

Biomass Gasification using Solar Thermal Energy

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Hydrogen from Biomass as an energy carrier has generated increasing interest in recent years. There are several different technologies to convert solid or liquid Biomass into a gas mix consisting of mainly hydrogen and carbon dioxide. Up to 30% of the energy stored in the product gas would originate from the sun by using solar thermal applications to source the conversion while the equivalent of 30% of the product gas would have to be burned using conventional approaches. This paper explains the principles of the main technical pathways for biomass gasification and shows their advantages and disadvantages especially in connection with the use of solar heat as energy source for the conversion reaction. Biomass gasification in supercritical water appears to be a simple and efficient and thus most convenient approach for solar thermal applications.

1. INTRODUCTION

With the world facing environmental problems like global warming and possible shortage of fossil fuels in the near future, interest in renewable energies has been growing rapidly in recent years. Direct conversion of solar radiation is one promising approach within the renewable energies to provide a significant fraction of the future energy consumption. However, with solar radiation not being available at all times, it is important to find ways of storing solar energy to make solar technologies viable for energy production. In addition, liquid hydrocarbon fuels have proved to be very effective as high energy density transport fuels. Gas derived from solar thermal conversion of biomass is one way to address both of these issues. The ANU Dish concentrator technology discussed elsewhere in these proceedings (Lovegrove and Zawadski 2006), is a possible source of energy input for solar driven biomass gasification. This paper presents a review of the established technologies for biomass gasification and discusses the issues associated with driving them via the input of solar energy from a dish system.

2. BASIC PRINCIPLES

Biomass gasification is the thermo chemical conversion of solid or liquid biomass into gaseous components. Gasification can be achieved either with or without the addition of water and so the processes are categorised as “dry” or “wet” accordingly. The generalised reaction pathways are:

“Dry” processes:



Milne *et al.* 2001 describe this as a two step process. In the first step, pyrolysis, volatile components of the biomass are vaporised at elevated temperatures from around 400°C. These vapours include hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, tars and water vapour. Through gas phase cracking processes the tar levels are further reduced. Non vaporised by-products of this first step are char (fixed carbon) and ash. The main pyrolysis pathways are shown in Figure 1. In the second step char is gasified through reactions with steam, carbon dioxide, hydrogen and oxygen (if available).

While pure pyrolysis itself is an anaerobic process, commercial techniques usually add air or oxygen for partial oxidation purposes. Combustive reactions in the second step then produce enough energy needed for turning the otherwise endothermic pyrolysis into an overall auto thermic gasification process.

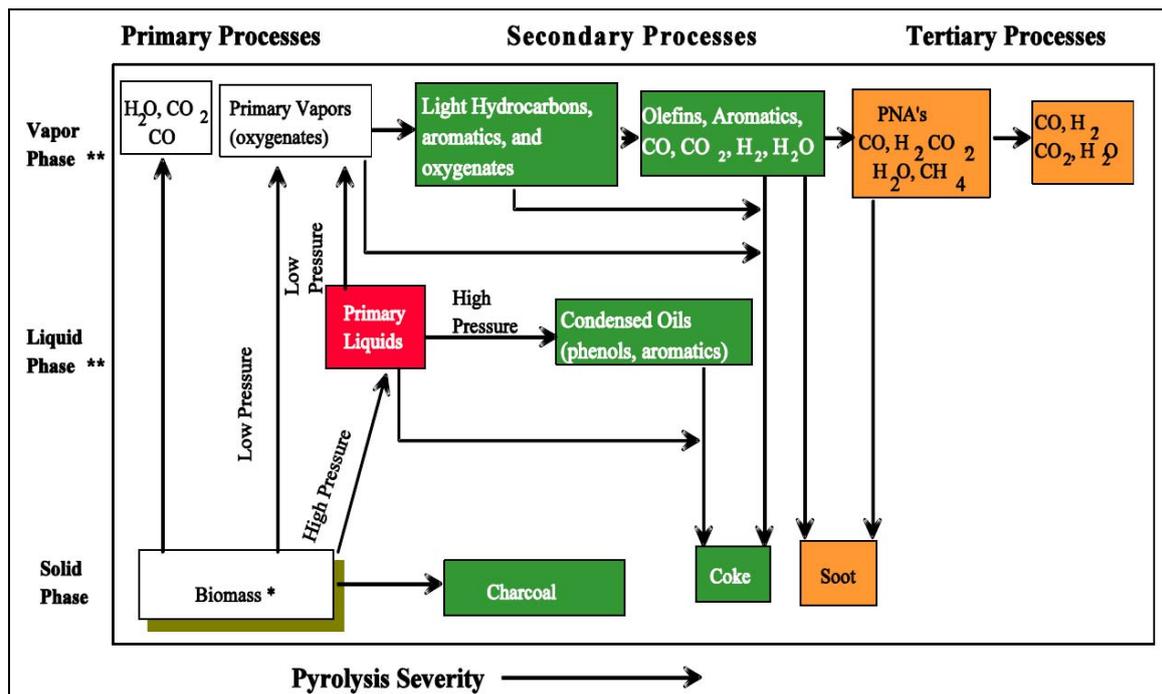
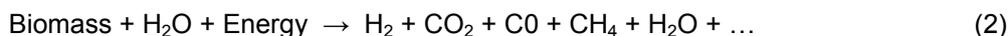


