Synergy effects on combining hydrogen and gasification for synthetic biogas

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Abstract: This paper focuses on biogas and suggests methods for strongly increasing its production potential by combining gasification with hydrogen addition. By utilizing hydrogen produced from non-fossil energy sources, synthetic biogas can be obtained. The suggested methods are gasification combined with the Sabatier reaction, and hydrogasification. Both processes utilize hydrogen as a co-feedstock which can be produced via electrolysis from renewable electricity. Hydrogen addition to the gasification enhances the conversion efficiency and this synergy effect leads to higher fuel output compared to separate use of biomass and hydrogen.

The exploitation of renewable sources such as wind- and solar power is rapidly increasing since many countries have introduced incentives for these alternatives to expand. Since these are intermittent sources it would be highly beneficial to use electrolysis for balancing excess power in the grid during e.g. high loads or off-peak periods. Additionally, there would be an economical benefit as well since the price of electricity during these periods often is reduced.

The suggested methods could increase the biogas output by 130 – 150 % from the same amount of biomass as in conventional gasification. Contrary to upcoming fuels and solutions in the transport sector, biogas can be considered as conventional since a developed distribution system and storage capacity exists. It would also be a first step of introducing renewable electricity to the transport sector.

Keywords: *Synthetic biogas, Gasification, Transport sector, Hydrogen, Renewable fuels Introduction*

1. Introduction

The transport sector today poses one of the largest emitting sources of carbon dioxide. In a global perspective CO_2 from transport is responsible for approximately 23 % of the total green-house gas (GHG) emissions [1]. Moreover, the share of fossil energy used in the transport sector amounts to almost 95 %, most of it originating from oil [1]. With such a high share of fossil energy, the global transport sector is highly vulnerable and dependent on the fossil fuel market. Therefore, many regional and intergovernmental goals have been set, aiming for heavy reductions of fossil energy usage in the future as an act of CO_2 mitigation as well as an increased security of supply for their region. However, it is still highly uncertain how these goals could be reached. Many proposed solutions, e.g. the hydrogen economy, electric vehicles; CCS etc. are concepts and technologies still under development which probably cannot be used in any significant magnitude in a near future.

The most noticeable reaction from society towards a more climate neutral transport sector has been an increased usage of biofuels (mainly ethanol) and hybridized vehicles. The use of biofuels has increased quite rapidly during the past decade. However, the potential of biofuels from biomass is quite limited. The topic has been studied by many research groups such as [2, 3, 4] using Sweden (or local regions in Sweden) as an example, which is a particularly rich country in terms of forest (lignocellulosic biomass). Their studies have shown that even a forest rich country like Sweden will only be able to support parts of the total energy needs in the transport sector. Moreover it is shown that it will be necessary to combine different solutions, both for the supply-side and the demand-side in order to reach highly reduced levels of fossil energy in the transport sector [2].

Another renewable fuel that lately has received more and more attention is biogas. Today biogas constitutes only a minor part of the energy usage in transport. Biogas consists mainly of methane and is usually produced through digestion of organic materials. The amount of biogas that could be obtained from each alternative depends on available raw material (waste water sludge, manure and to some extent crops). Among others, [5,6] have studied the biogas potential from waste water sludge and solid municipal waste depending on t he amount of inhabitants in a region and have estimated that it is possible to obtain a total of about 0.8 GJ biogas/person/year [5,6].

This paper suggests methods and technologies for strongly increasing the biogas potential by producing synthetic biogas from renewable energy sources. Synthetic biogas is a good alternative in the transport sector, which could contribute to large reductions of fossil fuel related CO_2 emissions. Biogas is in this paper defined as a biofuel containing mostly methane, independent of the route used to produce it.

1.1. Aim and Scope

The aim of the paper is to present possibilities for utilising biomass, mainly lignocellulosic, more efficiently than via conventional gasification. With the suggested methods it is possible to convert larger fractions of the tree into a propellant (in this case methane). It would result in an almost 100 % increase in fuel potential from forest biomass compared to when conventional methods are used. Such increase would have a substantial effect on t he total biomass potential as raw material for propellant production. Accordingly, the transport sector would take a leap towards the possibility of achieving a transport sector with no net emissions of greenhouse gases.

The paper suggests implementing:
- Gasification combined with the Sabatier reaction
- Hydrogasification

These methods use the same fundamental principle i.e. thermal degradation of a given material. However, there are some key differences that are presented, discussed and evaluated in this paper. Comparisons are made and suggestions given for where each process should be implemented to make the greatest contribution.

