas to the final synthesis pressure (30 bar).

It can be observed that lower heat losses and steam/oxygen ratios cut down the oxygen need from 0.64 to 0.49 kg kg⁻¹ and improve the syngas efficiency significantly from 58 to 70%. Rising the gasification pressure from 2.5 bar to 10 bar lowers the power requirement by 50% (from 4 to 2%).

3.2.2. The effects of filtration temperature and reformer conversion levels

When the filtration step has to be performed in a lower temperature than gasification, additional heat exchanger must be installed for cooling of the gas. After the filtration, the temperature needs to be elevated again for the reforming process by partial oxidation of the product gas, which leads to lower η_{syngas} and higher oxygen consumption. According to Fig. 6 the combined effects of elevated filtration temperature and higher reformer conversions amount to 8% points rise in the η_{syngas} . More detailed calculations show that elevated filtration temperature contributes 5% points and higher reformer conversions 3% points share in this total improvement from 70 to 78%.

The change in oxygen consumption between the IBC and Target case is a result of two phenomena driving the oxygen consumption in opposite directions: For the Target case, oxygen consumption in the reformer must rise in order to maintain the same temperature, as more endothermic reforming reactions are taking place. However, the higher filtration temperature of the Target case leads to a reduced need for reheating before the reformer, contributing to lower oxygen needs. According to the calculations, an aggregate effect of these two phenomena lowers the oxygen consumption from 49 to 43 kg kg⁻¹. The differences between power requirements are small, because gasification pressure is same for both of the cases.

3.2.3. The effect of reforming temperature

It is also important to study the effects of reforming temperature to the process performance, as higher temperatures require higher oxygen consumption and thus lead to lower syngas efficiency. Fig. 7 illustrates the effects of reforming temperature to the process performance, while keeping the

conversion levels constant. It can be observed, that if the target conversions are achieved only after 950 °C instead of 850 °C, it will lower the η_{syngas} from 78 to 76%, and raise the oxygen consumption from 43 to 46 kg kg⁻¹.

3.2.4. The effect of drying

A commercial-scale gasification plant produces several kinds of heat streams as a by-product. Some of these streams can be used to generate process steam and electricity, whereas some streams are associated with such a low temperature levels that the production of electricity is not anymore technically possible. However, these low quality heat streams can be used for feedstock drying. If process performance calculations are performed on LHV basis, the incorporation of fuel drying can lead to a significant rise in the efficiency. This can be observed also in Fig. 8, where η_{syngas} is calculated for three different drying levels. The first column represents a case where drying is not applied (fuel moisture already at the targeted 10 wt-%). The second column indicates a rise in η_{syngas} from 70 to 73% when the fuel is dried from 25 to 10 wt-%, and the third column indicates a rise in syngas efficiency up to 79% when fuel is dried from 50 to 10 wt-%.

4. Conclusions

Experimental data from a PDU-scale reactor was used to fit a semi-empirical model for steam/O₂-blown fluidised-bed gasification of biomass with catalytic reformer. The model is capable of predicting product gas composition with an average relative error of 12% for fuels with a reactivity close to that of clean wood. A parametric analysis indicated that higher reformer conversions and filtration temperature have the potential to improve syngas efficiency from 70 to 78%. Achieving target conversions at 950 °C instead of 850 °C would decrease syngas efficiency by 2% points and drying the fuel from 50 to 10 wt-% moisture content would improve the efficiency by 9% points.

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REFERENCES

- [1] Kurkela E. Formation and removal of biomass-derived contaminants in fluidized-bed gasification processes. In: VTT Publications, vol. 287. Technical Research Centre of Finland, VTT; 1996.
- [2] Kurkela E, Simell P, McKeough P, Kurkela M. Production of synthesis gas and clean fuel gas [[synteesikaasun ja puhtaan polttokaasun valmistus]]. In: VTT Publications, vol. 682. Technical Research Centre of Finland, VTT; 2008.
- [3] Rose L. Chemical reactor design in practise. Espoo, Finland: TKK; 1982.
- [4] Buekens A, Schoeters J. Mathematical modelling in gasification. In: Bridgwater A, editor. Thermochemical processing of biomass. London, Boston: Butterworths; 1984.
- [5] Gururajan V, Agarwal P, Agnew J. Mathematical modelling of fluidized bed coal gasifiers. Chem Eng Res Des 1992;70:211–38.
- [6] Konttinen J, Hupa M, Moilanen A, Kurkela E. Carbon conversion predictor for fluidized bed gasification of biomass fuels – model concept. In: Proceedings of the Science in Thermal and Chemical Biomass Conversion (STCBC) conference. 2004.
- [7] Kovacik G, Oguztoreli M, Chambers A, Özüm B. Equilibrium calculations in coal gasification. Int J Hydrogen Energy 1990; 15(2):125–31.
- [8] Kilpinen P, Hupa M, Leppälahti J. Nitrogen chemistry at gasification – a thermodynamic analysis. Åbo Akademi; 1991. Tech. Rep.
- [9] Schuster G, Löffler G, Weigl K, Hofbauer H. Biomass steam gasification – an extensive parametric modeling study. Bioresour Technol 2001;77(1):71–9.
- [10] Doherty W, Reynolds A, Kennedy D. The effect of air preheating in a biomass CFB gasifier using aspen plus simulation. Biomass and Bioenergy 2009;33(9):1158–67.
- [11] Nikoo M, Mahinpey N. Simulation of biomass gasification in fluidized bed reactor using aspen plus. Biomass and Bioenergy 2008;32(12):1245–54.
- [12] Kurkela E, Hepola J, Ståhlberg P, Lappi M. Sulphur removal by calcium-based sorbents in fluidized-bed gasification. In: International symposium on energy and environment. Espoo, Finland; 1991.
- [13] Simell P. Catalytic hot gas cleaning of gasification gas. Ph.D. thesis; Helsinki University of Technology, TKK; 1997.
- [14] Bruinsma O, Moulijn J. The pyrolytic formation of polycyclic aromatic hydrocarbons from benzene, toluene, ethylbenzene, styrene, phenylacetylene and n-decane in relation to fossil fuels utilization. Fuel Process Technol 1988; 18(3):213–36.
- [15] Simell P, Leppälahti J, Bredenberg J. Catalytic purification of tarry fuel gas with carbonate rocks and ferrous materials. Fuel 1992;71(2):211–8.
- [16] Kurkela E, Stahlberg P, Laatikainen J. Pressurized fluidized-bed gasification experiments with wood, peat, and coal at VTT [Espoo, Finland] in 1991–1992, Part 1. In: Test facilities and gasification experiments with sawdust. VTT Publications, vol. 161. Technical Research Centre of Finland, VTT; 1993.
- [17] Anderson J, Boudart M, editors. Catalysis Science and Technology, vol. 5. Berlin, Heidelberg: Springer-Verlag, ISBN 3-540-12665-1; 1984.
- [18] Tubular reforming and autothermal reforming of natural gas – an overview of available processes. Fuel Process Technol 1995;42(2–3):85–107. doi:10.1016/0378-3820(94)00099-F. Trends in Natural Gas Utilisation.
- [19] Channiwala S, Parikh P. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81(8): 1051–63. Cited by (since 1996) 61.
- [20] Hannula I, Kurkela E. A semi-empirical model for pressurised air-blown fluidised-bed gasification of biomass. Bioresour Technol 2010;101(12).