Figure 1 Pyrolysis pathways (Milne *et al.* 1998)

“Wet” processes:



Resulting basically in the same end products, wet processes differ quite a lot from dry processes in their pathways. With increasing water concentration and pressure hydrolysis reactions take place parallel to pyrolysis, where biomass directly reacts with water. Várhegyi *et al.* 1993, Minowa and Fang 1998, Minowa *et al.* 1998a, Minowa *et al.* 1998b, Minowa *et al.* 1997 use cellulose as model compound for biomass. According to them cellulose is broken up catalysed by water starting at temperatures as low as 200°C. They propose the following pathway for the hydrolysis process:

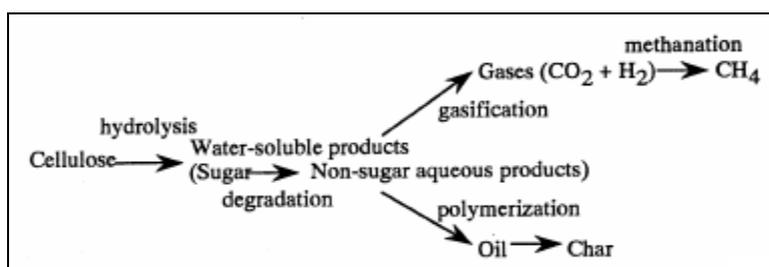
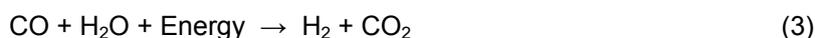


Figure 2 Hydrolysis pathways (Minowa and Fang 1998)

Depending on temperature and water content this pathway is accompanied by the respective pyrolysis pathways shown in Figure 1.

Supercritical fluids, ie fluids at temperatures and pressures above their critical point, are known to have differing and usually more active chemical properties. Water at or above critical pressure and high temperatures becomes nonpolar and hence a very good solvent for organic compounds. Dissolving of organic compounds restrains condensation reactions and thus char forming during pyrolysis (Su *et al.* 2004, Matsumura *et al.* 2005, Potic *et al.* 2002). The methanation reaction shown in Figure 2 is outperformed by the water-gas shift reaction (equation 3) under supercritical conditions especially above 660°C the hydrogen content in the product gas increases dramatically. At this temperature the water-gas shift reaction starts to become dominant (Lee *et al.* 2002). With biomass

having usually only a fairly low hydrogen content (around 6% versus 25% for methane [Milne *et al.* 2001]) the water-gas shift reaction can increase the hydrogen content of the product gas significantly. In fact up to half of the hydrogen produced during the reaction under supercritical conditions originates from water [Kruse *et al.* 2003].



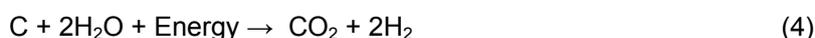
Generally it is possible to completely gasify biomass using supercritical water (Osada *et al.* 2006, Schmieder *et al.* 2000, Antal *et al.* 2000, Dinjus and Kruse 2004, Potic *et al.* 2004), leaving only clear water and some salts in the effluent.

Although it seems that supercritical techniques are more effective there are no commercially operated supercritical gasification plants yet. Compared to dry methods which were commercially used for centuries already, supercritical gasification is a fairly young field of research. Existing methods using the dry gasification process are often combined with “wet” pathways using steam-air mixtures just steam as gasification medium in a hybrid process in order to further reduce tar and hydrocarbon remainder in the product gas and increase the process efficiency, e.g. Collot *et al.* 1999, Corella *et al.* 1998, Czernik *et al.* 1999, Chen *et al.* 2004, Aznar *et al.* 2006.