2. The processes

Both suggested processes use biomass and hydrogen as raw materials for producing methane (synthetic biogas). They reach almost the same yield, however the main difference is that the hydrogen is introduced into the process at different stages. To keep the product (i.e synthetic biogas) CO_2 lean the suggested processes are will use hydrogen produced from renewable sources. In such case water electrolysis would be an excellent alternative. Electrolysis could be driven by renewable electricity (which often is intermittent) which gives the possibility of obtaining pure hydrogen at relatively low cost if run at e.g. off-peak periods when electricity is in excess. The two processes are illustrated and more thoroughly described in the following sections.

2.1. Gasification combined with the Sabatier reaction

Gasification is a known application and is commonly used to produce syngas, a mixture of mainly hydrogen and carbon monoxide. CO and H_2 in combination are suitable for production of hydrocarbons e.g. synthetic methane, methanol and Fischer-Tropsch fuels.
Generally, there is a shortage of hydrogen in syngas if the aim is to produce synthetic biogas. Therefore, WGS is used to increase the share of hydrogen before the methane synthesis. However, when applying WGS, carbon dioxide is formed as a by-product which must be separated. It is a target for removal in the upgrading step after the fuel synthesis and vented to the air. The biomass to biogas efficiency in terms of energy is approximately 60 % [7] even though most of the carbon feed (about 65 %) is removed as CO_2 [8]. Table 1 displays the general chemical reaction for methane production via gasification where oxygen is used as the gasification agent.

Table 1. Reaction and energy balance for oxygen gasification based on 1 mole produced methane.

Oxygen gasification								
Reaction	$2.7\ CH_{1.5}O_{0.6}$	+	$1.4\ O_2$	$\rightarrow CH_4$	+	reaction heat		$+1.7CO_2$
Energy	1127		0	676 (60 %)		450		[kJ/mol CH_4]

To increase the methane yield from biomass it would be possible to use the separated CO_2 for additional methane production. This could be done by implementing the Sabatier reaction which is showed in Eq. (1). Due to a very beneficial equilibrium in the Sabatier reaction it would be possible to convert most of the CO_2 to additional methane [9,10]. Hence, in this report it is assumed that 90 % of the input CO_2 is converted and such process would increase the total amount of methane produced, significantly.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H = -165\ kJ/mol \qquad (1)$$

As can be seen in Eq. (1), there is need for four hydrogen molecules per carbon dioxide molecule for the reduction of the carbon dioxide to methane according to the Sabatier reaction. As a by-product, two water molecules are produced for every molecule of methane; additionally the reaction is exothermal according to the equation. In Fig. 1 it is illustrated how the Sabatier process could be used to retrofit a gasification process.

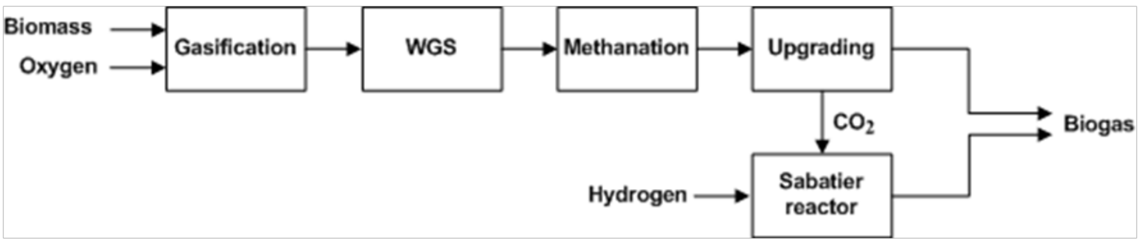

Fig. 1. Oxygen gasification combined with the Sabatier reaction.

After separation from the methane, the CO_2 stream could be directed to an external reactor where the Sabatier reaction takes place. The reaction could be run at atmospheric pressure but needs temperatures between 250 - 400°C. If running close to equilibrium it would be possible to increase the methane yield significantly, hence about 85 – 90 % of the carbon dioxide would be converted to additional methane [9,10]. To keep the "new" methane CO_2-clean the hydrogen is supposed to originate from electrolysis driven by a renewable source e.g wind power or photovoltaics (PV).