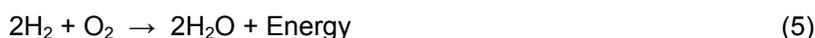
Also a wide range of catalysts has been successfully tested which support certain reactions within the gasification process and thereby influence the product gas composition, e.g. Kruse *et al.* 2000, Corella *et al.* 1998, Antal *et al.* 2000, Matsumura *et al.* 2002, Landon *et al.* 2005, Aznar *et al.* 2006.

2.1. The Potential for Solar Contribution

A promising way of combining biomass gasification with solar thermal technologies would be the generation of hot water/steam or air for feeding into the respective reactors as the gasification medium. The big advantage with using solar thermal technologies opposed to conventional gasification methods becomes obvious with looking at some reaction energy balances (All energies are calculated using enthalpies of formation at 298K and 1 atmosphere taken from Moran and Shapiro 2000). As a simple example the gasification of carbon with solar heated water or steam is given by:



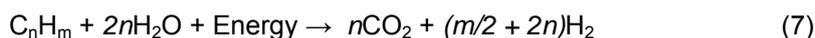
The energy input needed for this reaction is 178kJ/mol and this can potentially be provided by a high temperature solar thermal system. The resulting hydrogen in the product gas then can be burned/oxidized:



giving off 572 kJ/mol of carbon. Compared to just burning coal (carbon)



giving off 394kJ/mol. The solar enhanced gas contains $178/572 = 30\%$ solar energy from the thermochemical conversion, it can also be applied in much more efficient conversion processes such as fuel cells or combined cycle power plants. Other hydrocarbons are gasified according to:



The energy fraction in the products that is solar depends on the C/H ratio but will be around 20%.

These arguments also apply to solar gasification of coal. Such a process could provide a significant reduction in overall CO₂ emissions from coal use, whilst providing a stepping stone to a fully solar driven energy economy.

An important issue is how the heat from the hot gases is recovered afterwards. For solar driven gasification this affects the efficiency of the process but not the energy value of the final product. For conventional gasification, any loss in heat recovery is a loss of the original energy. Consequently the

effective fraction of direct solar contribution in gasification products is actually higher than these ideal values.

Since hydrogen storage itself is still a critical point, it is useful to consider the conversion into easier storable media. Looking more closely at the gasification reaction, it is actually two steps:



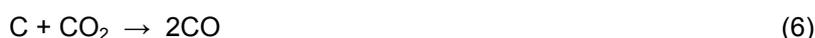
If one stops after the first step (which is the energy intensive one), the CO plus H₂ mix, called syngas, is the feed stock for making "Di Methyl Ether" (DME) which can then be transformed into a diesel substitute.

3. REACTOR TECHNOLOGIES

3.1. Fixed-Bed Gasification

Fixed bed gasifiers involve reactor vessels in which the biomass material is either packed in or moves slowly as a plug, with gases flowing in between the particles. A number of different reaction zones can be identified in such reactors:

- A : Drying Zone
Moist Biomass is heated up to about 200°C and the moisture is driven out.
- B : Pyrolysis Zone
The temperature is increasing up to about 500°C and the biomass is pyrolysed to tar-oil, charcoal and some gases.
- C : Reduction Zone
Temperatures here reach from 500 up to about 800°C. Hot gases from the combustion react with charcoal and are reduced:



- D : Combustion Zone
The temperature is greater than 800°C. Charcoal is burned with air or oxygen, which are fed in through a grate, sometimes mixed with steam. This produces the heat for the overall gasification process.

3.1.1. Counter-current ("up draft") gasifier

In a counter current gasifier, biomass enters the reactor from the top and travels downwards into a stream of hot gas, as shown in Figure 3. As the products from the pyrolysis zone are directly drawn into the product gas without any further decomposition, updraft gasifiers produce the largest amount of tar in the product gas compared to all other gasification technologies. Thus extensive gas cleaning is required before it can be used in other applications. On the other hand the resulting product gas has only a fairly low temperature (80-300°C (Kurkela 2002)) which results in a good thermal efficiency for this process. This is a consequence of the counterflowing arrangement allowing product gases to preheat incoming biomass as they leave. Counter current gasifiers are also not very demanding in the type of biomass used and usage of biomass with high moisture contents up to 50% is possible without having to pre-dry the feedstock (Beenackers and Maniatis 1996).

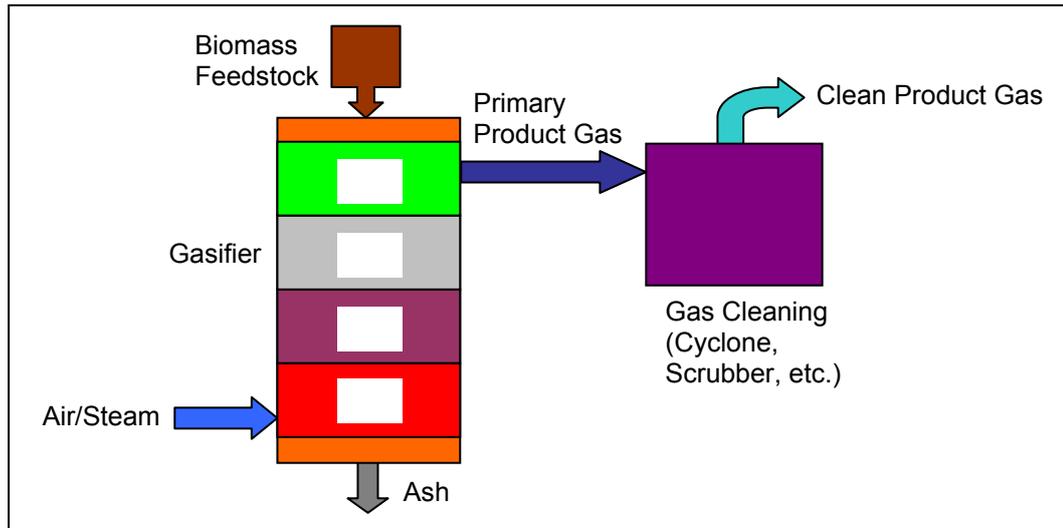


Figure 3 Up draft gasifier: schematic drawing

3.1.2. Co-current ("down draft") gasifier

In a Co-current gasifier, biomass is fed into the reactor from the top and air and/or steam are usually added in the middle in a narrowed section ("throat") as shown in Figure 4.

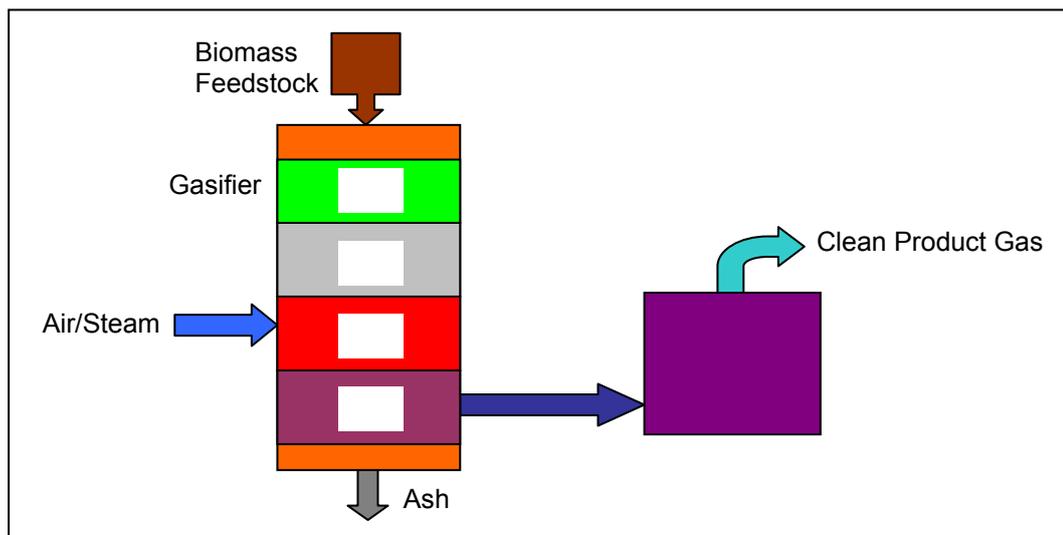


Figure 4 Down draft gasifier: schematic drawing

Since gases that contribute to reduction processes are only added in the middle and flow downwards, combustion and reduction zone are in changed order compared to up draft gasifiers. The fact that the pyrolysis products flow co-currently through the combustion and reduction zones results here in a very low tar content in the product gas. On the other hand the tars here are much more stable in comparison to an updraft gasifier which results into further problems for complete tar removal. Proper operation of this reactor type requires narrow specifications for fuel size and moisture content (typically 20% Wt db) (Beenackers and Maniatis 1996).