2.2. Hydrogasification

As stated in the previous section, the limiting factor for methane formation in the fuel synthesis is the low proportion of hydrogen in syngas. If WGS is used to obtain hydrogen, carbon dioxide is produced simultaneously and must be removed. By adding hydrogen in an earlier stage, i.e. in the gasifier, WGS can be avoided, moreover less or even no CO_2 removal is necessary. Adding hydrogen to the gasifier also has the positive effect of eliminating the need for oxygen as a gasification agent. Since the produced biogas has a low CO_2 content, the only upgrading that is needed is to remove the water by condensation. The process is illustrated in Fig. 2.

Fig. 2. Hydrogasification process

Table 2 shows the theoretical reaction and energy balance for hydrogasification which may be compared to oxygen gasification in Table 1. As can be seen, less reaction heat is produced and there are no CO_2 in the product (assuming total reaction).

Table 2. Reaction and energy balance for hydrogasification

Hydrogasification							
Reaction	$CH_{1.5}O_{0.6}$	+	1.85 H_2	$\rightarrow CH_4$	+	reaction heat	+ 0.6H_2O
Energy	420		448	676 (78 %)		192	[kJ/mol CH_4]

3. Potential for enhanced methane production

The mentioned processes are suggested as alternatives which significantly can enhance the yield of fuel obtained from biomass compared e.g. with biological processes. One must keep in mind though, that hydrogen is needed for both processes. The needed hydrogen is suggested to be produced through water electrolysis using a renewable energy source e.g. wind power or PV. It has been suggested by many researchers that electricity could be stored as hydrogen (which in turn can be used to produce propellants) through electrolysis [11-13]. This is especially beneficial when considering intermittent power i.e. wind- and solar power. Accordingly, electrolysis could act as stabilizer when electricity production is high and the grid load is low. In the Nordic countries the electricity price varies continuously and depends on supply and demand [14]. When high amounts of electricity are produced with few end users, the price will naturally decrease. Therefore, if running the electrolysis during these periods, the produced hydrogen will be as cheap as possible. It could also be stored for later use which could create possibilities for producing methane in a cost efficient manner.

In Table 3 and Table 4 examples for both processes are presented. The calculations are based on input biomass containing 100 moles of carbon (C). As stated earlier a 90 % conversion rate of the CO_2 is used in the calculations with the Sabatier reaction. It must be noted that in Table 3 the system boundaries for the gasification also includes the WGS reaction i.e. the flow is led in to the gasification and out from the upgrading process.

Table 3. Potential for increased biogas production by using the Sabatier reaction (input data for gasification from [7])

Gasification	Biomass	H_2	CO_2	CH_4
In (mol)	100 (mol C)	-		
Out (mol)		0.7	54	36
Sabatier				
In (mol)		217	54	
Out (mol)		22	5.4	49
Total CH_4 out				85

By using the removed carbon dioxide from the biogas, production can be increased by 136 %. In addition to the produced methane some un-reacted hydrogen is added to the biogas.

Table 4. Potential for increased biogas production by hydrogasification [7]

Hydrogasification	Biomass	H_2	CO_2	CH_4
In (mol)	100 (mol C)	178	12	
Out (mol)		8	8	83
Total CH_4 out				83

The input of CO_2 in the hydrogasifier is used as inert gas in the feeding process to avoid nitrogen in the system. The increase in biogas production can be calculated by comparing with the case of oxygen blown gasifier. In the case of hydrogasification the yield of methane will increase 130% compared to oxygen gasification (without Sabatier).

It is important to consider not only the yield of methane since biogas contains other combustible gases e.g. hydrogen which will increase the total energy output. In Table 5 it is possible to see the total energy balance. There are some facts to consider when reading Table 5 regarding the carbon input and the hydrogen content in the biogas. There is a higher carbon input in the hydrogasification process since carbon dioxide is used as feed, and it will also take part in the reaction and forms methane. Carbon dioxide is also used for feeding the oxygen-blown gasifier, but in that case a part of the produced carbon dioxide is re-circulated, thus no additional carbon source is added. The higher biogas output from the Sabatier reactor, despite the lower carbon input, can be traced to the higher hydrogen content in the produced biogas (20 mol-% from Sabatier and 8 mol-% from hydrogasification).