3.1.3. "Cross draft" gasifier

Cross draft gasifiers have the fastest response time and lowest thermal mass compared to all other gasifiers. Biomass is fed from the top again and air is blown in from the side through a nozzle at high velocity, as shown in Figure 5.

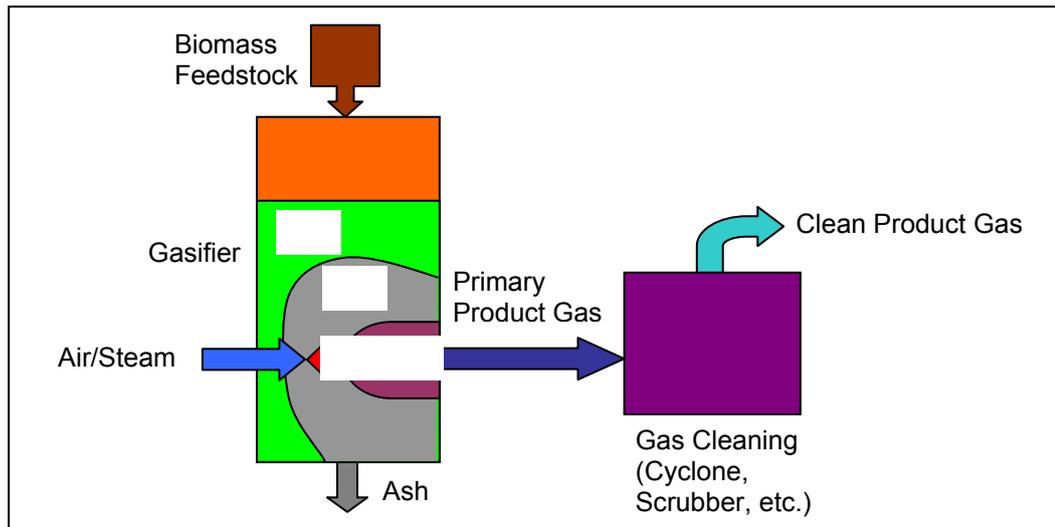


Figure 5 Cross draft gasifier: schematic drawing

This induces circulations and flow across the bed of fuel and char and generates very high temperatures. Thus it is required to use low ash fuel to prevent slagging. Air or water cooled nozzles are also often required. So far only small scale units are operating moderately successfully (max. proven commercial capacity appr. 150kW_{el} (Stassen and Knoef 2001)) and the concept seems to be not suitable for up scaling.

3.2. Fluidised-Bed Gasification

A fluidised bed, involves mixtures of particles in gases, with gas flow rates high enough that the fluid particles are entrained and mixed and become fluid like in their behaviour. The simplest arrangement is the bubbling fluidised bed.

3.2.1. Bubbling fluidised-bed gasifier

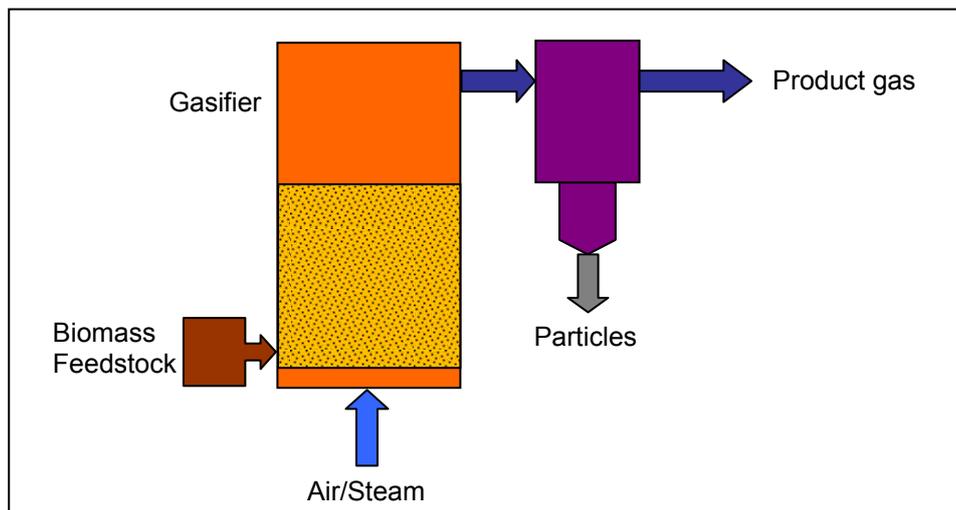


Figure 6 Bubbling fluidised bed gasifier: schematic drawing

A fluidised bed gasifier is usually partly filled with an inert medium like sand which can contain catalytically active particles as well. This medium is fluidised either by air or steam (designs using supercritical water as the fluidisation medium have been considered (Matsumura and Minowa 2004)). Biomass fuel is fed in either above or directly into the bed depending on the fuel size and density. Due to the fluidisation, fuel and heat are spread homogeneously through out the bed which results in an increased conversion rate in comparison to fixed bed gasifiers.

Because of the intense continuous mixing of the whole bed it cannot be distinguished between drying, reduction, combustion and pyrolysis zone. This type of gasifier is able to handle fuel types with relatively high moisture and ash contents. The resulting hot product gas still contains significant amounts of tar which have to be removed.

3.2.2. Circulating fluidised-bed gasifier

Circulating fluidised bed gasifiers differ mainly in using a faster fluidisation velocity than bubbling fluidised bed gasifiers. This results in bed particles being lifted off and taken into the product gas stream. A cyclone following after the reactor filters the particles out of the gas stream and feeds them back into the reactor. This recycling process results in higher heat and mass transfer rates and improved gasification efficiency in comparison to bubbling fluidised bed gasifiers (Bingyan *et al.* 1994).

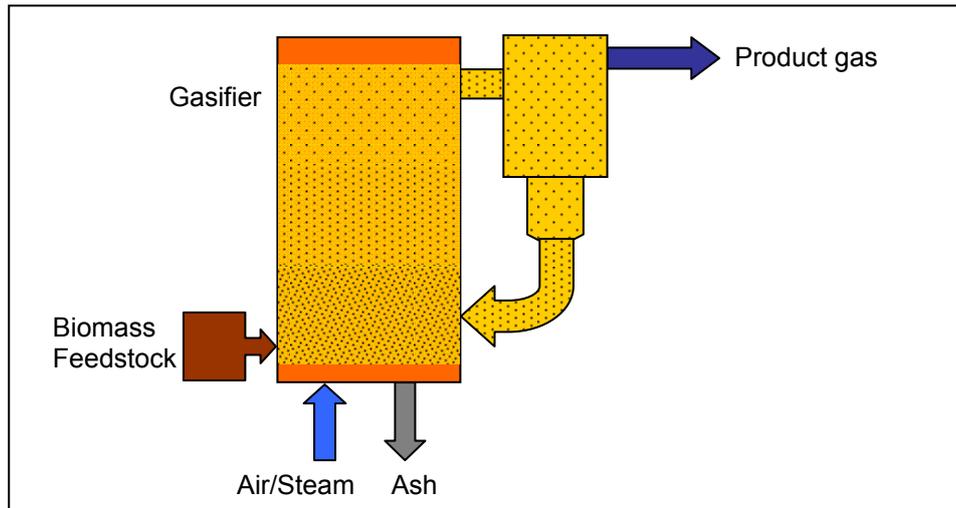


Figure 7 Circulating fluidised bed gasifier: schematic drawing

3.3. Supercritical Water Gasification

Supercritical water gasification is usually realised in two main reactor types: continuous flow reactors and batch reactors. Batch reactors are generally used only for research purposes. Figure 8 illustrates a typical arrangement.