Table 5. Example of the efficiency of SNG production [7]

SNG production		**Hydrogasification**	**Gasification + Sabatier**	**Oxygen gasification**
Input	Biomass [MW]	100	100	100
	Hydrogen [MW]	94.8	117.7	
Output	Biogas [MW]	154	165.9	66.3
Efficiency		79 %	76.2 %	66.3 %
Hydrogen efficiency[1]		92.5 %	84.6 %	

[1]Hydrogen efficiency refers to the increase in fuel production compared with amount added hydrogen. In the hydrogasification case, 94.8 MW hydrogen is added which increases the output by 87.7 MW compared to the oxygen blown gasifier. The efficiency is obtained by dividing the increase (87.7MW) with added hydrogen (94.8 MW), 87.7/94.8 = 0.925

Adding hydrogen increases the efficiency which gives a high yield based on the LHV of hydrogen, 92 % for the hydrogasification case and 85 % when the Sabatier reactor is used. Table 5 also shows that the suggested methods could increase the biogas output with 130 – 150 % from the same amount of green carbon. Furthermore, the hydrogasification has a positive power balance with the possibility to export 4.5 MW; meanwhile oxygen gasification requires an import of 2.7 MW. If the oxygen is taken from the electrolysis in the case of oxygen gasification, the plant would lower the electric demand by 4 MW resulting in a 1.3 MW power export[7].

4. Discussion

Biogas' corresponding fossil fuel is CNG (compressed natural gas). The main difference between biogas and CNG is that biogas, when upgraded for vehicle usage, contains about 98 % pure methane and the remaining carbon dioxide. Natural gas however, contains mainly methane (about 80-90 %), higher hydrocarbons and carbon dioxide. Today many vehicles are driven by CNG, e.g. private cars, buses, trucks, taxicabs etc. In many urban areas (and to some extent in rural areas), there is a grid for CNG distribution. Hence, existing grids would be suitable for introducing biogas since both gases can be used in the same applications due to similar combustion qualities and energy content.

In both suggested processes small amounts of hydrogen are present in the product flow. Technically, the hydrogen does not need to be separated. According to test runs from 2006 in Malmö, Sweden, natural gas buses have tried driving on hydrogen blended CNG (HCNG) with promising results. The buses used up to 25 vol-% hydrogen with no, or only minor changes, in the system depending on blend [15].

Acquiring the essential hydrogen is one of the key issues for the processes. In this paper, electrolysis has been suggested for hydrogen production. However, electrolysis is energy demanding with an efficiency of about 70 % from electricity to hydrogen (LHV) [16]. Additionally, energy is lost when the actual reaction takes place. On the other hand, using electrolysis opens for possibilities of storing electricity in a manner the does not exist today; especially intermittent power which is growing rapidly. Moreover it is possible to produce a variety of different valuable products from hydrogen. Battery electric vehicles or plug-in hybrids have been suggested as possible electricity depots, however the technology and infrastructure for this kind of usage is still not commercially available.

An important matter regarding synthetic biogas is that it depends on renewable electricity for hydrogen production. Wind power and PV are renewable energy sources that have shown promising future potential. However, these sources produce intermittent power which is entirely controlled by current weather conditions. Hydrogen production through electrolysis would therefore be an effective method to regulate the fluctuations when excess power is produced.

Transporting and storing hydrogen for use as a vehicle fuel are issues that have not been solved yet. In such terms, it would be more favorable to use the hydrogen as a component for further conversion, in this case to produce synthetic biogas. One of the main problems when storing hydrogen is that a significant compression work is needed if stored as compressed gas. Biogas contains over 3 times more energy per volume than hydrogen which makes compression of biogas much more beneficial compared to hydrogen. Additionally, storage and infrastructure for biogas is more developed and the vehicles are available today, both as private cars and buses for public transportation.

As can be seen in the results, both processes show a significant increase in biogas production with the highest hydrogen efficiency when using hydrogen in the gasifier. An advantage of the Sabatier reaction however, is that it is not limited to gasification processes; basically any process with CO_2 emissions would be possible to retrofit. The fact that energy is lost as heat when adding hydrogen to the processes, could be solved (to some extent) by recovering the heat for power production in a steam cycle. Excess heat from the electrolysis could also be integrated in the steam cycle as preheating energy or used in e.g biomass drying.

5. Conclusions

Based on the presented information in this paper, it would be feasible to implement the suggested methods for fuel production. These would increase the capacity of biogas production greatly in areas where sufficient sustainable electricity is available.

It would be an excellent synergy opportunity to use intermittent electricity from renewable power production, to run the electrolysis when loads are high on the grid or during off-peak periods.

In a short time scale, the methods would be feasible options, since gasification and the Sabatier reaction are known technologies and furthermore biogas is used as vehicle fuel commercially.

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