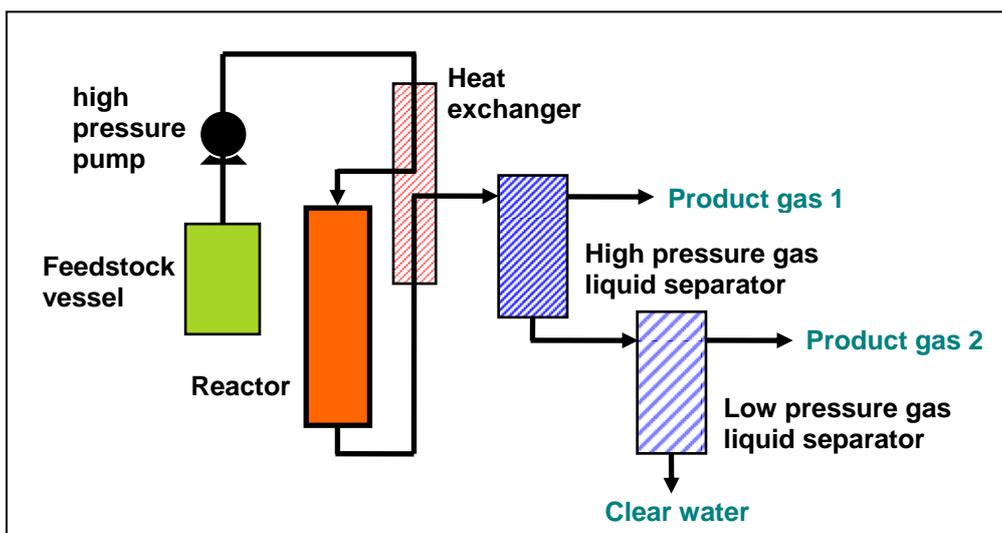


Figure 8 Supercritical water gasification continuous flow reactor: schematic drawing

In a continuous flow reactor biomass is fed as slurry into the reactor. The biomass used needs to be ground to a sufficient small size in order to produce well pumpable slurry. Using a high pressure pump, the slurry is pressurised up to 25-30MPa. In the reactor the slurry is heated up to about 700°C which causes the biomass particles to dissolve and break down. Complete gasification is possible, producing mainly hydrogen and carbon dioxide as well as small amounts of carbon monoxide and methane. The water-gas shift reaction almost doubles the amount of hydrogen that can be obtained from biomass otherwise. While passing through a heat exchanger afterwards, the water-gas mixture is cooled down to below 100°C and then moves on into the high pressure gas-liquid separator. With temperatures around 50°C and pressures still at 25-30MPa carbon dioxide dissolves very well in water. This results in product gas 1 being almost pure hydrogen. In the low pressure gas-liquid separator the pressure is then brought down to ambient and the remaining gases are separated from the liquid effluent, which should not contain anything else, except some salts. Salts generally can cause problems within the reactor due to their low solubility in supercritical water. They fall out of solution and can lead to blockages. This can be overcome by switching from feedstock to fresh water and turning the heating off. Precipitated salts will then be dissolved and washed out again.

3.4. Approaches to Solar Input

Whilst the potential benefits of providing solar energy input to gasification processes are clear, it is challenging to develop technically feasible methods for coupling solar input to reactor systems. This is particularly so for a dish system with a moving receiver. A range of innovative solar receiver reactors have been demonstrated for solid phase reactions using solar furnace facilities where receivers are stationary and can be fitted with windows. Using this approach, any of the gasification reactor types can potentially be solar powered. For a dish based system, it is hard to imagine other than fluid phase transport to and from the receiver being feasible.

If a secondary high temperature heat transport fluid is used, then any of the reactor types could be driven if they are fitted with suitable heat exchange tubes. This approach has the disadvantages that temperature drops would be associated with the heat exchange and heat losses would be suffered in transporting the fluid. The first of these issues could be overcome if steam were heated in the receiver and then injected into the reactor. This approach could work for either low pressure or supercritical reactors. There would be challenges in balancing the energy input and the desired ratio of steam to biomass however.

Alternatively if finely ground biomass could be mixed with water as a slurry, this could be transported direct to the receiver and gasified in situ. Use of counterflow heat exchangers in such an arrangement would minimize thermal losses.

Consideration of solar reactor designs will be a main area of investigation for this ongoing investigation.

4. CONCLUSION

Solar gasification of biomass or coal can provide high value gaseous fuels, with an energy content that is around 30% attributable to the direct solar input. As well as this energy increase, gaseous fuels can be the feed-stocks for synthesis of transport fuels or can be used in high efficiency conversion processes such as fuel cells or combined cycle power plants.

Gasification using Supercritical water has been shown to be highly effective. It results in all reactions driving to completion with enhanced reaction rates and also offers the side benefit of providing separation of the hydrogen from the other gases if desired.

In order to couple gasification to a dish solar concentrator, use of slurries of biomass and water as the feed to an integrated receiver reactor system has great appeal. In this context, operation at supercritical conditions will also minimise the potential for the deposits of un-reacted solids.

5. ACKNOWLEDGMENTS

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